Structural Characterization of a Sol−Gel-Prepared Anhydrous Proton-Conducting Electrolyte

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We have prepared a hybrid inorganic/organic, anhydrous proton-conducting polymer electrolyte $(MePEG_3SiO_3)_n$. Structural characterization of this $MePEG_3$ polymer through ^{29}Si NMR spectroscopy and gel-permeation chromatography indicates that our $MePEG_3$ polymer is composed of several different structures giving a distribution of molecular weights and silicon resonances. In this article, we show that the sol−gel-prepared $MePEG_3$ polymer is primarily composed of incompletely condensed T_8 silsesquioxane clusters. These incompletely condensed T_8 clusters are seen in the ^{29}Si NMR spectra at chemical shifts between −62 and −70 ppm. The minority composition of the $MePEG_3$ polymer contains a small amount of completely condensed T_6 silsesquioxane clusters, observed at −55.5 ppm, and T_2 dimers from −48 to −50 ppm. End-group analysis shows the presence of 0.67 uncondensed Si−OH groups per silicon atom in the $MePEG_3$ polymer, supporting the presence of incompletely condensed or ladder-type structures. The completely condensed POSS cluster $(MePEG_3)_8T_8$ was synthesized for study as a model compound, showing ^{29}Si NMR peaks between −65.5 and −69 ppm. "Q"-type silicon species are observed in the ^{29}Si NMR spectra of the $MePEG_3$ monomer and $MePEG_3$ polymer at approximately −80 to −90 and −101 ppm, respectively. The Q-type structures are generated from a coupling of triethoxysilane formed in the hydrosilation reaction.

Introduction

In this article, we present the results of ^{29}Si NMR spectroscopy and gel-permeation chromatography studies designed to determine the structure of our anhydrous proton-conducting polymer electrolyte, $(MePEG_3SiO_3)_n$ (the "$MePEG_3$ polymer"; Scheme 1). We have previously reported the synthesis of this material, a member of the relatively rare class of polymer electrolytes capable of conducting protons in the absence of plasticizing solvent or water.[1−3] Our goal is to understand the molecular-level details of ion transport in our anhydrous $MePEG_3$ polymer as a function of structure. We have previously described measurements that led us to believe that our system displays Grotthus-type proton conductivity at low to moderate temperatures, with the contribution from the vehicle mechanism of conductivity increasing at high temperatures.

Similarly structured polyhedral silsesquioxane (POSS) macromolecules are synthesized by a sol−gel polymerization of trichloro- or triethoxyorganosilanes [e.g., (phenyl)$SiCl_3$ or (phenyl)$Si(OMe)_3$].[4,5] The structures of these POSS macromolecules are denoted as T_n or $T_n(OH)_m$ (where n and m denote the numbers of silicon atoms and uncondensed OH groups, respectively, in the cluster and T indicates a trifunctional organosilane starting material). The size and type of these POSS clusters can be differentiated by the chemical shift of the silicon atoms in the ^{29}Si NMR spectra, with larger clusters showing more negative silicon ressonances.[6−8] In smaller clusters (i.e., T_2 and T_6 structures), the silicon peaks are shifted downfield (less negative) by the influence of ring strain present in the small clusters.[6,7]

Gel-permeation chromatography has shown that POSS clusters can be prepared with polydispersity indices very close to 1 (i.e., very monodisperse polymer molecular weights).[9,10] In contrast, a polydispersity index (PDI) >1 indicates the presence of a distribution of structures of different molecular weights in the sample.[8,11] Furthermore, the synthesis of different POSS structures can be accomplished by varying the polymerization conditions and the pendant R groups.[8,12] That is, an $R-Si(OR)_3$ monomer with bulky R groups will tend to favor the formation of silsesquioxane clusters.

Experimental Section

^{29}Si NMR Experiments. NMR experiments were performed on a Bruker DRX-500 instrument. Proton-decoupled ^{29}Si NMR spectra

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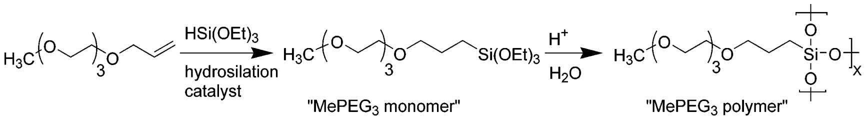
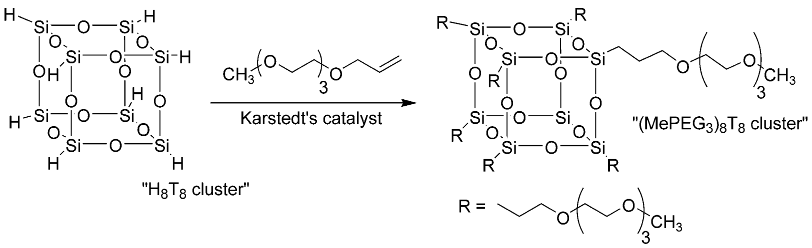
Scheme 1. Synthesis of the MePEG$_3$ Polymer



Scheme 2. Synthesis of the (MePEG$_3$)$_8$T$_8$ Cluster



were measured at 99.36 MHz using a broadband probe and tetramethylsilane as an internal standard (0 ppm). All silicon NMR samples were prepared with a high concentration (∼100 mg) of sample in $CDCl_3$ with 0.02 M $Cr(acac)_3$ as a relaxation agent and one drop of TMS. Experiments were run for 10000 scans with a 5-s delay time.

Gel-Permeation Chromatography. GPC experiments were performed using two 30-cm Polymer Laboratories Mixed-D columns and a Polymer Laboratories ELS-2100 evaporative light scattering detector using a THF mobile phase. Molecular weights were calculated by the PL-Cirrus software package using poly(styrene) molecular weight standards (PL-EasiCal PS-2, 10 standards with MW range 400000−580).

Synthesis of the MePEG$_3$ Polymer, (MePEG$_3$SiO$_3$)$_n$. The MePEG$_3$ monomer was prepared from tri(ethylene glycol) monomethyl ether [$CH_3(OCH_2CH_2)_3OH$ is referred to as MePEG$_3$OH] as previously reported.[2] Briefly, MePEG$_3$OH was coupled to allyl bromide to form the alkene-terminated MePEG$_3$CH$_2$CHCH$_2$, which was then coupled to $HSi(OEt)_3$ through a PtO_2-catalyzed hydrosilation reaction, yielding the MePEG$_3$ monomer [MePEG$_3$Si(OEt)$_3$; Scheme 1]. The MePEG$_3$ monomer was then hydrolyzed and allowed to gel, forming the MePEG$_3$ polymer, which is a viscous liquid that was dried under vacuum at ∼60 °C for several days. MePEG$_3$ monomer: ^{29}Si{H}NMR (99.36 MHz, $CDCl_3$, ppm) −48.46, −55.52, −56.47, −56.59, −58.16, −60.59, −62.17 to −69.84, −91.05 (br), −100.23 (relative to TMS).

End-Group Analysis. Chlorotrimethylsilane (0.14 mL, 1.1 mmol, 0.12 g; TMS−Cl, Aldrich) was added to a solution of 0.0281 g (1.00 mmol) of MePEG$_3$ polymer in 20 mL of toluene in an Ar-purged flask. After the reaction mixture had been stirred for 6 h under Ar at room temperature, 2.0 g of K_2CO_3 (14 mmol) was added, and the mixture was stirred for 1 h. The toluene was removed by rotary evaporation, and then the crude product was evacuated at ∼100 mTorr for 30 min to remove excess TMS−Cl. The resulting product was a clear and colorless viscous liquid. ^{1}H NMR (500 MHz, $CDCl_3$, ppm) 0.109 (s, 6H), 0.503 (br, 2H), 1.591 (br, 2H), 3.381 (s, 3H), 3.401 (br, 2H), 3.553−3.665 (br, 12H).

Synthesis of H-Terminated T$_8$ Cluster. The Si−H terminated, "naked" H_8T_8 cluster (Scheme 2) was prepared according to a literature procedure.[13] Briefly, in a 3-L round-bottom flask, concentrated HCl (20 mL) was added to 50 g of anhydrous $FeCl_3$ (Aldrich). Methanol (40 mL), hexane (350 mL), and toluene (50 mL) were then added. A solution of trichlorosilane ($HSiCl_3$, 20 mL, 0.20 mol) in 150 mL of hexane was slowly added to the stirred reaction mixture (∼10 h). The upper hexane layer was removed and stirred overnight with 14 g of K_2CO_3 and 10 g of $CaCl_2$. The mixture was filtered, and the volume was reduced. After fractional crystallization, 1.2 g of H_8T_8 (white crystals) was collected ($H_8Si_8O_{12}$, 2.8 mmol, 11% yield). ^{1}H NMR (C_6D_6, 500 MHz, ppm) 4.21 (s).

Synthesis of MePEG$_3$-Capped T8 Cluster. The MePEG$_3$−T$_8$ cluster was prepared according to the literature procedure (Scheme 2).[11] Briefly, in a 25-mL round-bottom flask, 0.2 g (0.47 mmol) of the H_8T_8 cluster was added with 2-fold molar excess (1.54 g, 7.52 mmol) of the MePEG$_3$CH$_2$CHCH$_2$ alkene in the presence of 50 μL of Karstedt's catalyst (Aldrich) and heated to 100 °C overnight. Completion of the hydrosilation reaction was monitored by the disappearance of the Si−H peak in the ^{1}H NMR spectrum. After complete disappearance of the Si−H peak, 20 mL of toluene and activated charcoal were added, and the reaction mixture was filtered. Evaporation of the solvent yielded 1.43 g of (MePEG$_3$)$_8$T$_8$. Although ^{1}H NMR spectroscopy indicated no remaining alkene at the completion of this reaction, the recovered mass indicated that the product contained excess MePEG$_3$. This excess MePEG$_3$ would not affect the ^{29}Si NMR measurements of this model compound, which was further dried under vacuum for 24 h prior to NMR measurements. ^{29}Si{^{1}H} NMR [$CDCl_3$, 99.36 MHz, 0.02M $Cr(acac)_3$, ppm] −65.76, −65.86, −66.33, −66.57, −68.83, −101.27.

Coupling of Triethoxysilane. $HSi(OEt)_3$ (1.64 g, 10.0 mmol) was combined with ∼1 mg of PtO_2 catalyst and heated to 65 °C using the same hydrosilation conditions described for synthesis of the MePEG$_3$ monomer above except without the MePEG$_3$CH$_2$CHCH$_2$ alkene. The workup procedure was halted before hydrolysis, and a small amount of oily product was recovered. Crude coupling product: ^{29}Si{^{1}H} NMR [$CDCl_3$, 99.36 MHz, 0.02M $Cr(acac)_3$, ppm] −77.02, −79.06, −81.69, −82.65, −86.08, −88.64, −88.75, −96.14.

Result and Discussion

^{29}Si NMR Spectroscopy. The solution ^{29}Si NMR spectrum (Figure 1A) of our MePEG$_3$ polymer shows several broad absorbances in the "T" region between −48 and −70 ppm.[6−8] One broad and small-area peak is apparent at −100 ppm, which is in the Q-type silica region. The ^{29}Si NMR spectrum of the unhydrolyzed MePEG$_3$ monomer also shows a small amount of Q-type silicon between −80 and −90 ppm (Figure 1B).

The ^{29}Si NMR spectra taken in our laboratory are complicated by the presence of glass in the probe and NMR tube. The data presented for all ^{29}Si NMR spectra are the result of a subtraction of a blank solution spectra containing

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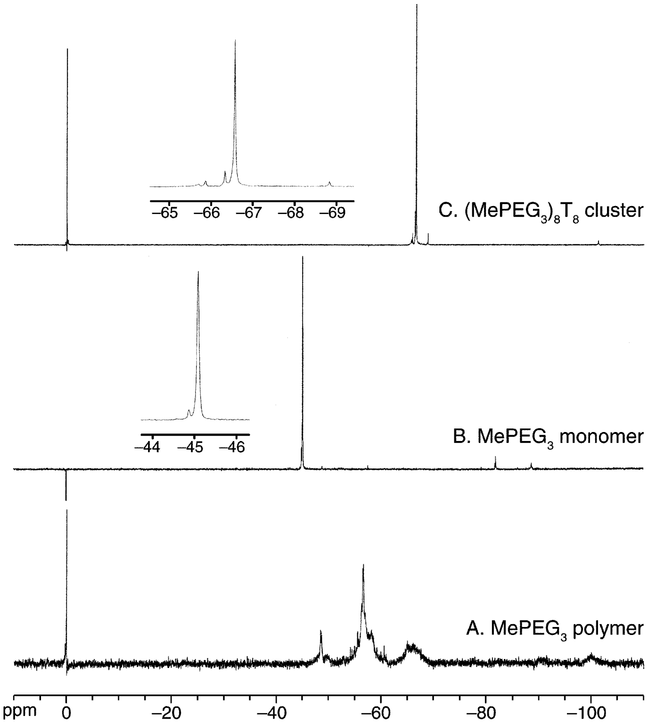

Figure 1. ^{29}Si NMR spectra for (A) the MePEG$_3$ polymer, (B) the MePEG$_3$ monomer, and (C) the (MePEG$_3$)$_8$T$_8$ cluster.

only TMS from the sample spectra. Spectral subtraction was accomplished using the “Dual” and “Diff” commands in the XWINNMR software package (Bruker). As an example, the original spectra of the MePEG$_3$ polymer, the blank spectra, and the results of the subtraction are presented in the Supporting Information (Figure S1).

Formation of Q-Type Silicon. In the ^{29}Si NMR spectra, large negative chemical shifts (−75 to −110 ppm) are common for Q-type silicon atoms [e.g., silica where silicon is attached to four oxygens, Si(−O)$_4$].[14−17] The presence of Q-type silicon in the ^{29}Si NMR spectra of our MePEG$_3$ polymer is intriguing because we expected that all of the Si atoms should be of the T-type [i.e., organosilicon bonded to three oxygen atoms and one organic group, RSi(−O)$_3$]. There are at least three plausible mechanisms for the creation of Q-type silicon in our material: (1) oxidation of the Si−H bond in triethoxysilane, HSi(OEt)$_3$, to HO−Si(OEt)$_3$ before, during, or after the hydrosilation reaction (Scheme 3A); (2) hydrolysis of the C−Si bond in the MePEG$_3$ polymer during the gelling phase (Scheme 3B); or (3) coupling of two HSi(OEt)$_3$ groups under hydrosilation conditions to form (OEt)$_3$Si−Si(OEt)$_3$, which can later be easily oxidized to two HO−Si(OEt)$_3$ groups (Scheme 3C).

We can discount the first mechanism of formation of Q-type silicon, which relies on the oxidation of HSi(OEt)$_3$ at some point before or during the reaction (Scheme 3A).[14] Upon receipt, triethoxysilane is pumped into the drybox where it is stored and handled under an inert atmosphere. We have verified through ^{1}H NMR spectroscopy that our triethoxysilane starting material contains no visible peaks indicating Si−OH or other impurities. For reactions, the HSi(OEt)$_3$ is dispensed into degassed Schlenk flasks in the drybox and is never exposed to O$_2$ during the reaction. The hydrosilation reaction is carried out on the Schlenk line, under Ar, and monitored by ^{1}H NMR spectroscopy until the Si−H peak disappears. Any excess HSi(OEt)$_3$ is then removed on the Schlenk line under vacuum. Thus, no SiH(OEt)$_3$ is left over to be oxidized and hydrolyzed to form Q-type structures. Therefore, we conclude that this mechanism cannot be responsible for the formation of Q-type silicon in our MePEG$_3$ polymer.

We can discount the second mechanism of formation of Q-type silicon, which relies on the hydrolysis of the C−Si bond in the formed MePEG$_3$ polymer (Scheme 3B). Carbon−silicon bond cleavage (or rearrangement) has been found in some POSS clusters at very high temperature (400 °C);[18,19] however, our material has never been exposed to temperatures in excess of 90 °C. Nevertheless, we explored this unlikely mechanism by taking ^{1}H and ^{13}C NMR spectra of the MePEG$_3$ polymer and MePEG$_3$ monomer. In each spectrum, no hydrolysis peaks were observed. Furthermore, the integration of the CH_2−Si peak in the ^{1}H NMR spectra indicates no loss of intensity upon condensation to the polymer. From these spectra, we conclude that our MePEG$_3$ polymer is not forming Q-type silicon atoms through hydrolysis of the C−Si bond of the MePEG$_3$ polymer.

The third possible mechanism of formation of Q-type silicon relies on the coupling of two Si−H functionalities in triethoxysilane under hydrosilation conditions to form a polysilane Si−Si bond.[11] This Si−Si bond can subsequently be oxidized to give Q-type silicon (Scheme 3C).[20−22] The oxidation of any formed Si−Si bonds is likely catalyzed by the addition of acidic water used to initiate the condensation of the monomer. To investigate this mechanism, a coupling reaction was run under the above-described hydrosilation conditions but without the alkene (i.e., only triethoxysilane and catalyst) to see if any coupling products were produced. After a workup identical to that in the MePEG$_3$ monomer synthesis, ^{29}Si NMR spectroscopy was performed on the small amount of resulting product. The ^{29}Si NMR spectrum of the coupling product showed two peaks at −81.69 and −88.75 ppm, which are consistent with Q-type silicon (Figure 2C). These peaks are very similar to the two small silicon peaks at −81.74 and −88.74 ppm observed with our MePEG$_3$ monomer (Figure 1B).

To further explore this hypothesis, we also prepared a MePEG$_3$ polymer using a 2-fold molar excess of HSi(OEt)$_3$ in the hydrosilation step (in a typical reaction, we use equimolar amounts of silane and alkene). Because the

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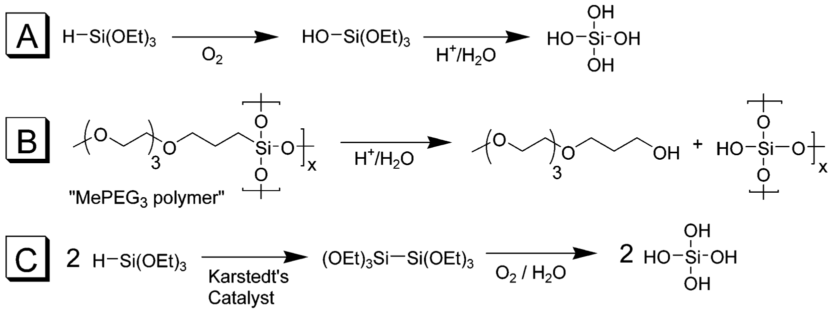
Scheme 3. Possible Routes for Q-type Silicon Formation



hydrosilation reaction is faster,[22] we expect less polysilane coupling product to be formed in the equimolar reaction. Consequently, we expect the reaction with excess triethoxysilane to produce more Si−Si couplings because of the excess and higher concentration of silane. This should lead to significantly more Q-type silicon in the excess triethoxysilane reaction.

After workup, hydrolysis, and condensation, the ^{29}Si NMR spectrum (Figure 2B) of the MePEG$_3$ polymer synthesized with excess triethoxysilane showed four broad peaks between −80 and −115 ppm (Q-type silicon). The MePEG$_3$ polymer formed from the reaction with equimolar silane and alkene shows two small broad peaks in the Q region of the ^{29}Si NMR spectrum at −91.05 and −100.30 ppm (Figure 1A). These peaks are presumably formed from the two peaks at −81.74 and −88.74 ppm in the MePEG$_3$ monomer (Figure 1B). Thus, we conclude that the small amount of Q-type silicon in our MePEG$_3$ polymer originates from a coupling of HSi(OEt)$_3$ during the hydrosilation reaction.

Because the formation of Q-type silicon atoms arises from an excess of triethoxysilane in the hydrosilation step, the formation of Q-type silicon can be diminished by reducing the concentration of triethoxysilane. Thus, we can add triethoxysilane to the hydrosilation reaction slowly over several hours such that the concentration of the triethoxysilane will be minimized at any time during the reaction, resulting the less chance of Si−Si coupling leading to less Q-type silicon in the polymer product.

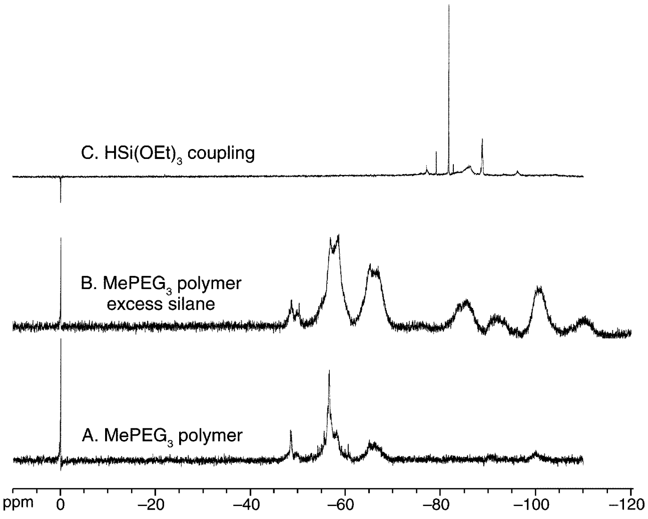


Figure 2. ^{29}Si NMR spectra for (A) the MePEG$_3$ polymer, (B) the MePEG$_3$ polymer synthesized from excess HSi(OEt)$_3$, and (C) the HSi(OEt)$_3$ coupling products.

We have previously described that conductivity in our MePEG$_n$ polymer is controlled by the volume fraction of PEG ($V_{\mathrm{f,PEG}}$) and is primarily of a Grotthus-type mechanism of ionic conductivity where the H^+ cations are handed off from one hydrogen-bonding site to another.[2] Although it is possible that the Si−OH groups present at Q-type silicon atoms might serve as basic sites, these Si−OH sites are located in a part of the MePEG$_3$ polymer that is separated from the other more numerous PEG segments. Thus, we expect that there is a lack of additional hydrogen-bonding sites near the Q-type silicon atoms that is not likely to allow for Grotthus-type proton conductivity at these Q-type sites.

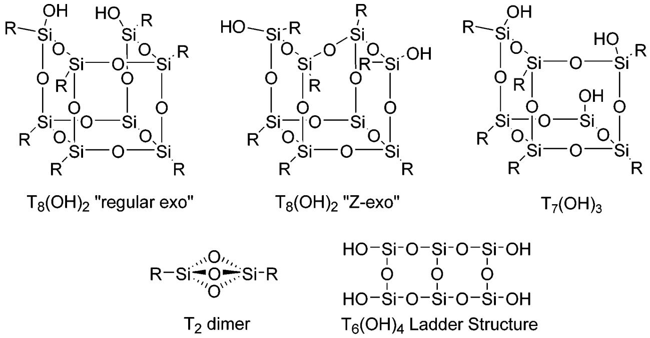
It is more likely that the fourth Si−OH site present in a Q-type silicon atom can condense with another Si−OH site, which serves to cross-link the MePEG$_n$ polymer. We expect that this cross-linking will increase the viscosity of the MePEG$_n$ polymer, resulting in an overall decrease of H^+ conductivity. For example, this increase in viscosity will slow both the frequency of PEG segmental reorganization (leading to a slowing of Grotthus conductivity) and the physical diffusion of small molecules (leading to a slowing of the vehicle mechanism of conductivity). We are currently studying how the ionic conductivity and mechanism of ionic conductivity in our MePEG$_n$ polymer are affected by cross-linking and the presence of Q-type structures.

Polymer Structure. The ^{29}Si NMR spectrum of the unhydrolyzed MePEG$_3$ monomer shows a small shoulder at −44.87 on the main peak at −45.08 ppm and a very small peak at −48.76 ppm (Figure 1B). The peak at −45.08 ppm in the MePEG$_3$ monomer is assigned as the favorable α-hydrosilation product, whereas the −44.87 ppm is the β-hydrosilation. The integration of these peaks shows that the MePEG$_3$ monomer is >90% α-hydrosilation product. The very small peak at −48.76 ppm is likely due to the formation of a small amount of the incompletely condensed T_2 dimer in the presence of moisture from the air (Chart 1). This dimer peak is also present in our MePEG$_3$ polymer samples at the same chemical shift.

After hydrolysis and condensation of the MePEG$_3$ monomer to form the MePEG$_3$ polymer, a mixture of different T-type structures was obtained. The ^{29}Si NMR spectrum of the MePEG$_3$ polymer shows the absence of any peak around the −45.00 ppm region, indicating the complete hydrolysis of the MePEG$_3$ monomer (Figure 1A).

The small peaks at −48.46 and −49.22 ppm indicate the presence of incompletely and fully condensed T_2 dimers (Chart 1). The large, broad peak between −55 and −59 ppm

Chart 1. Condensed and Incompletely Condensed Cluster Structures



mainly corresponds to Si atoms present in incompletely condensed T_8 structures with a small contribution of silicon atoms in strained T_6 triangular structures. The main two peaks in this cluster of peaks at −56.59 and −58.17 ppm correspond to the incompletely condensed T_8 structures and are assigned as "regular exo" and "Z-exo", respectively, for $T_8(OH)_2$ structure.[23,24] The small sharp peak at −60.59 ppm was assigned to the presence of small amount of the incompletely formed trisilanol $T_7(OH)_3$ (Chart 1).[7,8,24] The small peak at −55.52 ppm is assigned as the completely condensed and strained T_6 structure.[6,7,25]

The broad peak with a maximum at −66.28 ppm is consistent with the fully condensed T_8 structure where each Si atom is attached with three Si−O−Si bonds.[6] It is also possible that a small amount of T_{10} cluster and ladder polymer might be hidden under this broad peak between −62.2 and −69.8 ppm.

Residual, uncondensed −OH groups in our $MePEG_3$ polymer are difficult to detect using FT-IR and ^1H NMR spectroscopies. To investigate the presence of incompletely condensed structures observed in the ^{29}Si NMR spectra, we exposed the polymer samples to chlorotrimethylsilane (TMS−Cl) to label residual −OH groups. The very reactive TMS−Cl reacts with exposed −OH groups to yield an −OTMS group that is easily detected and quantified in the ^1H NMR spectra (nine protons in a very sharp peak in a known location vs one proton in a broad and variable peak). After reaction with TMS−Cl, the modified $MePEG_3$ polymer shows a new, sharp peak at 0.109 ppm in the ^1H NMR spectra having an area of 6H (referenced to the terminal CH_3O− group in the MePEG) (Figure S2). Assuming that each exposed −OH group couples to a TMS−Cl to yield 9H, our result of 6H indicates that each silicon atom in the $MePEG_3$ polymer has an average of 0.67 exposed −OH groups. Thus, our $MePEG_3$ polymer contains a significant fraction of uncondensed structures.

The presence of fully condensed T_8 structure (observed in the ^{29}Si NMR spectra) was confirmed by synthesizing the $(MePEG_3)_8T_8$ polymer cluster as a model (Scheme 2). This T_8 structure was synthesized by first preparing the hydrogen-terminated H_8T_8 structure and then hydrosilating the H_8T_8 with the $MePEG_3$−alkene.[11] The ^{29}Si NMR spectrum of $(MePEG_3)_8T_8$ gives a small sharp peak at −66.33 ppm and a large sharp peak at −66.57 ppm (Figure 1C). These two peaks are due to the small fraction of β- (−66.33 ppm) and large fraction of α-hydrosilation attachment (−66.57 ppm) of the alkene to form the $(MePEG_3)_8T_8$ polymer cluster. In addition, the formation of two β sites on the same $(MePEG_3)_8T_8$ cluster yields a pair of diastereomers (the product of the β-hydrosilation is chiral). The two small peaks in Figure 1C at −65.86 and −68.83 ppm are the two resulting diastereomers.[11] As expected, the intensities of the diastereomeric peaks are less than the intensity of the β-peak owing to their lower probability of formation. The β-peak, in turn, is lower in intensity than the main α-peak. One small peak is also seen at −101.23 ppm (in the Q-type silica region), likely resulting from the Si−Si coupling of two T_8 cluster that is possible in the presence of Pt catalyst.[11]

The NMR peaks from the $(MePEG_3)_8T_8$ polymer cluster are significantly sharper than the peaks from the sol−gel-synthesized $MePEG_3$ polymer. This broadening of the peaks in the sol−gel $MePEG_3$ polymer is likely due to the presence of different combinations of α- and β-hydrosilation products and different incompletely condensed structures, including small amounts of dimers and Q-type silicon. The presence of Q-type silicon atoms can result in a distribution of structures and correspondingly broad NMR peaks. Bulky substituents can increase the broadening of the ^{29}Si NMR peaks.[7,26] Interestingly, the ^{29}Si NMR spectrum of the $(MePEG_3)_8T_8$ cluster gives sharp and well-resolved peaks for α- and β-hydrosilation products because there is no structural inhomogeneity in the T_8 cluster skeleton. This is also true in the case of the $MePEG_3$ monomer where sharp peaks were resolved for both α- and β-products. However, upon sol−gel condensation to the $MePEG_3$ polymer, the presence of structural variability and incomplete condensation significantly broaden the observed NMR peaks.

Gel-Permeation Chromatography. GPC of our $MePEG_3$ monomer (Scheme 1, Figure 3A) shows a weight-average molecular weight (M_w) of 931 g/mol and a number-average molecular weight (M_n) of 688 g/mol, with a polydispersity index (PDI) of 1.35 (calculated MW = 368 g/mol). The expected PDI for the monomer should be close to 1 for a monodisperse molecular material (our instrument gives PDIs as low as 1.04 for our narrow-molecular-weight standards). In fact, the GPC-measured molecular weight of a monodisperse Cl-functionalized T_8−POSS clusters has been reported to have a very small polydispersity index (PDI = 1.10), indicating a very narrow molecular weight distribution.[9] Interestingly, the authors noted a significant underestimation of the true M_w and M_n values calculated from poly(styrene) molecular weight standards.

The calculated molecular weight of our $MePEG_3$ monomer is 368 g/mol, which is below the smallest poly(styrene) MW standard of 580 Da. In addition, it was necessary to inject a large concentration of the monomer into the GPC, because the ELS detector has difficulty detecting low-MW analytes

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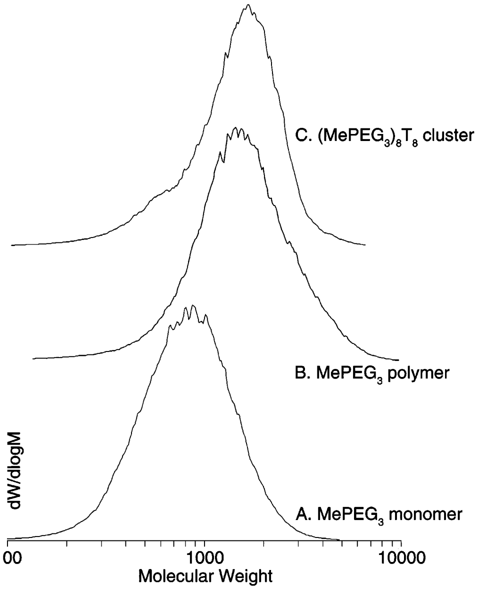

Figure 3. Molecular weight distribution plots of the (A) the $MePEG_3$ monomer, (B) the $MePEG_3$ polymer, and (C) the $(MePEG_3)_8T_8$ cluster.

(for ELS detectors, $I \propto MW^2$). This high concentration can saturate the pores in the GPC column, allowing a portion of the analyte to elute out faster (i.e., high-molecular-weight side) than it would at a lower concentration. This broadening on the high-molecular-weight side (as seen in Figure 3A) will appear as a greater polydispersity and an overestimation of the molecular weight. In addition, it is possible that the $MePEG_n$ polymers might have an affinity interaction with the polystyrene/divinylbenzene gel stationary phase of the MIXED-D GPC column, leading to band broadening. Furthermore, the presence of a small amount of dimer and Q-type silicon (as seen in the ^{29}Si NMR spectra) could also lead to a band broadening and a larger PDI.[11]

The GPC of our sol−gel-synthesized $MePEG_3$ polymer yields a broad peak (Figure 3B; M_w = 1817 g/mol, M_n = 1264 g/mol, PDI = 1.44). The moderate PDI value of 1.44 indicates some dispersity in the molecular weight distribution, which supports the presence of a distribution of different cluster structures with a small amount of Q-type silicon. The poly(styrene)-based linear calibration standards are known to underestimate the number-average molecular weights (M_n) of branched polymers. The three-dimensional structures of these macromolecules give high PDI values as calculated by M_w/M_n.[5,9,27,28] Thus, the true M_n value should be higher, leading to a smaller true PDI.

The GPC was also measured for the $(MePEG_3)_8T_8$ cluster (Figure 3C; M_w = 1587 g/mol, M_n = 1137 g/mol, PDI = 1.39). The moderate PDI suggests that this cluster contains some different structures (i.e., T_8−T_8 dimers) that can be generated from the coupling of two H_8T_8 oligomers or Q-type silicon structures in the presence of Karstedt's catalyst or some higher oligomers.[11] This is supported by the ^{29}Si NMR spectrum, which shows a Q-type peak at −101.23 ppm. The sol−gel $MePEG_3$ polymer that was synthesized using excess $HSi(OEt)_3$ yields larger molecular weights and dispersity (M_w = 3151 g/mol, M_n = 1132 g/mol, PDI = 2.78). This large PDI and mass are likely due to the presence of a larger concentration of Q-type silicon atoms (as seen in the ^{29}Si NMR spectrum) than are present in the previously prepared $MePEG_3$ polymer.

Conclusions

We have shown that our sol−gel-prepared $MePEG_3$ polymer contains a distribution of several different structures, with the majority of the $MePEG_3$ polymer composed of incompletely condensed T_8 clusters (and possibly T_{10} and ladder structures). The ^{29}Si NMR spectra of the $MePEG_3$ monomer show that our hydrosilation step produces >90% α-attachment of the $MePEG_3$ oligomer. This α-attachment is carried through into the $MePEG_3$ polymer, yielding a product composed primarily of α-substituted units. The presence of the incompletely condensed structures is shown through end-group labeling of residual −OH groups. GPC measurements of the molecular weight and polydispersity index show that our $MePEG_3$ polymer has a molecular weight distribution that is similar to and consistent with the synthesized $(MePEG_3)_8T_8$ cluster.

We have also shown that a small amount of Q-type silicon structures are formed in our $MePEG_3$ polymer during the hydrosilation attachment of the $MePEG_3$ oligomers. We have shown that these Q-type structures are generated by the coupling of triethoxysilane in the presence of the hydrosilation catalyst. The incorporation of these Q-type structures leads to structural inhomogeneity and increased molecular weights and polydispersity in the resulting polymers.

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Supporting Information Available: Two plots showing (1) the subtraction of glass peaks from the ^{29}Si NMR spectra, and (2) the NMR spectra of the end-group labeling of residual −OH groups in the $MePEG_3$ polymer. This material is available free of charge via the Internet at http://pubs.acs.org.

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