Star-Shaped Block Copolymer-Based Proton Exchange Membranes with Continuous Ionic Phase Domains and Their Conductivity: Postprint

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Abstract

Using octafunctional silsesquioxane (BCP-POSS) as the initiator, a star-shaped POSS-(PMMA-b-PS)8 block copolymer with poly(methyl methacrylate)-b-polystyrene arms was synthesized via two-step atom transfer radical polymerization (ATRP). A sulfonated hybrid polymer POSS-(PMMA-b-SPS)8 with identical sulfonation degree was prepared through post-sulfonation and employed to fabricate proton exchange membranes (PEMs). The conductivity of both PEMs at various hydration states was analyzed as a function of humidity, revealing that the PEM with longer SPS segments exhibited higher proton conductivity under equivalent low hydration conditions. Thermogravimetric analysis (TGA) results demonstrated that both PEMs possess high-temperature water retention capability and elevated initial thermal decomposition temperatures. The microphase structures of PEMs with different block ratios were investigated using transmission electron microscopy (TEM) and atomic force microscopy (AFM), which revealed that the PEM with longer SPS segments favored a bicontinuous microphase morphology conducive to proton conduction. Low-field nuclear magnetic resonance spectroscopy was utilized to determine the spin-spin relaxation time T2 and segmental molecular mobility characteristics of the different copolymers under low hydration states, demonstrating that the PEM with longer SPS segments exhibited a narrow, elongated microphase-separated morphology with favorable connectivity, displaying a higher proton spin diffusion coefficient and consequently superior proton conductivity under low humidity environments.

Full Text

Proton Exchange Membrane Based on Star-Shaped Block Copolymer with Well-Connected Ionic Domains and Its Conductivity Properties

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ABSTRACT

A star-shaped block copolymer, POSS-(PMMA-b-PS)$_8$, with poly(methyl methacrylate)-b-polystyrene arms was synthesized via a two-step atom transfer radical polymerization (ATRP) using octafunctional polyhedral oligomeric silsesquioxane (POSS) as the initiator. The sulfonated hybrid polymer POSS-(PMMA-b-SPS)$_8$ was subsequently prepared through post-sulfonation and used as the polymer matrix for proton exchange membranes (PEMs). The conductivity of two PEMs with different hydration states was analyzed as a function of humidity, revealing that the PEM with longer SPS blocks exhibited higher proton conductivity under low hydration conditions at the same sulfonation degree. TGA analysis demonstrated that both PEMs possessed high-temperature water retention capability and high initial thermal decomposition temperatures. Transmission electron microscopy (TEM) and atomic force microscopy (AFM) analysis of the microphase structure of PEMs with different block ratios showed that longer SPS blocks favored the formation of a well-connected microphase morphology conducive to proton conduction. Low-field nuclear magnetic resonance spectroscopy was employed to measure the spin-spin relaxation time T_2 and characterize the molecular motion of chain segments under low hydration states. The results indicated that the PEM with longer SPS blocks formed a narrower and better-connected microphase-separated morphology, exhibiting a higher proton spin-diffusion coefficient and consequently higher proton conductivity under low humidity conditions.

KEY WORDS organic polymer materials, proton exchange membrane, atom transfer radical polymerization (ATRP), star-shaped block copolymer, polyhedral oligomeric silsesquioxane, microstructure

1. Introduction

Proton exchange membranes (PEMs) are critical components in proton exchange membrane fuel cells (PEMFCs), serving to separate the anode and cathode while conducting protons. The performance of PEMs directly affects fuel cell efficiency. The next generation of PEMs aims to achieve higher water retention and stability at elevated temperatures while maintaining high proton conductivity under low humidity conditions [1-7].

Research on sulfonated PEMs has shown that the distribution of sulfonic acid groups on the polymer backbone influences the microphase structure, which in turn affects proton conduction properties. Takimoto [8] found that although highly sulfonated membranes exhibited high water uptake, the irregular distribution of sulfonic acid groups created "dead-end" hydrophilic domains with poor connectivity, resulting in low proton conductivity under low humidity. Einsla et al. [9] demonstrated significant differences in phase structures between block copolymers and random copolymers with identical compositions. Random sulfonated polymers formed small microphase domains with poor connectivity between hydrophilic segments, whereas block copolymers exhibited highly separated hydrophilic and hydrophobic domains with well-connected hydrophilic regions. Such block copolymer PEMs showed reduced humidity dependence and maintained high proton conductivity under low humidity conditions. Therefore, controlling the microphase-separated structure of hydrophilic/hydrophobic domains in PEMs can yield membranes with well-connected ionic domains, which is beneficial for enhancing proton conductivity at low humidity. However, understanding what type of connected ionic domain structure facilitates proton transport and how to obtain such microphase structures in PEMs remains a key challenge.

Compared with linear block copolymers, polymers with complex topologies such as comb-shaped and hyperbranched structures offer richer microphase morphologies that facilitate control over sulfonic acid group distribution, thereby creating efficient ionic domains for proton transport and ensuring high conductivity [10-13]. Polyhedral oligomeric silsesquioxane (POSS)-containing block copolymers [14] possess strong designability and rich self-assembly behavior, showing promising applications in ordered nanostructure design. In this work, POSS was employed as an intramolecular crosslinking agent to initiate the synthesis of star-shaped block copolymers. The inner PMMA block near the POSS core provides excellent film-forming properties, while the outer SPS block serves as the ionic domain. By adjusting the block ratio of the hybrid copolymer, the distribution of sulfonic acid groups (ionic domains) can be controlled at the terminal blocks of the star-shaped copolymer, thereby improving the connectivity between ionic and non-ionic domains to enhance proton conductivity under low humidity. The microstructure of the PEMs was analyzed, and low-field NMR was used to investigate the effect of block composition on chain dynamics under low hydration states, providing a theoretical foundation for designing high-performance PEMs for low-humidity applications.

2. Experimental

2.1 Materials

Methyl methacrylate (MMA, analytical grade), styrene (St, analytical grade), pentamethyldiethylenetriamine (PMDETA, 98% purity), cuprous chloride (analytical grade), neutral alumina (chemical grade), N,N-dimethylformamide (DMF, analytical grade), anhydrous methanol (analytical grade), and 1,2-dichloroethane (DCE, analytical grade) were used as received. Octachloropropyl polyhedral oligomeric silsesquioxane (POSS-Cl_8) was synthesized in our laboratory and characterized by ^{1}H, ^{13}C, and ^{29}Si NMR, confirming its symmetric octafunctional cage structure [15].

2.2 Synthesis of POSS-(PMMA -b-SPS $)_8$

POSS-(PMMA -b-SPS $)_8$ was synthesized via ATRP using POSS-Cl_8 as the initiator in a two-step process.

(1) Synthesis of POSS-(PMMA-Cl$)_8$ macroinitiator: Appropriate amounts of POSS-Cl_8, PMDETA, cuprous chloride, MMA, and toluene were added to a 100 mL three-neck flask equipped with a condenser and magnetic stirrer. The mixture was stirred under nitrogen protection and gradually heated to 100–110°C for 24 h. The product was dissolved in tetrahydrofuran, passed through a neutral alumina column to remove the catalyst, and precipitated in anhydrous methanol. After vacuum drying, the white solid macroinitiator POSS-(PMMA-Cl$)_8$ was obtained.

(2) Synthesis of POSS-(PMMA -b-PS $)_8$ block copolymer: The macroinitiator POSS-(PMMA-Cl$)_8$, PMDETA, cuprous chloride, styrene, and toluene were reacted at 100–110°C for 48 h. After catalyst removal and precipitation in anhydrous methanol, followed by vacuum drying, the POSS-(PMMA -b-PS $)_8$ block copolymer was obtained. By adjusting the feed ratio of MMA to St, two copolymers with different block ratios were synthesized and designated as POSS-(PMMA -b-PS $)_8$-a and POSS-(PMMA -b-PS $)_8$-b. The yields ranged from 34.2% to 38.7%, and the block copolymers were used without further purification.

For sulfonation, the block copolymer was placed in a three-neck flask with 1,2-dichloroethane (25 mL) as solvent. Excess concentrated sulfuric acid was added based on the styrene content, and the mixture was stirred at 50°C for 24 h to ensure similar sulfonation degrees for both copolymers. The product was concentrated, precipitated in deionized water, washed to neutral pH, and dried to constant weight to obtain POSS-(PMMA -b-SPS $)_8$.

2.3 Membrane Preparation

Appropriate amounts of POSS-(PMMA -b-SPS $)_8$ polymer were dissolved in DMF with heating and ultrasonication. The solution was cast onto a petri dish and dried in a vacuum oven at 65°C for 8 h, followed by post-treatment at 80°C for 2 h to obtain the PEM.

2.4 Polymer Characterization

^{1}H NMR spectra were recorded on a Bruker AV400 spectrometer using $CDCl_3$ as solvent and tetramethylsilane (TMS) as internal standard. Molecular weight and polydispersity were determined by gel permeation chromatography (GPC) on a Waters 150C system equipped with a Shodex OHpak SB-803 HQ column (300 × 8 mm) using THF as eluent.

2.5 PEM Performance Testing and Morphological Observation

Ion Exchange Capacity (IEC): The IEC was determined by titration. A dried membrane sample (mass m) was immersed in 0.01 mol/L NaOH solution (volume V_1) for 12 h at 80°C, then back-titrated with 0.005 mol/L standard H_2SO_4 solution (volume V_2). The IEC was calculated as:

$$IEC = \frac{0.01(V_1 - V_2)}{m} \quad (\mathrm{meq} \cdot \mathrm{g}^{-1})$$

Water Uptake (λ): The hydration number (λ, number of water molecules per sulfonic acid group) at 30°C and various relative humidities (0%, 50%, 70%, 90%, 98%) was measured by thermogravimetric analysis (TGA) using a TA Instruments Q5000SA. The water uptake was calculated as:

$$\lambda = \frac{w_{\mathrm{wet}} - w_{\mathrm{dry}}}{w_{\mathrm{dry}} \times IEC} \times 1000$$

Proton Conductivity (σ): Proton conductivity was measured by AC impedance spectroscopy using a Solartron 1260A frequency response analyzer over a frequency range of 100 Hz-1 MHz. Measurements at different humidities were performed in an Espec SH-241 temperature/humidity chamber at 30°C, with each humidity condition maintained for 1 h before measurement. The conductivity was calculated as:

$$\sigma = \frac{L}{R \times W \times T}$$

where L is the distance between platinum electrodes (0.776 cm), R is the membrane resistance, and W and T are the membrane width and thickness (in cm), respectively.

Thermal Stability and Water Retention: These properties were evaluated by TGA (TA Instruments Q500) under two conditions: (1) hydrated membranes were heated from room temperature to 160°C at 5°C/min in nitrogen to evaluate water retention; (2) after cooling to room temperature, the samples were reheated to 600°C at 10°C/min to determine polymer decomposition temperature.

Morphology: TEM images were obtained on a Hitachi H-7650 microscope. Membranes were stained in 2% lead acetate solution for one week to visualize ionic domains, then embedded in epoxy resin, cryo-microtomed into ~50 nm thick sections, and examined at 80 kV accelerating voltage. AFM surface morphology was examined on an Asylum Research FP-3D-SA system in tapping mode. Membranes were cast from DMAC solutions and annealed at 80°C for >2 h.

NMR Analysis: Spin-spin relaxation time T_2 and proton spin-diffusion coefficients were measured at room temperature on a VTMR20-010V-T low-field NMR analyzer using the CPMG method to obtain free induction decay (FID) curves. A biexponential model was fitted using linear least-squares regression [16] with Matlab software and PSO algorithm to determine T_2 and T_2 :

$$M(t) = M_{0r} \exp\left(-\frac{t}{T_{2r}}\right) + M_{0f} \exp\left(-\frac{t}{T_{2f}}\right)$$

where M_0 and M_0 are the initial magnetizations, and T_2 and T_2 are the relaxation times for the rigid and flexible phases, respectively. The proton spin-diffusion coefficient $D(T_2)$ was calculated following the method in reference [17].

3. Results and Discussion

3.1 Synthesis of POSS-(PMMA -b-SPS $)_8$ Block Copolymers

The synthetic route for star-shaped hybrid polymers POSS-(PMMA -b-PS $)_8$ and their sulfonated derivatives POSS-(PMMA -b-SPS $)_8$ is shown in [Figure 1: see original paper]. The arm structures of the two copolymers were analyzed by ^{1}H NMR, with spectra presented in [Figure 2: see original paper]. The signals at 3.67, 2.12–0.77 ppm correspond to methylene protons from both PMMA and PS main chains, while the resonances at 6.44–7.25 ppm are assigned to the five aromatic protons of PS. These results confirm successful polymerization of MMA and St from the POSS macroinitiator. Based on peak area ratios, the block compositions were determined to be m:n = 26:156 and 16:200 for the two products (see).

GPC traces are shown in [Figure 3: see original paper]. Both copolymers exhibit monomodal distributions, indicating the absence of homopolymer or ungrafted species (which would appear as additional peaks or broad molecular weight distributions). The polydispersity indices (PDI) of 2.44 and 1.90 are narrower than conventional free radical polymerization but broader than typical linear block copolymers from living polymerization. This is attributed to steric hindrance during polymerization of topologically complex structures, initiator efficiency, and differences in hydrodynamic volume of star-shaped polymers compared to linear analogs. Similar results have been reported for POSS-(PCL-b-PTFEA)$_8$ [18] and other star-like block copolymers [19].

Combining NMR and GPC data, the two polymers were identified as POSS-(PMMA$_{26}$-b-PS$_{156}$)$_8$ and POSS-(PMMA$_{16}$-b-PS$_{200}$)$_8$. Sulfonated membranes prepared from POSS-(PMMA$_{26}$-b-SPS$_{156}$)$_8$ and POSS-(PMMA$_{16}$-b-SPS$_{200}$)$_8$ exhibited IEC values of 2.77 and 3.85 $\text{meq}\cdot\text{g}^{-1}$, respectively, as determined by titration. The difference in IEC primarily arises from the relative length of the PS blocks.

3.2 Water Uptake and Proton Conductivity as Functions of Humidity

[Figure 4: see original paper] shows the hydration number (λ, water molecules per sulfonic acid group) at 30°C as a function of relative humidity. Both PEMs show increasing λ with humidity, with POSS-(PMMA$_{26}$-b-SPS$_{156}$)$_8$ exhibiting higher λ values, reaching a maximum of 6 at 98% RH. This indicates low water uptake even at high humidity for both membranes.

Proton conductivity versus humidity is plotted in [Figure 5: see original paper]. Throughout the humidity range, POSS-(PMMA$_{16}$-b-SPS$_{200}$)$_8$ consistently shows higher conductivity than POSS-(PMMA$_{26}$-b-SPS$_{156}$)$_8$. At low humidity (30% RH), the conductivities are $1.33 \times 10^{-4}\ \text{S}\cdot\text{cm}^{-1}$ and $2.07 \times 10^{-3}\ \text{S}\cdot\text{cm}^{-1}$, respectively—a difference of approximately one order of magnitude. This demonstrates that longer SPS blocks significantly enhance proton conductivity under low humidity, surpassing Nafion 117 ($1.4 \times 10^{-4}\ \text{S}\cdot\text{cm}^{-1}$ at 34% RH) [20] by an order of magnitude.

The relationship between conductivity and λ is shown in [Figure 6: see original paper]. At equivalent λ values, the longer SPS block copolymer POSS-(PMMA$_{16}$-b-SPS$_{200}$)$_8$ exhibits higher conductivity. Under low hydration, the higher density of sulfonic acid groups in the longer SPS blocks reduces the resistance for proton hopping between acid sites and facilitates the formation of continuous proton transport channels.

3.3 Water Retention and Thermal Stability

Water retention and thermal stability were evaluated by TGA under two conditions: (1) heating hydrated membranes from room temperature to 160°C to assess water retention, and (2) reheating the dried samples to 600°C to determine polymer decomposition temperatures.

As shown in [Figure 7a: see original paper], the water retention at 100°C is 45% and 50% for POSS-(PMMA$_{26}$-b-SPS$_{156}$)$_8$ and POSS-(PMMA$_{16}$-b-SPS$_{200}$)$_8$, respectively. The longer SPS block membrane exhibits better water retention due to its higher sulfonic acid group density. [Figure 7b: see original paper] shows the second heating stage, with initial decomposition temperatures (5% weight loss) of 262°C and 318°C, respectively, indicating excellent thermal stability. The combination of high-temperature water retention and high decomposition temperature makes these PEMs promising for high-temperature PEMFC applications.

3.4 Microphase-Separated Morphology

TEM micrographs of the PEMs are presented in [Figure 8: see original paper], where dark regions correspond to ionic SPS domains and bright regions to non-ionic PMMA domains [21,22]. The block length significantly affects the microphase morphology. POSS-$(PMMA_{26}$-b-$SPS_{156})_8$ exhibits ~100 nm cylindrical SPS domains, while the longer SPS block copolymer POSS-$(PMMA_{16}$-b-$SPS_{200})_8$ forms narrower (30–40 nm), more elongated, and interconnected ionic domains. During solvent evaporation, the POSS core imposes greater constraints on shorter SPS blocks, favoring larger domain structures. In contrast, longer SPS blocks have greater mobility, enabling the formation of narrow, tortuous, and interconnected morphologies.

AFM surface morphology and phase images in [Figure 9: see original paper] confirm these observations. The longer SPS block membrane shows more elongated and better-connected hydrophilic channels (dark regions), consistent with TEM results.

3.5 Chain Dynamics and Proton Spin Diffusion

Low-field NMR was used to measure T_2 relaxation times and probe chain dynamics in different phases. The FID curves and biexponential fits are shown in [Figure 10: see original paper], with fitting parameters listed in . The fast-relaxing component (T_2) corresponds to the rigid SPS phase, while the slow-relaxing component (T_2) corresponds to the flexible PMMA phase. The SPS phase dominates the relaxation due to its higher magnetization.

Interestingly, the longer SPS block copolymer POSS-$(PMMA_{16}$-b-$SPS_{200})_8$ exhibits a shorter T_2 , indicating stronger proton confinement and slower chain motion in the rigid phase. However, it shows a larger proton spin-diffusion coefficient $D(T_2)$, which correlates with higher proton conductivity. This apparent contradiction is resolved by the microstructural analysis: the longer SPS blocks form a well-connected, interpenetrating morphology that provides efficient proton transport pathways, overcoming the effect of stronger proton confinement. Thus, the connected microphase-separated structure plays a decisive role in proton conduction in this system.

4. Conclusion

Using octafunctional POSS as an initiator, two star-shaped block copolymers, POSS-(PMMA$_{26}$-b-PS$_{156}$)$_8$ and POSS-(PMMA$_{16}$-b-PS$_{200}$)$_8$, were successfully synthesized via ATRP. After sulfonation and solution casting, PEMs were prepared. Under identical humidity conditions, the membrane with longer SPS blocks demonstrated higher proton conductivity. Both PEMs exhibited excellent high-temperature water retention and high initial decomposition temperatures. Although the longer SPS blocks showed slower chain motion, they formed a connected, interpenetrating microphase-separated structure that provided efficient proton transport channels, ensuring high proton conductivity under low humidity. These findings provide a theoretical basis for designing high-performance PEMs for low-humidity applications.

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Note: Figure translations are in progress. See original paper for figures.