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Effect of Polymer Structure on Ion Transport in an Anhydrous Proton Conducting Electrolyte

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We have studied the effect of polymer structure of a proton-conducting polymer electrolyte on proton conductivity. Proton conducting electrolytes composed of mixtures of a $MePEG_7SO_3H$ acid, our $MePEG_n$ polymer, and a PEG containing cross-linker have been prepared. We have independently varied two structural parameters in our polymer electrolyte, viscosity and free volume, and studied the effects of these changes on the H^+ conductivity. The copolymerization of a PEG_{13} cross-linker increases the viscosity and the molecular weight distribution (i.e., PDI) of our $MePEG_n$ polymers. In addition, the fractional free volume of our $MePEG_n$ polymers increases as the length of the PEG side chains in the polymer increases from $n = 7$ to $n = 12$. Under certain conditions, high-viscosity, cross-linked $MePEG_n$ polymers show almost the same ionic conductivity as less viscous, uncross-linked $MePEG_n$ polymers. The effect of this change in viscosity is compensated by a simultaneous change in the free volume of the $MePEG_n$ polymer. These results indicate that both free volume and viscosity are important factors in predicting the ionic conductivity in our polymer electrolyte. When shown as a Walden plot, the data appear below the ideal Walden line, indicating that the $MePEG_7SO_3H$ acid is behaving as a weak acid in our anhydrous $MePEG_n$ polymer.

Introduction

This paper focuses on how the structure of a polymer electrolyte affects proton conductivity in our sol−gel-based $MePEG_n$ polymer electrolyte. We seek a fundamental understanding of the dependence of H^+ transport on polymer structure.[1−5] In this work, we will focus on two important parameters of structure: viscosity and free volume. We have developed a strategy in which we can independently alter the viscosity and free volume in our $MePEG_n$ polymer electrolyte.

In recent years, proton conducting polymer electrolytes have become a very interesting and exciting material due to their applications in fuel cells, electrochemical sensors, and electrochromic displays.

Nafion (a sulfonated fluoropolymer) is a very widely used proton-conducting polymer electrolyte because of its mechanical properties, chemical stability, and high proton conductivity when wet. Unfortunately, Nafion membranes require hydration to achieve this high proton conductivity, which limits the maximum operating temperature to around 100 °C. The steam reforming of natural gas and coal to synthesize the hydrogen used to power PEM fuel cells produces carbon monoxide. At these relatively low temperatures, the tolerance of the electrocatalyst against CO poisoning is low, but at temperatures above 150 °C, anodes are available that can efficiently deal with a small concentration of CO. Thus, we need new polymer electrolytes with high conductivity and good mechanical stability that are capable of operating at high temperatures and low humidities.[6]

We have adopted an approach used by several research groups to increase the conductivity of an amorphous polymer by increasing the frequency of segmental motions of side chains attached to a polymer backbone.[7] Here, a high frequency of segmental motions of the side chains allows for fast reorganization, which according to our understanding of proton transport in our material,[1−5] leads to faster ion conduction. Polyethylene oxide (PEO) and Polyethylene glycol (PEG) side chains have been attached to polymer backbones in order to increase the rate of reorganization of a polymer. Shriver and coworkers have reported polysiloxane comb polymer electrolytes that contain flexible PEG side chains. Shriver noted that these flexible side chains can increase the conductivity of their comb polymer by increasing the number of ether oxygens on PEG side chains.[8]

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Although fast segmental motions of side chains leads to high conductivity, good dimensional stability is also required for practical applications of ion-conducting polymers and is especially desirable for high-temperature applications. Cross-linkers and high-molecular-weight polymers can increase the dimensional stability of polymer electrolytes. West and co-workers have improved the dimensional stability of their polysiloxane-based, cross-linked polymer electrolytes by using α,ω-diallyl poly(ethylene glycol) as cross-linkers. These solid polymer electrolytes display room temperature Li^+ ion conductivity in excess of 1×10^{-4} S/cm, a value that is comparable to their liquid polysiloxane counterparts.[9]

Several research groups have analyzed the effect of flexible side chains (like PEG) on ionic conductivity and transport properties in terms of free volume. Murray showed that the increase in transport properties in their redox polyether molten salts, as a function of the variation in length of PEG side chains, was in fact an effect of increasing free volume.[10] Murray was also able to duplicate this effect by adding supercritical CO_2 to their redox polyether molten salts in order to increase the free volume. Here, an increase in P_{CO_2} from 0 to 2000 psi causes swelling of the system, thus increasing the free volume. This increase in free volume results in an increase of the physical diffusion coefficient of the $Co(II)(bipy)_3$ species from 2.4×10^{-11} to 7.0×10^{-10} cm^2/s.[11]

In addition to free volume, the effect of viscosity on ionic conductivity has been studied by several groups. West has described how free volume and viscosity work together to control the conductivity of Li^+ ion in their ion conducting polymer.[12] They compared the conductivity of cyclic and linear oligoether substituted siloxanes with a similar number of backbone repeating units (i.e., same M_w). They showed that the linear siloxane system has a higher conductivity than cyclic siloxane even though the linear siloxane has a higher viscosity. This is due to the larger free volume of the linear siloxane compared to the cyclic siloxane.

Previously, we have shown that H^+ transport is dependent on the volume fraction of PEG present in the MePEG polymer and acid mixtures.[2] The volume fraction of PEG in this case was used as a proxy for free volume. Our hypothesis in this work is that the proton conductivity is dependent on both the free volume (i.e., void volume) and viscosity of our MePEG polymer.

To test our hypothesis, we have developed methods separately altering the free volume, and viscosity (η). Here, we have specifically synthesized $MePEG_n$ polymers with different viscosities and free volumes. Viscosities of the $MePEG_n$ polymers were changed by adding a PEG-based cross-linker, which we expect to restrain the reorganization of the system,[2,13] thus increasing the viscosity. We expect that higher viscosities will also increase the dimensional stability of the polymers. Free volumes were altered by using different $MePEG_n$ chain lengths in the MePEG polymers. The longer MePEG chains contribute more free volume.

Experimental Section

Poly(ethylene glycol) ($H(OCH_2CH_2)_nOH = PEG_n$, $M_n = 600$, $n = 13$; Acros), Poly(ethylene glycol) monomethyl ether ($CH_3(OCH_2CH_2)_nOH = MePEG_nOH$, $M_n = 350$, 550; Aldrich) were dried at 60 °C under a vacuum (~10 mtorr) for 24 h. For clarity, this paper will refer to the polyethylene glycol $M_n = 600$ as PEG_{13}, the $M_n = 350$ poly(ethylene glycol) monomethyl ether as $MePEG_7$, and the $M_n = 550$ material as $MePEG_{12}$. Triethoxysilane (Aldrich), sodium hydride (Aldrich), sodium sulfite (Fisher), and 1.0 M phosphorus tribromide in CH_2Cl_2 solution (Aldrich) were used as received. Dry tetrahydrofuran and ethyl ether were dried and purified by passing them through alumina using a contour glass solvent delivery system.

The densities of dry polymer and acid samples were measured gravimetrically by drawing the neat liquid into a tared 2 μL micropipet which was weighed using an ATI Cahn C-33 microbalance. Concentrations of mixtures of the $MePEG_nSO_3H$ acid and $MePEG_n$ polymer were calculated by (1) converting the mass of the $MePEG_n$ polymer to volume (using their densities), (2) converting the masses of the $MePEGSO_3H$ acid to moles, and (3) dividing by the total volume of the (acid + polymer). This approach specifically assumes that the volumes are additive.

AC-impedance measurements were made with a PAR 283 potentiostat equipped with a Perkin-Elmer 5210 lock-in amplifier using PowerSine software. The construction and use of the electrodes have been described previously.[2,14] Variable-temperature measurements were made with electrodes sealed in a jacketed cell connected to a circulator and vacuum pump.[14]

Gel permeation chromatography (GPC) measurements were made using two 30 cm Polymer Laboratories Mixed-D analytical columns and analyzed using a Polymer Laboratories ELS-2100 evaporative light scattering detector. Polystyrene molecular weight standards (Polymer Laboratories - EasiCal PS-2, MW range 580−400K) were used to calibrate the instrument prior to running unknown samples.

Viscosity measurements were performed on Brookfield DV-III ULTRA Programmable Rheometer by using a CPE-40 Spindle under the flow of N_2.

Poly(ethylene glycol) Allyl Methyl Ether. ($MePEG_7OCH_2CHCH_2$) (**2a**) and ($MePEG_{12}OCH_2CHCH_2$) (**2b**) and the $MePEG_n$ monomers $MePEG_7(CH_2)_3Si(OEt)_3$ (**3a**) and $MePEG_{12}(CH_2)_3Si(OEt)_3$ (**3b**) were all prepared as previously described.[2]

Synthesis of α,ω-Diallyl poly(ethylene glycol) Cross-Linker CH_2CHCH_2O-PEG_{13}-CH_2CHCH_2 (5; Scheme 1). NaH (1.70 g, 70.8 mmol) and THF (35 mL) were added to an air-free round-bottom flask. Dry polyethylene glycol ($M_n = 600$; HO-PEG_{13}−OH, 20.0 g, 33.3 mmol), was dissolved in 20 mL of dry THF and added dropwise to the NaH/THF slurry. The mixture was stirred at room temperature, under argon, for 30 min to complete the deprotonation. Allyl bromide (8.25 g, 68.2 mmol, 2.05 equiv) was dissolved in 10 mL of THF and added dropwise

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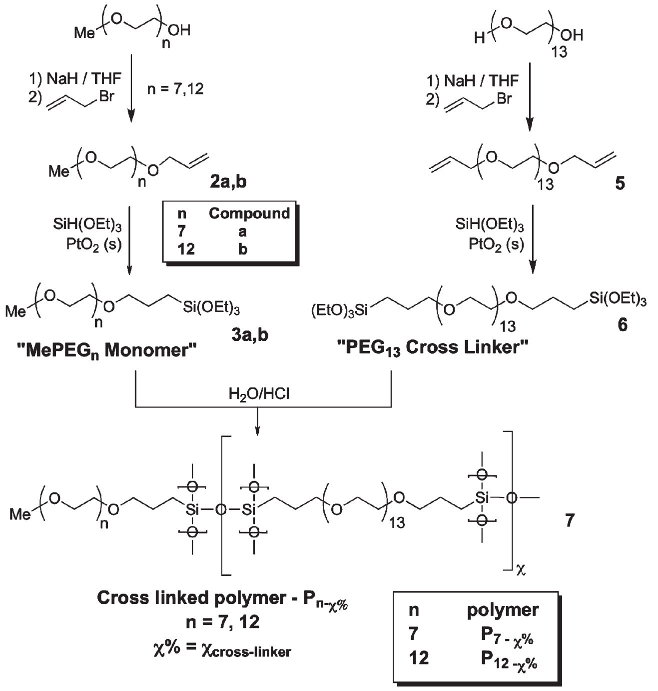
Scheme 1. Synthesis of MePEG$_n$ Cross-Linked Polymer

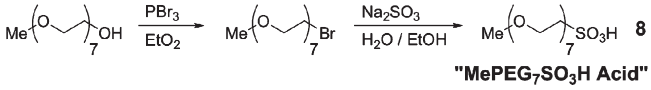


to the reaction mixture (a white precipitate of NaBr appeared upon addition). The reaction was stirred at room temperature for 5 h, followed by the addition of 5 mL of wet acetone to quench any unreacted NaH. The NaBr precipitate was removed by filtration, and the filtrate was extracted with 50 mL of 0.5 M NaCl and 3 × 75 mL of $CHCl_3$. The organic fraction was dried (Na_2SO_4) and concentrated by rotary evaporation, yielding a clear and colorless liquid (21.2 g, 31.2 mmol, 94%). NMR (^1H, $CDCl_3$, δ ppm) 3.35−3.65 (m, 53H), 4.01 (m, 4H), 5.22 (dd, 4H), 5.89 (m, 2H). NMR (^{13}C, $CDCl_3$, δ ppm) 58.51, 68.89, 69.99−70.09, 71.39, 71.67, 116.55, 134.26.

Synthesis of PEG$_{13}$ Cross-Linker $(EtO)_3Si(CH_2)_3PEG_{13}(CH_2)_3Si(OEt)_3$ (6). The hydrosilylation catalyst PtO_2 (~2 mg) was added to an air-free Schlenk tube followed by triethoxysilane ($SiH(OEt)_3$, 10.1 g, 61.6 mmol, 2.09 equiv) and α, ω-diallyl poly(ethylene glycol) (20.0 g, 29.4 mmol). The tube was shaken and then heated to 70 °C in an oil bath under argon. ^1H NMR analysis after 10 h showed the complete disappearance of the allyl protons and a slight excess of silane protons, indicating completion of the reaction. The reaction mixture was then heated under vacuum (~50 mtorr) at 50 °C for 2 h to remove excess $SiH(OEt)_3$ (bp = 134−135 °C). The PtO_2 catalyst was removed by filtration with activated charcoal in THF in an inert atmosphere glovebox. Two successive filtrations were needed to completely remove the highly colored PtO_2. The THF solvent was removed by rotary evaporation, yielding a clear and colorless viscous liquid (22.4 g, 22.2 mmol, 76%). NMR (^1H, $CDCl_3$, δ ppm) 0.64 (m, 4H), 1.19 (m, 18H), 1.67 (m, 4H), 3.38 (m, 4H), 3.52−3.68 (m, 53H), 3.77 (m, 12H).

Preparation of Sol−Gel Cross-Linked Polymer $(MePEG_7(CH_2)_3SiO_{1.5})$ $(O_{1.5}Si(CH_2)_3PEG_{13}(CH_2)_3SiO_{1.5})_\chi$ (7; $P_{7-0\%}$ to $P_{7-30\%}$; Scheme 1). The "PEG$_{13}$ cross-linker" (**6**) was mixed with the $MePEG_7Si(OEt)_3$ monomer (**3a**) with 0, 5, 10, 15, 20, 25, and 30 mol % cross-linker (see Table S1 in the Supporting Information). Ten equivalents of acidic water (one drop of concentrated HCl in 100 mL of water) was then added to the mixture. The solution was mixed well and allowed to hydrolyze for 12 h at room temperature. The solution was then concentrated on a rotovap and placed in a vacuum oven at 60 °C for 48 h. The resulting 0, 5, 10, and 15% cross-linked MePEG$_7$ polymers (**$P_{7-0\%}$−$P_{7-15\%}$**, Scheme 1) were clear and colorless viscous liquids. The 20, 25, and 30% cross-linked MePEG$_7$ polymers (**$P_{7-20\%}$−$P_{7-30\%}$**, Scheme 1), however, were clear and colorless soft solids. NMR analysis of **$P_{7-0\%}$** through **$P_{7-15\%}$** cross-linked polymers showed that the ethoxy (Si-OEt) peaks had completely disappeared, indicating complete hydrolysis.

Scheme 2. Synthesis of MePEG$_7$SO$_3$H Acid



Preparation of the Sol−Gel Cross-Linked Polymer $(MePEG_{12}(CH_2)_3SiO_{1.5})$ $(O_{1.5}Si(CH_2)_3PEG_{13}(CH_2)_3SiO_{1.5})_\chi$ ($P_{12-0\%}$ − $P_{12-30\%}$; Scheme 1). The "PEG$_{13}$ cross-linker" (**6**) was mixed with $MePEG_{12}Si(OEt)_3$ monomer (**3b**) with 5, 10, 15, 20, 25, and 30 mol % cross-linker (see Table S2 in the Supporting Information). These mixtures were treated using the same method as explained above for the **$P_{7-0\%}$** − **$P_{7-30\%}$** polymers. The resulting 0%, 5%, 10% and 15% polymers (**$P_{12-0\%}$** through **$P_{12-15\%}$**; Scheme 1) were clear and colorless viscous liquids, while the 20%, 25% and 30% polymers (**$P_{12-20\%}$** through **$P_{12-30\%}$**) were clear and colorless soft solids.

Synthesis of MePEG$_7$SO$_3$H Acid (8; Scheme 2). (*i*). *Synthesis of MePEG$_7$Br.* In an air-free round-bottom flask, PBr_3 (43.0 mL, 43.0 mmol, 1.00 M PBr_3 solution in CH_2Cl_2) was slowly added to a solution of poly(ethylene glycol) monomethyl ether ($MePEG_7OH$, 30.0 g, 85.7 mmol) in 50 mL of dry diethyl ether. The reaction was stirred overnight at room temperature. The reaction was then poured over 100 g of ice and extracted with 100 mL of diethyl ether and 2 × 100 mL dichloromethane. After the mixture was dried with Na_2SO_4 and concentrated by rotary evaporation, 30.0 g of the clear and colorless $MePEG_7Br$ (72.6 mmol, 84.7% yield) was recovered. NMR (^1H, $CDCl_3$, δ ppm) 3.34 (s, 3H), 3.56 (m, 2H), 3.60 (m, 28H), 3.71 (t, 2H). NMR (^{13}C, $CDCl_3$, δ ppm) 29.00, 58.89, 70.06−70.49 (several peaks), 71.05, 71.77.

(*ii*). *Synthesis of MePEG$_7$SO$_3$H.* This material (Scheme 2) was prepared by the same procedure as reported previously.[2] The following amounts of materials were used: $MePEG_7Br$ (15.00 g, 36.32 mmol) and sodium sulfite (Na_2SO_3, 9.15 g, 72.6 mmol; 2.00 equiv). Yield: $MePEG_7SO_3H$ acid (6.40 g, 7.86 mmol, 63.4%). NMR (^1H, $CDCl_3$, δ ppm) 3.22 (t, 2H), 3.35 (s, 3H), 3.50−3.70 (m, 65H), 3.88 (t, 2H). The acidity of (**8**) was measured at 101%. Neat $MePEG_7SO_3H$ has a density 1.237 g/mL.

Results and Discussion

Synthesis. The MePEG$_n$ monomers (**3a**, **3b**) and cross-linker (**6**) synthesized for this study were prepared from a PtO_2-catalyzed[2,15] hydrosilylation reaction between triethoxysilane and poly(ethylene glycol) allyl methyl ether (Scheme 1). The completion of these hydrosilylation reactions were monitored by following the ^1H NMR signal of the alkene and silane protons. After complete disappearance of the alkene proton, a small excess of triethoxysilane typically remained. The excess silane was removed from the reaction mixture by heating at 50 °C under a vacuum.

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The MePEG$_n$ monomers (**3a**, **3b**) were mixed with different mole fractions of the PEG$_{13}$ cross-linker (**6**). These mixtures were hydrolyzed and condensed to form the cross-linked polymers. By increasing the mole fraction of PEG$_{13}$ in the cross-linker, we are able to increase the viscosities of the resulting polymers. We synthesized the (MePEG$_n$)(PEG$_{13}$)$_\chi$ cross-linked polymer with MePEG$_n$ chain lengths of both n = 7 repeat units ($\mathbf{P_{7-0\%}}$ through $\mathbf{P_{7-30\%}}$, Scheme 1), and n = 12 repeat units ($\mathbf{P_{12-0\%}}$ through $\mathbf{P_{12-30\%}}$, Scheme 1).

In the notation used in this paper, a cross-linked polymer (e.g., $\mathbf{P_{7-10\%}}$) is noted as **P**, followed by the a subscript with the number of side chains in the MePEG$_n$ group (in this case 7) followed by a dash and the mole percent of the PEG$_{13}$ cross-linker. For example, a cross-linked polymer prepared from the MePEG$_7$ monomer and 10 mol % PEG$_{13}$ cross-linker would be called: $\mathbf{P_{7-10\%}}$.

The preparation of cross-linked polymers from both the MePEG$_7$ and MePEG$_{12}$ polymers allow for the control of free volume and volume fraction of PEG in the polymer. Cross-linked polymers with 0, 5, 10, 15, 20, 25, and 30 mol % PEG$_{13}$ cross-linker were synthesized from both the MePEG$_7$ and MePEG$_{12}$ polymers. Cross-linked polymers with 0% ($\mathbf{P_{7-0\%}}$, $\mathbf{P_{12-0\%}}$), 5% ($\mathbf{P_{7-5\%}}$, $\mathbf{P_{12-5\%}}$), 10% ($\mathbf{P_{7-10\%}}$, $\mathbf{P_{12-10\%}}$), and 15% ($\mathbf{P_{7-15\%}}$, $\mathbf{P_{12-15\%}}$) mol % cross-linker were clear and colorless viscous liquids, whereas the 20% ($\mathbf{P_{7-20\%}}$, $\mathbf{P_{12-20\%}}$), 25% ($\mathbf{P_{7-25\%}}$, $\mathbf{P_{12-25\%}}$), and 30% ($\mathbf{P_{7-30\%}}$, $\mathbf{P_{12-30\%}}$) mol % cross-linked polymers were soft solids for both MePEG$_7$ and MePEG$_{12}$ chain lengths.

We measured the molecular weight of the $\mathbf{P_{7-0\%}}$ to $\mathbf{P_{7-15\%}}$ and $\mathbf{P_{12-0\%}}$ to $\mathbf{P_{12-15\%}}$ cross-linked polymers (i.e., all the liquid polymers) using gel permeation chromatography. We expected that the GPC-measured polydispersity index (PDI, a measurement of molecular weight distribution) of our polymer would increase as the mole fraction of cross-linker increased. Figure 1 shows the change in molecular weight distribution with respect to the mole fraction of cross-linker. All of the cross-linked polymers showed two peaks, one with high M_w and one with low M_w. The high M_w peaks show a larger PDI than the low M_w peaks. The PDI increases from the un-cross-linked polymers [$\mathbf{P_{7-0\%}}$, PDI = 1.26 (high M_w) and 1.24 (low M_w); $\mathbf{P_{12-0\%}}$, PDI = 1.24 (high M_w) and 1.22 (low M_w)] to the 15% cross-linked polymers [$\mathbf{P_{7-15\%}}$, PDI = 1.77 (high M_w) and 1.41 (low M_w); $\mathbf{P_{12-15\%}}$, PDI = 1.36 (high M_w) and 1.34 (low M_w)] for cross-linked polymers made from the MePEG$_7$ and MePEG$_{12}$ polymers. This increase in PDI supports our hypothesis for both the high- and low-molecular-weight (M_w) peaks.

Figure 1 shows molecular weight distribution plots for both the MePEG$_7$ and MePEG$_{12}$ cross-linked polymers. In both plots, the low M_w peaks for both the cross-linked MePEG$_7$ and MePEG$_{12}$ polymers are narrower than the high M_w peaks. These low M_w peaks seem to be due to the formation of T$_2$-type dimers.[1] In addition, as seen in Figure 1, the width of the high-molecular-weight peaks increases as the concentration of the PEG$_{13}$ cross-linker increases in both the MePEG$_7$ and MePEG$_{12}$ polymers.

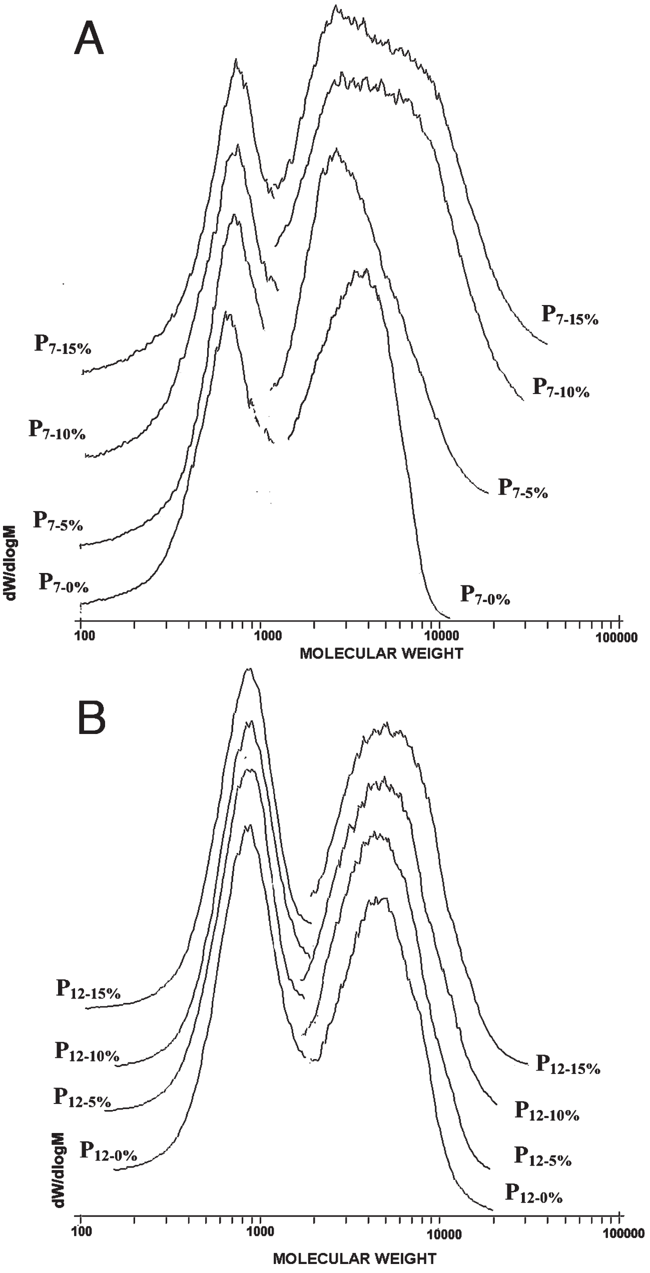

Figure 1. GPC-derived molecular weight distribution plots of (A) MePEG$_7$ and (B) MePEG$_{12}$ cross-linked polymers with respect to the mol % cross-linker.

Fluidity. We measured viscosities (η) of mixtures of the cross-linked polymers with a high (1.32 M) and low (0.26 M) concentration of the MePEG$_7$SO$_3$H acid as a function of mol % cross-linker in the polymers. Before each measurement, samples were dried at 55 °C under a vacuum for 18 h and viscosities were measured under the flow of dry nitrogen. Fluidities (η^{-1}) of the polymers and acid mixtures were calculated from the inverse of measured viscosities.

High-concentration (1.32 M) mixtures of the MePEG$_7$SO$_3$H acid in the MePEG$_n$ polymer show higher fluidities than for the low-concentration (0.26 M) mixtures of polymer and acid (Figures 2 and 3). Here, the high-concentration samples have a larger mass % of the MePEG$_7$SO$_3$H

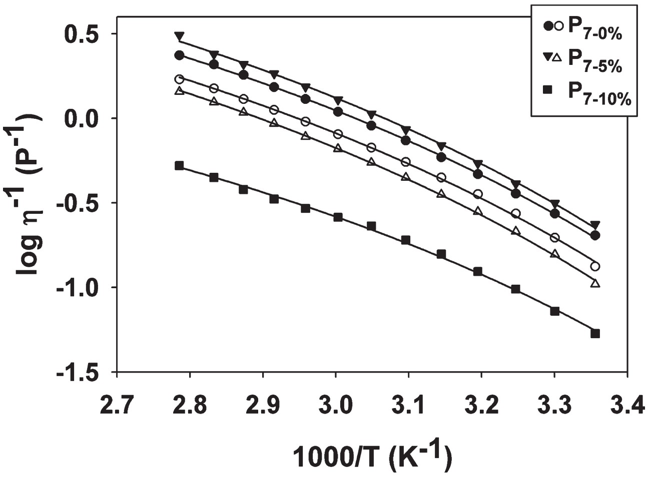

Figure 2. Arrhenius plot of fluidity (η^{-1}) of MePEG$_7$ non-cross-linked (**P$_{7-0\%}$**) and cross-linked (**P$_{7-5\%}$**–**P$_{7-10\%}$**) polymers and MePEG$_7$SO$_3$H acid mixtures at high (1.32 M; closed symbols ●, ▼, ■) and low concentrations (0.26 M; open symbols ○, ▽). Polymers shown: 0% cross-linked MePEG$_7$ polymer (**P$_{7-0\%}$**, ●, ○); 5% cross-linked MePEG$_7$ polymer (**P$_{7-5\%}$**, ▼,▽); 10% cross-linked MePEG$_7$ polymer (**P$_{7-10\%}$**, ■).

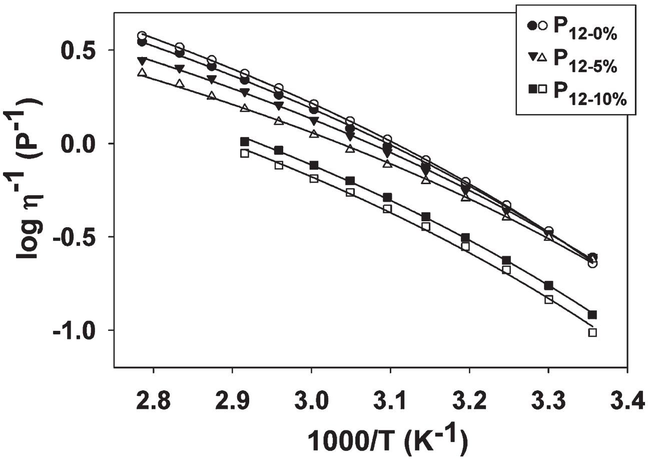

Figure 3. Arrhenius plot of fluidity (η^{-1}) of MePEG$_{12}$ noncross-linked (**P$_{12-0\%}$**) and cross-linked (**P$_{12-5\%}$**–**P$_{12-10\%}$**) polymers and MePEG$_7$SO$_3$H acid mixtures at high (1.32 M; closed symbols ●, ▼, ■) and low concentrations (0.26 M; open symbols ○, ▽, □). Polymers shown: 0% cross-linked MePEG$_7$ polymer (**P$_{12-0\%}$**, ●, ○); 5% cross-linked MePEG$_7$ polymer (**P$_{12-5\%}$**, ▼, ▽); 10% cross-linked MePEG$_7$ polymer (**P$_{12-10\%}$**, ■, □).

acid, which as we have previously noted, adds fluidity into the mixture.[2]

Figure 2 shows the activation of fluidity (η^{-1}) for the 0% (**P$_{7-0\%}$**), 5% (**P$_{7-5\%}$**) and 10% (**P$_{7-10\%}$**) cross-linked MePEG$_7$ polymer at low (0.26 M) and high (1.32 M) concentrations of dissolved MePEG$_7$SO$_3$H acid. In general, we expect that adding the PEG$_{13}$ cross-linker will decrease the fluidity (increase the viscosity) of the resulting cross-linked polymers. In comparing the **P$_{7-0\%}$** and **P$_{7-5\%}$** polymer–acid mixtures, we see that **P$_{7-0\%}$** polymer–acid mixture has a slightly lower fluidity than the **P$_{7-5\%}$** cross-linked polymer–acid mixture. In the low-concentration (0.26 M) mixtures of **P$_{7-0\%}$** and **P$_{7-5\%}$** polymers, the **P$_{7-5\%}$** polymer–acid mixture has a slightly lower fluidity than **P$_{7-0\%}$** polymer, as would be expected. Furthermore, the **P$_{7-10\%}$** cross-linked polymer, as expected, has a substantially smaller fluidity than the **P$_{7-0\%}$** and **P$_{7-5\%}$** cross-linked polymers. Thus, with the exception of the **P$_{7-5\%}$** polymer, this trend supports our hypothesis that added cross-linker will decrease fluidity.

Table 1. Results of VTF Fits of Fluidity Plots (Figures 2 and 3)

sample	[MePEG$_7$SO$_3$H] M	A ($\times$ 10^{-3})	B
P$_{7-0\%}$	1.32	10.3	564 ± 3
	0.26	13.5	570 ± 5
P$_{7-5\%}$	1.32	7.88	577 ± 7
	0.26	14.4	587 ± 4
P$_{7-10\%}$	1.32	70.8	504 ± 7
P$_{12-0\%}$	1.32	5.11	612 ± 5
	0.26	3.90	638 ± 2
P$_{12-5\%}$	1.32	8.40	566 ± 4
	0.26	13.8	524 ± 5
P$_{12-10\%}$	1.32	11.8	595 ± 6
	0.26	13.0	600 ± 12

Because of the excessively high viscosities of the low (0.26 M) concentration **P$_{7-10\%}$** polymer–acid mixture and both concentrations of the **P$_{7-15\%}$** polymer–acid mixtures, we were not able to measure the viscosity for these samples.

The fluidity plots in Figure 2 were fit to the VTF equation using eq 1,[16] The slopes of the data for the **P$_{7-0\%}$** and **P$_{7-5\%}$** samples appear similar indicating similar activation energies. Indeed, the pseudoactivation energies (B) for fluidity, determined from the VTF fits, are very similar (Table 1; B values between 564 and 587 K). The 10% cross-linked **P$_{7-10\%}$** sample appears to have a smaller slope, and again the pseudoactivation energy for **P$_{7-10\%}$** is significantly lower at 504 K.

$$\frac{1}{\eta} = -A\exp\left(\frac{B}{T-T_0}\right) \qquad (1)$$

Figure 3 shows a similar Arrhenius plot of the activation of fluidity (η^{-1}) for the MePEG$_{12}$ cross-linked polymer. In this data, the MePEG$_7$SO$_3$H acid is dissolved in 0% (**P$_{12-0\%}$**), 5% (**P$_{12-5\%}$**) and 10% (**P$_{12-10\%}$**) cross-linked MePEG$_{12}$ polymer at low (0.26 M) and high (1.32 M) concentrations of the MePEG$_7$SO$_3$H acid. At high concentration (1.32 M) of acid, the fluidity decreases from **P$_{12-0\%}$** to **P$_{12-5\%}$** to **P$_{12-10\%}$**, as we expected. Low concentrations (0.26 M) of the polymer–acid mixture follow the same trend. The fluidity of **P$_{12-10\%}$** polymer–acid mixtures at both concentrations (0.26 and 1.32 M) are much lower than **P$_{12-0\%}$** and **P$_{12-5\%}$** polymer–acid mixtures at the same concentrations.

The activation energy for fluidity for each of these samples, as measured by the pseudoactivation energy term B in eq 1, are similar varying between 524 and 638 K (Table 1). We were not able to measure the viscosity of the **P$_{12-15\%}$** polymer–acid mixtures because these samples had much larger viscosities, which exceeded the capabilities of our instrument.

From the fluidity data in Figures 2 and 3, we can conclude that in our MePEG polymer samples a greater concentration of cross-linker decreases the fluidity, and an increasing concentration of the MePEG$_7$SO$_3$H acid

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(16) Vogel, H. *Phys. Z* **1921**, *22*, 645.

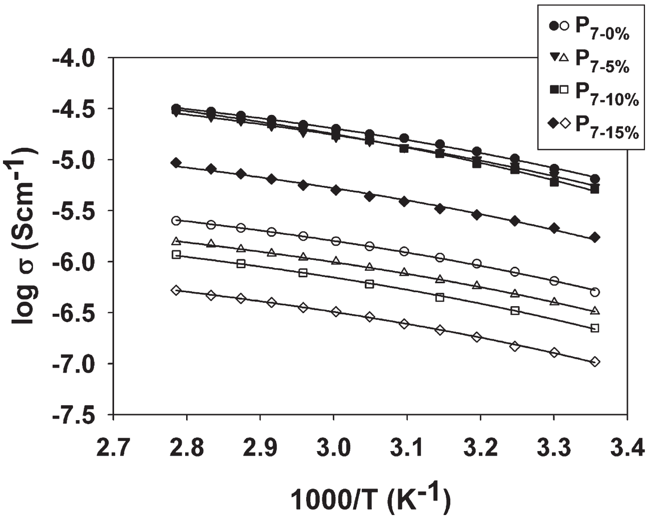

Figure 4. Activation of ionic conductivity (σ) of the MePEG$_7$SO$_3$H acid (**7a**) dissolved in noncross-linked (**P$_{7-0\%}$**) and cross-linked (**P$_{7-5\%}$**–**P$_{7-15\%}$**) MePEG$_7$ polymers at high (1.32 M; closed symbols ●, ▼, ■, ◆) and low concentration (0.26 M; closed symbols ○, ▽, □, ◇). Polymers shown: 0% cross-linked MePEG$_7$ polymer (**P$_{7-0\%}$**, ●, ○); 5% cross-linked MePEG$_7$ polymer (**P$_{7-5\%}$**, ▼,▽); 10% cross-linked MePEG$_7$ polymer (**P$_{7-10\%}$**, ■, □); 15% cross-linked MePEG$_7$ polymer (**P$_{7-15\%}$**, ◆, ◇).

increases the fluidity when added to the MePEG$_7$ polymer (both cross-linked and non-cross-linked).

Ionic Conductivity. Ionic conductivity measurements were performed on anhydrous samples of polymers and acids that had been dried on the electrode under a vacuum at 55 °C for at least 18 h. After 18 h, the conductivity was checked at 55 °C until a constant conductivity (σ) was obtained. Conductivities were measured by ac-impedance on an electrode consisting of two Pt electrodes.[2,5]

Figure 4 shows the activation of ionic conductivity (σ) for MePEG$_7$SO$_3$H acid dissolved in non-cross-linked (**P$_{7-0\%}$**) and three cross-linked (**P$_{7-5\%}$**, **P$_{7-10\%}$**, **P$_{7-15\%}$**) MePEG$_7$ polymers at low (0.26 M) and at high concentration (1.32 M). As expected, the high concentration of the acid in polymer shows larger ionic conductivities than low concentrations of the acid in polymer.[1–4] Moreover, the change in ionic conductivities as a function of added cross-linker in the polymer–acid mixtures are larger at low acid concentration than at high acid concentration. Interestingly, the conductivities of the 0, 5, and 10% cross-linked polymers are very similar at high concentration of the MePEG$_7$SO$_3$H acid, despite a significantly lower fluidity for the **P$_{7-10\%}$** cross-linked polymer compared to the **P$_{7-0\%}$** and **P$_{7-5\%}$** polymer–acid mixtures (Figure 2). This high ionic conductivity, despite lower fluidity, seems to be an effect of increased free volume in this sample.

Free Volume. The free volume (FV) of a material is essentially the volume present in the bulk material that is not directly occupied by the molecules of the polymer. The presence of a large amount of free volume, or void volume, aids the polymer in rearrangement by allowing room for the polymer to reorganize into during segmental motions. This leads to an increase in the frequency of segmental motions of the polymer and a corresponding increase in transport properties within the material. Free volume is a scalar property, and is not the best choice for comparing the behavior of these materials. The fractional free volume (FFV) is a better choice to employ to compare different materials. The FFV is the ratio of the free volume in the material to the specific volume, and is essentially a measurement of the concentration of free volume in a material. The free volume of a sample is calculated using eq 2,[11]

$$FV_{\text{sample}} = V_{\text{sp}} - V_{\text{w}} \tag{2}$$

where V_{sp} is the specific volume of the sample (concentration^{-1}) and V_{w} is the van der Waals volume of the sample (how much space the molecules directly occupy).

To calculate the FFV of our cross-linked polymer samples, we will first need to calculate the V_{sp} and V_{w} for each component in the MePEG$_n$ polymer + PEG$_{13}$ cross-linker + MePEG$_7$SO$_3$H acid mixture. We will then calculate the FFVs of the various mixtures used in this report.

The V_{sp} of the sample was calculated from density using eq 3

$$V_{\text{sp}} = \frac{\text{MW(g/mol)}}{\text{density(g/cm}^3)} = \frac{\text{cm}^3}{\text{mol}} \tag{3}$$

The density of the sample was measured at room temperature. The molecular weight (MW$_{\text{poly}}$) of the cross-linked polymer was calculated from eq 4

$$\text{MW}_{\text{poly}} = (\text{MW}_{\text{MePEG}}\chi 1) + (\text{MW}_{\text{PEG}_{13}}\chi 2) \tag{4}$$

Here, MW$_{\text{MePEG}}\chi 1$ and MW$_{\text{PEG13}}\chi 2$ are the molecular weight contributions from one monomer unit of the MePEG$_n$ polymer and one monomer unit of the PEG$_{13}$ cross-linker multiplied by their respective mole fractions (χ) in the cross-linked polymer (MW$_{\text{poly}}$). From the calculated molecular weight (MW$_{\text{poly}}$) of the cross-linked polymers, we calculated the specific volumes ($V_{\text{sp-poly}}$) using eq 3 (the calculation is detailed in Table S3 in the Supporting Information). This $V_{\text{sp-poly}}$ result is the specific volume of the cross-linked MePEG polymer (i.e., MePEG$_n$ polymer + PEG$_{13}$ cross-linker).

We can then continue, and calculate the van der Waals volume (V_{w}) of the cross-linked polymer using the "group contribution" method.[10,11,17,18] In this method, each functional group in the polymer is assigned a van der Waals volume, and these group contributions are summed to determine the total van der Waals volume of the cross-linked polymer ($V_{\text{w-poly}}$) according to eq 5

$$V_{\text{w-poly}} = (\chi\text{MePEG})(V_{\text{w-MePEG}}) + (\chi\text{PE}G\text{13})(V_{\text{w-PEG}_{13}}) \tag{5}$$

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(17) Lee, D.; Harper, A. S.; DeSimone, J. M.; Murray, R. W. *J. Am. Chem. Soc.* **2003**, *125*, 1096–1103.

(18) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441–451.

Table 2. Calculated Free Volume and Fractional Free Volume of Acid−Polymer Mixtures

polymer sample +$MePEG_7SO_3H$	[$MePEG_7SO_3H$] (M)[a]	$V_{\text{sp-mixture}}$ (cm^3/mol)[b]	$V_{\text{W-mixture}}$ (cm^3/mol)[c]	FV_{mixture} (cm^3/mol)[d]	FFV_{mixture}[e]
$\mathbf{P_{7-0\%}}$	1.32	360	231	129	**0.358**
	0.26	378	242	136	**0.360**
$\mathbf{P_{7-5\%}}$	1.32	368	236	133	**0.360**
	0.26	393	250	143	**0.364**
$\mathbf{P_{7-10\%}}$	1.32	375	240	135	**0.360**
	0.26	406	258	148	**0.365**
$\mathbf{P_{7-15\%}}$	1.32	381	244	138	**0.361**
	0.26	420	266	153	**0.365**
$\mathbf{P_{12-0\%}}$	1.32	434	275	159	**0.365**
	0.26	535	336	199	**0.372**
$\mathbf{P_{12-5\%}}$	1.32	435	277	158	**0.363**
	0.26	537	339	198	**0.369**
$\mathbf{P_{12-10\%}}$	1.32	437	278	159	**0.363**
	0.26	542	342	200	**0.369**
$\mathbf{P_{12-15\%}}$	1.32	439	279	160	**0.363**
	0.26	547	345	202	**0.369**

[a] Concentration of $MePEG_7SO_3H$ acid in the cross-linked polymer + acid mixture. [b] Specific volume of the cross-linked polymer + $MePEG_7SO_3H$ acid mixture (see Table S4 in the Supporting Information). [c] Van der Waals volume of the cross-linked polymer + $MePEG_7SO_3H$ acid mixture (see Table S4 in the Supporting Information). [d] Overall free volume of the cross-linked polymer + $MePEG_7SO_3H$ acid mixture (eq 2). [e] Overall fractional free volume of the cross-linked polymer + $MePEG_7SO_3H$ acid solution (eq 8).

In eq 5, $V_{\text{w-MePEG}}\chi$MePEG and $V_{\text{w-PEG13}}\chi$PEG13 are the sum of the "group contributions" to the van der Waals volumes for one monomer unit of the $MePEG_n$ polymer and one monomer unit of the PEG_{13} cross-linker multiplied by their respective mole fractions (χ) in the polymer (the calculation is detailed in Table S3 in the Supporting Information). This $V_{\text{w-poly}}$ result is the van der Waals volume of the cross-linked MePEG polymer (i.e., $MePEG_n$ polymer + PEG_{13} cross-linker).

Now that we have calculated the specific volume ($V_{\text{sp-poly}}$) and the van der Waals volume ($V_{\text{w-poly}}$) of the cross-linked polymer, we need to calculate these same values for the mixture of the cross-linked polymer and the $MePEG_7SO_3H$ acid. Again, the free volume of the acid and polymer mixture can be calculated by using eq 2. In this case, we will be calculating the specific volume of the $MePEG_7SO_3H$ acid + cross-linked polymer mixture ($V_{\text{sp-mixture}}$) and the analogous van der Waals volume ($V_{w\text{-}mixture}$). We calculate $V_{\text{sp-mixture}}$ by using eq 6 (see Table S4 in the Supporting Information)

$$V_{\text{sp-mixture}} = \frac{n_{\text{acid}} V_{\text{sp-acid}} + n_{\text{poly}} V_{\text{sp-poly}}}{n_{\text{acid}} + n_{\text{poly}}} \tag{6}$$

Here, n_{acid} and n_{poly} are the moles of $MePEG_7SO_3H$ acid and $MePEG_n$ cross-linked polymer in the mixture, $V_{\text{sp-acid}}$ and $V_{\text{sp-poly}}$ are the specific volumes of acid and cross-linked polymer per mole (Table S4 in the Supporting Information shows the detailed calculation of specific volumes for the acid and cross-linked polymer mixtures).

The van der Waals volume of the $MePEG_7SO_3H$ acid + cross-linked polymer mixture ($V_{\text{w-mixture}}$) was calculated using eq 7.

$$V_{\text{w-mixture}} = \frac{n_{\text{acid}} V_{\text{w-acid}} + n_{\text{poly}} V_{\text{w-cross-linked-poly}}}{n_{\text{acid}} + n_{\text{cross-linked-poly}}} \tag{7}$$

Here, n_{acid} and n_{poly} are the moles of acid and polymer in mixture respectively, $V_{\text{w-acid}}$ and $V_{\text{w-poly}}$ are the van der Waals volume of acid and polymer per mole (Table S4 in the Supporting Information shows the detailed calculation of van der Waals volumes for the acid and cross-linked polymer mixtures).

The Fractional free volume (FFV_{mixture}) of a mixture can be calculated using eq 8

$$FFV_{\text{mixture}} = \frac{FV_{\text{mixture}}}{V_{\text{sp-mixture}}} \tag{8}$$

The free volume of the $MePEG_7SO_3H$ acid + cross-linked polymer mixture was then calculated using eq 2, and the FFV according to eq 8, with the results shown in Table 2.

The free volume in a solution is temperature dependent: generally, as the temperature rises, the specific volume (V_{sp}) of the sample increases, but the molecular weight (MW_{poly}) and the van der Waals volume (V_w) remain constant. Thus, the free volume increases with increasing temperature. In this report, we assume that as the temperature changes, the free volumes for all of the samples will change similarly over the temperature range. Others have also ignored the free volume change with temperature.[17]

In Table 2, we see that there are almost no changes of the FFV from $\mathbf{P_{7-0\%}}$ to $\mathbf{P_{7-15\%}}$ polymer−acid mixtures at low (0.26 M) and high (1.32 M) concentration. That is, as we increase the concentration of the PEG_{13} cross-linker in the $MePEG_7$ polymer, we are not increasing the FFV of the mixture. For these samples, we have changed the viscosity of the samples, without appreciably changing the FFV. In high acid concentration (1.32 M) samples of the $MePEG_7$ cross-linked polymer, conductivities do not change much for $\mathbf{P_{7-0\%}}$, $\mathbf{P_{7-5\%}}$, and $\mathbf{P_{7-10\%}}$ cross-linked polymer mixtures even though the $\mathbf{P_{7-10\%}}$ mixture has a much higher viscosity than $\mathbf{P_{7-0\%}}$ and $\mathbf{P_{7-5\%}}$ mixtures (Figure 4). This effect appears to be due to similar fractional free volumes of all polymer−acid mixtures.

In low-acid-concentration (0.26 M) samples of the $MePEG_7$ cross-linked polymer, conductivities decrease from $\mathbf{P_{7-0\%}}$ polymer−acid mixture to $\mathbf{P_{7-15\%}}$ polymer−acid mixtures, even though the fractional free volumes (FFV) remain the same for all polymer−acid mixtures. This

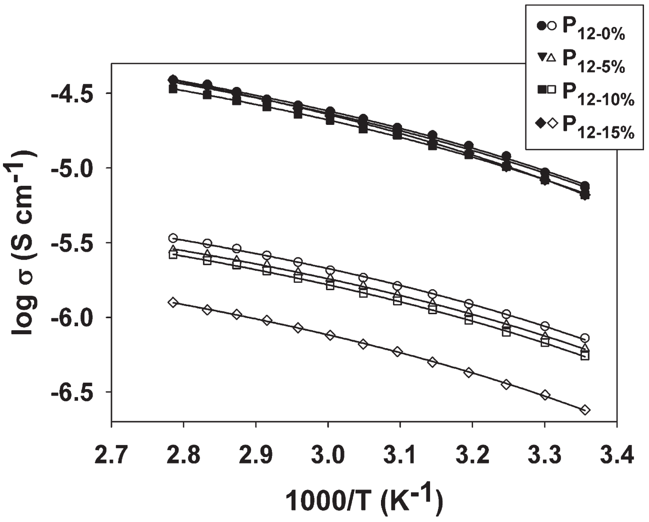

Figure 5. Activation of ionic conductivity (σ) of the MePEG$_7$SO$_3$H acid dissolved in non-cross-linked (**P$_{12-0\%}$**) and cross-linked MePEG$_{12}$ (**P$_{12-5\%}$**−**P$_{12-15\%}$**) polymers at high (1.32 M; closed symbols ●, ▼, ■, ◆) and low concentration (0.26 M; open symbols ○, ▽, □, ◇). Polymers shown: 0% cross-linked MePEG$_{12}$ polymer (**P$_{12-0\%}$**, ●, ○); 5% cross-linked MePEG$_{12}$ polymer (**P$_{12-5\%}$**, ▼, ▽); 10% cross-linked MePEG$_{12}$ polymer (**P$_{12-10\%}$**, ■, □); 15% cross-linked MePEG$_{12}$ polymer (**P$_{12-15\%}$**, ◆, ◇).

conductivity trend follows a similar change of viscosities for these materials (Figure 2). So, we can conclude that the effects of viscosity and free volume are interplaying in our polymer−acid mixture simultaneously. Furthermore, effect of viscosity appears to be more pronounced in low-acid-concentration (0.26 M) samples.

Figure 5 shows the activation of ionic conductivity (σ) for MePEG$_7$SO$_3$H acid dissolved in noncross-linked (**P$_{12-0\%}$**) and three cross-linked (**P$_{12-5\%}$**, **P$_{12-10\%}$**, **P$_{12-15\%}$**) MePEG$_{12}$ polymers at low (0.26 M) and high acid concentration (1.32 M). In contrast to Figure 4, Figure 5 shows that there is almost no difference in ionic conductivities between the **P$_{12-15\%}$** polymer−acid mixture and **P$_{12-0\%}$** polymer−acid mixture at high acid concentration (1.32 M). This is the case even though the fluidity of the **P$_{12-15\%}$** polymer-−acid mixture at high concentration (1.32 M) is much lower than that of the **P$_{12-0\%}$** polymer−acid mixture at high concentration (Figure 3). There is very little change in the FFV from the **P$_{12-0\%}$** to the **P$_{12-15\%}$** samples.

The effect of longer PEG chains on conductivity can also be seen in the low acid concentration (0.26 M) polymer/acid mixtures. At low concentrations (0.26 M), the difference in conductivities between **P$_{12-0\%}$**, **P$_{12-5\%}$**, and **P$_{12-10\%}$** polymer−acid mixtures (Figure 5) are smaller than **P$_{7-0\%}$**, **P$_{7-5\%}$**, and **P$_{7-10\%}$** polymer−acid mixtures (Figure 4). At high concentrations (1.32 M), all four of the mixtures, **P$_{12-0\%}$**, **P$_{12-5\%}$**, **P$_{12-10\%}$**, and **P$_{12-15\%}$**, have very similar ionic conductivity. However, at low concentration (0.26 M), the conductivities of **P$_{12-0\%}$**, P$_{12-5\%}$, and **P$_{12-10\%}$** are all similar because of the effect of free volume. From Table 2, we see that fraction free volumes (FFV) of all **P$_{12}$** polymers at both high concentration and low concentration are all between 0.36 and 0.37. Thus, it appears that at high concentration (1.32 M), all of these polymer−acid mixtures have the same ionic conductivity, which may be due to the fact that they all have similar fractional free volumes.

Table 3. Results of VTF Fits for Ionic Conductivity Data (Figures 4 and 5)

sample	[MePEG$_7$SO$_3$H] M	A ($\times 10^{-3}$)	B
P$_{7-0\%}$	1.32	7.27	377 ± 5
	0.26	0.59	380 ± 4
P$_{7-5\%}$	1.32	7.14	393 ± 6
	0.26	0.37	382 ± 3
P$_{7-10\%}$	1.32	10.4	438 ± 5
	0.26	0.30	398 ± 6
P$_{7-15\%}$	1.32	2.21	397 ± 10
	0.26	0.13	391 ± 4
P$_{12-0\%}$	1.32	9.53	388 ± 4
	0.26	0.76	376 ± 3
P$_{12-5\%}$	1.32	9.16	388 ± 6
	0.26	0.63	372 ± 2
P$_{12-10\%}$	1.32	8.23	388 ± 3
	0.26	0.61	379 ± 2
P$_{12-15\%}$	1.32	11.8	422 ± 3
	0.26	0.33	398 ± 2

In both Figures 4 and 5, the slopes of the data all appear similar. The pseudo activation energies (B; eq 9) were calculated from VTF fits of the activation data in Figures 4 and 5, according to eq 9 (Results in Table 3)

$$\sigma = \frac{A}{\sqrt{T}} \exp\left(\frac{-B}{T - T_0}\right) \qquad (9)$$

Walden Plot. Angell has quantitatively explored the relationship between conductivity and viscosity for ionic liquids based on the Walden rule, which relates the ionic mobility (represented by molar equivalent conductivity (Λ)) to the fluidity (η^{-1}) of the medium through which the ions move. The classical Walden rule (eq 10) is represented by

$$\Lambda\eta = \text{constant} \qquad (10)$$

This rule applies for an ideal solution where there are no ion−ion interactions. However, this relationship is not valid for real ion conducting electrolytes where ion−ion interactions present. Here, Angell has developed the "fractional" Walden rule (eq 11)[19]

$$\Lambda\eta^{\alpha} = \text{constant} \qquad (11)$$

Alpha (α) is a constant between zero and one, where α = 1 indicates ideal behavior of the solution (i.e., viscosity is the only force impeding the mobility of ions).[19] Alpha is interpreted as the ratio of activation energies for conductance and viscous flow.

The Walden rule is explored using a plot of the log of molar equivalent conductivity (Λ) versus the log of fluidity (η^{-1}). The data takes the form of a straight line where the slope of the line is equal to α. Dilute aqueous KCl solutions generally give α values near 1. In addition, the position of data points on the Walden plot reflects the behavior of the ion conducting system. For example, data points on or above the ideal Walden line (α = 1) indicate

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(19) Xu, W.; Cooper, E. I.; Angell, C. A. *J. Phys. Chem. B* **2003**, *107*, 6170–6178.

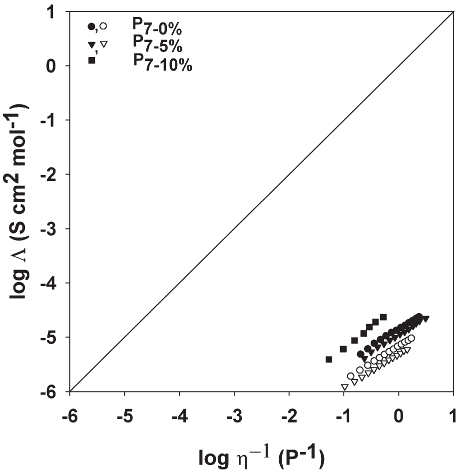

Figure 6. Walden plot of $MePEG_7$ polymers and $MePEG_7SO_3H$ acid mixture at high (1.32 M; closed symbols ●, ▼, ■) and low (0.26 M; open symbols ○, ▽) concentration. Polymers shown: 0% cross-linked $MePEG_7$ polymer (**$P_{7-0\%}$**, ●, ○); 5% cross-linked $MePEG_7$ polymer (**$P_{7-5\%}$**, ▼, ▽); 10% cross-linked $MePEG_7$ polymer (**$P_{7-10\%}$**, ■).

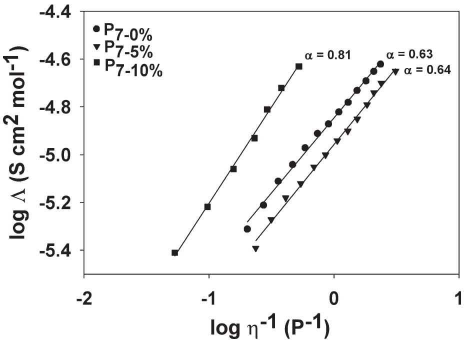

Figure 7. Walden plot of $MePEG_7$ polymers and $MePEG_7SO_3H$ acid mixture at high (1.32 M) concentration.

the behavior of good ionic liquid. Data below the ideal Walden line are generally termed poor ionic liquids.

The molar equivalent conductivity (conductivity/concentration) is proportional to ionic mobility, thus in our case, the Walden plot is a correlation of the ionic mobility of the H^+ and the fluidity of the H^+ electrolyte. Each data point in Figure 6 (and Figure S1 in the Supporting Information) represents the molar equivalent conductivity (Λ) versus the fluidity at a common temperature. All data points in Figure 6 (and Figure S1 in the Supporting Information) are below the ideal Walden line. This shows that our MePEG-based conducting polymer acid mixtures are in the region of poor ionic liquid.[20] This likely means that our $MePEG_nSO_3H$ acid does not fully dissociate in the anhydrous $MePEG_n$ polymer, but rather acts as a weak acid in the polymer solution.

One interesting result was found from the Walden Plot of $MePEG_7$ polymer−acid mixture at high concentration (1.32 M). Figure 7 shows that the molar equivalent conductivity (Λ) of the **$P_{7-10\%}$** polymer−acid mixture is almost same with the **$P_{7-0\%}$** polymer-acid mixtures though they have different viscosities. This supports our conclusion regarding the data in Figure 4 (Figures S2 and S3 in the Supporting Information show similar trends for $MePEG_{12}$ polymer−acid mixtures at low and high acid concentrations). The **$P_{7-10\%}$** sample has a higher viscosity and a larger activation energy of conductivity than the **$P_{7-0\%}$** sample. Interestingly, the alpha value of **$P_{7-10\%}$** ($\alpha = 0.81$) is larger than the alpha value of the **$P_{7-0\%}$** ($\alpha = 0.63$). According to the general interpretation of the fractional Walden rule, this difference in alpha reflects the ratio of activation energies for conductance and viscous flow.

These alpha values are close to the values that would be predicted from the ratios of the pseudoactivation energies of ion conductance (Table 3) and fluidity (Table 1). Using this data, you would predict an alpha of 0.87 for the **$P_{7-10\%}$** (actual $\alpha = 0.81$), and an alpha of 0.67 for the **$P_{7-0\%}$** (actual $\alpha = 0.63$).

Conclusions

We have shown that the viscosity and the molecular weight distribution (i.e., PDI) of our $MePEG_n$ polymers change when a PEG_{13} cross-linker is copolymerized. We have also shown that our $MePEG_n$ polymers of high viscosities can show almost the same conductivities as less-viscous $MePEG_n$ polymer systems. This effect is more prominent in the $MePEG_{12}$ polymers than the $MePEG_7$ polymers because of the longer PEG side chains. Here, the effect of increased viscosity on conductivity is offset by the lack of a change in free volume. From these results, we conclude that both structural parameters, viscosity and free volume, play an important role in controlling proton conductivity in our $MePEG_n$ polymer electrolytes. In the Walden plot, all of the data points appear below the ideal Walden line. This likely reflects that the $MePEG_7SO_3H$ acid is not fully dissociated in our $MePEG_n$ polymer and behaves as a weak acid in the polymer solution.

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Supporting Information Available: Additional tables and figures (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(20) Yoshizawa, M.; Xu, W.; Angell, C. A. *J. Am. Chem. Soc.* **2003**, *125*, 15411–15419.