Synthesis and Characterization of Highly Proton Conducting Sulfonated Polytriazoles

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ABSTRACT: This article describes the synthesis and characterization of highly sulfonated polytriazole copolymers (PTSQSH-I to IV) with IECw values ranging from 2.41 to 3.49 mequiv g\(^{-1}\). The copolymers were synthesized by click reaction between equimolar amount of a dialkyne monomer, potassium 2,5-bis(2-propyn-1-xylo)benzenesulfonate, and a mixture of two different diazide monomers, 4,4-bis[3′-trifluoromethyl-4′-(4-azidobenzenoxygen)]benzyl[biphenyl and 4,4′-diazido-2,2′-stilbene disulfonic acid disodium salt. The copolymers were characterized by Fourier transform infrared and NMR spectroscopy techniques. The membranes were prepared by dissolving the salt form of the copolymers in dimethyl sulfoxide. The copolymers showed high thermal, mechanical, and oxidative stabilities, and the acidified membranes showed very high proton conductivity (43−173 and 132−304 mS cm\(^{-1}\) at 30 and 80 °C, respectively). Transmission electron microscopy images confirmed the formation of well-phase-separated morphology with interconnected hydrophilic domains (20−150 nm).

INTRODUCTION

The last few decades have witnessed a remarkable growth on proton exchange membrane (PEM) materials as an alternative to sulfonated perfluoropolymers, for example, Nafion 117, Aciplex, and Flemion.\(^{1−4}\) In this context, a variety of proton exchange membranes (PEMs) based on sulfonated poly-(arylene ether sulfone)s,\(^{5−7}\) sulfonated poly(arylene ether ketone)s,\(^{8−10}\) sulfonated poly(arylene thioether sulfone)s,\(^{11−12}\) sulfonated copolyimides,\(^{13}\) and sulfonated poly-(benzimidazole)s,\(^{14−16}\) have been prepared and their properties been studied.

The copper(I)-catalyzed azide−alkyne click (CuAAC) reactions were extensively studied in organic synthesis because of their outstanding features, for example, versatility, high efficiency, regioselectivity, functional group tolerance, easy product isolation, and high yields.\(^{20−21}\) Because of all of these unique features, the click reactions were extended to the synthesis of polymers and accordingly several linear, hyper-branched, graft, and cross-linked polymers were prepared.\(^{22−28}\) Recently, the CuAAC reaction was used for the synthesis of PEM materials.\(^{29−36}\) The proton conductivity of a PEM material is associated with a combination of ion exchange capacity (IECw) or degree of sulfonation (DS) and the interconnected phase-separated morphology.\(^{34}\) Typically, high IECw values always result in high proton conductivity; however, they have a negative effect on dimensional swelling and mechanical properties of membranes. Moreover, high IECw values also increase the fuel permeability.\(^{34}\) Crosslinking is an effective method for the reduction of dimensional swelling; however, it sometimes results in brittle and insoluble membranes.\(^{34}\) These problems can be resolved by the introduction of fluorine in the polymer backbone. This approach improves not only the processability of the polymers but also their thermal, chemical, and swelling properties.\(^{1}\) In addition, fluorine also helps in the formation of phase-separated morphology, which helps in improving proton conductivity of the membranes.\(^{37}\) Therefore, in recent years, several classes of fluorinated sulfonated copolymers have been prepared that showed improved proton conductivity and dimensional stability.\(^{38−44}\) In the search of new PEM materials, we have already reported several new fluorinated sulfonated copolytriazoles (Scheme 1), and their detailed properties have been investigated.\(^{30−35}\)

In the present work, we targeted to increase the IECw values of polymers and to study their properties. Accordingly, a low-molar-mass sulfonated dialkyne monomer, potassium 2,5-bis(2-propyn-1-xylo)benzenesulfonate (TS), was synthesized and a new set of polytriazoles was prepared using two different diazide monomers, 4,4-bis[3′-trifluoromethyl-4′-(4-azidobenzenoxygen)]benzyl[biphenyl (QAZ) and 4,4′-diazido-2,2′-stilbene disulfonic acid disodium salt (SAZ). The additional sulfonic acid group in the dialkyne monomer resulted in high IECw value copolytriazoles (Scheme 2) compared with analogous copolymers with the same DS values.\(^{30−35}\)

The PEM properties of the copolytriazoles, such as proton conductivity, water uptake (WU), swelling ratio, oxidation and mechanical stability, and morphology, were studied and were compared to those of the analogous copolytriazoles.\(^{29−35}\)
RESULTS AND DISCUSSION

Synthesis of Monomers. A sulfonated dialkyne (TS) monomer was prepared from potassium salt of hydroquinone sulfonic acid and propargyl bromide as shown in Scheme 3. The structure of TS was confirmed by Fourier transform infrared (FTIR) and NMR spectroscopy techniques. The absorption bands at 3293 cm$^{-1}$ (strong) and 2123 cm$^{-1}$ (weak) in the FTIR spectrum (Figure 1) of the TS monomer were assigned to the characteristic of stretching of $\equiv C-H$ and $C\equiv C$ bonds, respectively. In the proton NMR spectrum, the acetylenic and propargyl protons appeared at 3.51 and 4.74 ppm and the aromatic protons were found between 6.96 and 7.35 ppm. The fluorinated diazide monomer (QAZ) was synthesized according to the previously reported procedure and was characterized by FTIR and NMR spectroscopic techniques. The FTIR spectra of QAZ in the range of 600–4000 cm$^{-1}$ are given in Figure 1 for better realization of the polymer formation through the azide–alkyne click reaction.

Synthesis and Characterization of Sulfonated Polytriazoles. The sulfonated polytriazole copolymers

![Scheme 1. Chemical Structures of Various Sulfonated Polytriazoles Reported Earlier](image1)

![Scheme 2. Chemical Structure of the Polytriazole](image2)

![Scheme 3. Reaction Scheme for the Synthesis of Potassium 2,5-Bis(2-propyn-1-yloxy)benzenesulfonate (TS)](image3)
(PTSQSH-I to IV) were synthesized by click polymerization of TS, SAZ, and QAZ, shown in Scheme 4. The salt and acid forms of the copolymers are reported as PTSQS-I to IV and PTSQSH-I to IV, respectively.

The copolymers of different degree of sulfonation (DS) were prepared by varying the molar ratio of the diazide monomers (SAZ to QAZ), i.e., $n/n - 1$. The copolymers (both salt form and acid form) were soluble in several common organic solvents, such as N-methyl-2-pyrrolidone (NMP), dimethyl sulfoxide (DMSO), dimethylformamide (DMF), and dimethylacetamide (DMAc), at a polymer concentration of $\sim 5\%$ (w/v) and were insoluble in tetrahydrofuran, dichloromethane, methanol, and water. The solution-cast membranes were prepared from the copolymers using DMSO as the solvent, and the acid form of the membranes was obtained after acidification of the membranes. The thickness of the acidified membranes was between 55 and 65 $\mu$m. The molecular weight, inherent viscosity, and degree of sulfonation (DS) are listed in Table 1, indicating the formation of high-molar-mass polymers.

The FTIR spectra of monomers and PTSQSH-I copolymer as one of the representatives are shown in Figure 1. It can be found that the absorption bands at 3293 cm$^{-1}$ (C≡C–H), 2123 cm$^{-1}$ (C≡C), and 2119 cm$^{-1}$ (−N≡N≡N≡N) disappear after the polymerization reaction, indicating the high conversion of the monomers. In addition, the bands at 1334 and 1484 cm$^{-1}$ are the characteristics of aromatic asymmetric C–O–C stretching, and the band at around 1051 cm$^{-1}$ corresponds to the symmetric C–O–C stretching. The band at around 1124 cm$^{-1}$ is due to the C–F stretching, and two bands at around 1020 and 1085 cm$^{-1}$ are due to asymmetric and symmetric stretching of $\text{−SO}_3\text{H}$ groups, respectively. These results support the formation of sulfonated copolymers by click polymerization.

The chemical structures and compositions of the PTSQS-I to IV copolymers were confirmed by $^1$H NMR spectroscopy. The $^1$H NMR spectrum of the salt form of PTSQS-I is shown in Figure 2. The peaks at around 8.92 ppm correspond to the aromatic protons (H₁ and H₇) of the triazole moieties. The peaks at around 8.35 and 8.26 ppm correspond to the H₅ and H₁₇ protons of the hydroquinone sulfonic acid potassium salt (TS) and stilbene disulfonic acid sodium salt (S) moieties, respectively. All protons in the copolymers are well assigned, which suggests that the PTSQSH-I to IV copolymers are successfully synthesized by copper(I)-catalyzed azide–alkyne click chemistry (CuAAC) polymerization reactions. Furthermore, the chemical composition and degree of sulfonation of the copolymers were...
determined using the peak integration values in the regions I_1−I_2−I_3 (Figure 2), and the values are presented in Table 1.

**Thermal Studies.** Thermal behavior of the copolymers was studied by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) techniques. All TGA experiments were carried out under a synthetic air environment. TGA thermograms for the acidified membranes with different compositions are shown in Figure 3, and the 10% weight loss temperature (T_{d10}) was in the range of 243–254 °C (Table 2). The copolymers showed two-step degradation, the initial weight loss at approximately 185–270 °C was due to the loss of the −SO_3H groups and the second weight loss at around 270–360 °C was a result of degradation of the main triazole backbone. None of these polymers showed any transition in DSC till their degradation temperature, which is typical of the sulfonic acid group containing polymers and attributed to the strong ionic interactions of the sulfonic acid groups.

**Mechanical and Oxidative Stability.** The stress–strain plots for the PTSQSH-I to IV membranes (dry form) are shown in Figure 4, and the results are summarized in Table 2. PTSQSH-I to IV membranes showed higher tensile strength (30–51 MPa) in contrast to Nafion 117 (tensile strength, 22 MPa). Young’s moduli for all membranes were also higher (1.25–2.02 GPa) than those of Nafion 117 (0.16 GPa). However, the elongation at break of PTSQSH-I to IV membranes was lower (9–14%) than that of Nafion 117 (200%).

The oxidative stability of the membranes was checked by putting them into Fenton’s reagent (2 ppm of iron(II) sulfate heptahydrate in 3% hydrogen peroxide) at 80 °C. None of these polymers showed any transition in DSC till their degradation temperature, which is typical of the sulfonic acid group containing polymers and attributed to the strong ionic interactions of the sulfonic acid groups.

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**Table 1. Molar Ratios of Different Monomers and Physical Properties of PTSQSH-I to IV Copolymers**

| polymer       | TS/SAZ/QAZ | M_n/a | D/b   | η_inh/c (dL g⁻¹) | DS (×2) |
|---------------|------------|-------|-------|-----------------|---------|
| PTSQSH-I      | 100:50:50  | 63200 | 2.78  | 1.23            | 2.00    |
| PTSQSH-II     | 100:60:40  | 60700 | 2.95  | 1.16            | 2.20    |
| PTSQSH-III    | 100:70:30  | 67600 | 2.28  | 1.12            | 2.40    |
| PTSQSH-IV     | 100:80:20  | 75300 | 2.54  | 1.24            | 2.60    |

*a* Number-average molecular weight. *b* Polydispersity index. *c* Inherent viscosity of PTSQSH-I to IV copolymers in NMP at 30 °C. *d* Degree of sulfonation, calculated from monomer feed ratio. *e* Calculated from ¹H NMR signal intensities.

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**Figure 2.** ¹H NMR spectrum of the PTSQS-I copolymer at room temperature (DMSO-d_6) (I_1: peak area under H_1,7; I_2: peak area under proton H_5,17, and I_3: peak area under H_9,10). DS = (I_2 + I_3)/(2.5 × I_1).³⁰,³¹

**Figure 3.** TGA thermograms of PTSQSH-I to IV copolymers.

**Table 2. Thermal and Mechanical Properties of PTSQSH-I to IV Copolymers**

| polymer       | T_{d10}a (°C) | tensile strength (MPa) | Young’s modulus (GPa) | elongation at break (%) | oxidative stabilityb (h) |
|---------------|---------------|------------------------|-----------------------|-------------------------|-------------------------|
| PTSQSH-I      | 254           | 51                     | 2.02                  | 13                      | >24                     |
| PTSQSH-II     | 249           | 36                     | 1.31                  | 11                      | >24                     |
| PTSQSH-III    | 247           | 34                     | 1.39                  | 14                      | ~8                      |
| PTSQSH-IV     | 243           | 30                     | 1.25                  | 9                       | ~2                      |

*a* 10% weight loss temperature, determined by TGA, heating rate 10 °C min⁻¹ under synthetic air (N_2/O_2 = 80:20). b Time to dissolve the membranes in Fenton’s reagent (2 ppm of iron(II) sulfate heptahydrate in 3% hydrogen peroxide) at 80 °C.
titrimetric analyses. In this work, a sulfonated dialkyn monomer (TS) was used to increase the IECw, and at the same time, the nonsulfonated diazide monomer (QAZ) with high fluorine content from 1.68 to 3.06 was added to the copolymers. As shown in Table 3, the IECw values for the PTSQSH-I to IV copolytriazoles obtained from titrimetric analyses were in compliance with the theoretical values. The oxide stability of the PTSQSH-I to IV membranes decreased with the decrease in the molar concentration of the QAZ monomer (or DS increases). However, PTSQSH-I to IV membranes showed oxidative stability similar to that of the previously reported QAZ-based copolymers in the current work showed oxidative stability in Figure 4. The theoretical IECw of the copolymers was calculated from the molecular weight of the repeat unit structure, whereas the experimental IECw was determined by 1H NMR and titr. NMR (ref 30). Similar to the previous studies, the oxidative stability of the copolymers decreases with the decrease in the molar concentration of the QAZ monomer (or DS increases). However, PTSQSH-I to IV membranes showed oxidative stability similar to that of the previously reported QAZ-based copolymers (PTFQSH-XX, PTAQSH-XX, and PTPQSH-XX) with the same DS values.30,31,36

**Ion Exchange Capacity, Water Uptake, and Swelling Ratio.** The theoretical IECw of the copolymers was calculated from the molecular weight of the repeat unit structure, whereas the experimental IECw was determined by 1H NMR and titrimetric analyses. In this study, a sulfonated dialkyn monomer (TS) was used to increase the IECw and at the same time, the nonsulfonated diazide monomer (QAZ) with high mole percentage (50–80 mol %) was used to increase the fluorine percentage of the copolymers. This resulted in an increase in IECw from 1.66 to 2.82 and fluorine percentage from 1.68 to 6.08. The IECw values for the PTSQSH-I to IV copolytriazoles obtained from titrimetric and 1H NMR analyses were in compliance with the theoretical values. This also supported that –SO3H-containing monomers (SAZ and TS) were successfully incorporated in the polymer chain by the CuAAC reaction.

The volumetric ion exchange capacity (IECv) of the copolymers in dry and wet states was also determined by the multiplication of IECw with the respective density values of the membranes.30,31 The results are listed in Table 3. The weight- and volume-based water uptake (WUw) of the PTSQSH-I to IV copolymers as a function of IECw are shown in Figure 6a. The water uptake (wt %) and IECw values for the PTSQSH-I to IV copolymers displays a similar trend as in the case of IECw in Figure 5a. However, Figure 6b shows a different trend because of high water uptake (vol %) and reduced IECw values for the PTSQSH-I to IV copolymers as a function of IECw. The hydration number (λ) is the number of absorbed water molecules per −SO3H group in the ionomer, and it is directly related to IECw, WUw, and temperature.30–33 It can be observed from Tables 3 and 4 that hydration number increases with IECw and temperature, and as a consequence, proton conductivity increases.

Table 3. PEM Properties of PTSQSH-I to IV Copolymers and Structurally Similar Polymers

| copolymer     | MW repeat unit (g mol−1) | fluorine content (%) | IECw-theo. (mequiv g−1) | IECw-titr. (mequiv g−1) | IECw-NMR (mequiv g−1) | WUw (wt %) | σ (mS cm−1) | Ea° (kJ mol−1) | ref       |
|---------------|--------------------------|----------------------|--------------------------|--------------------------|------------------------|------------|-------------|----------------|-----------|
| PTSQSH-I      | 832                      | 6.85                 | 2.41                     | 2.38                     | 2.38                   | 19         | 43          | 132            | 20.9      |
| PTSQSH-II     | 803                      | 5.68                 | 2.74                     | 2.72                     | 2.74                   | 31         | 69          | 173            | 17.1      |
| PTSQSH-III    | 775                      | 4.42                 | 3.10                     | 3.06                     | 3.08                   | 46         | 91          | 124            | 14.9      |
| PTSQSH-IV     | 746                      | 3.06                 | 3.49                     | 3.45                     | 3.51                   | 64         | 141         | 173            | 9.9       |
| PTHQSH-90     | 637                      | 1.68                 | 2.82                     | 2.79                     | 2.82                   | 31         | 65          | 142            | 15.6      |
| PTPQSH-90     | 863                      | 14.52                | 2.09                     | 2.04                     | 2.00                   | 15         | 30          | 86             | 19.5      |
| PTFSH-100     | 835                      | 13.66                | 2.40                     | 2.36                     | 2.40                   | 26         | 42          | 136            | 16.2      |
| PTAQSH-90     | 755                      | 1.51                 | 2.38                     | 2.34                     | 2.33                   | 36         | 40          | 76             | 9.0       |
| PTPASH-90     | 748                      | 1.53                 | 2.40                     | 2.35                     | 2.38                   | 31         | 36          | 90             | 9.5       |
| PTEHS90-100   | 727                      | 0                    | 2.75                     | 2.67                     | 2.75                   | 46         | 57          | 112            | 14.7      |
| PTEHS100-100  | 738                      | 1.55                 | 2.96                     | 2.83                     | 2.89                   | 57         | 73          | 163            | 11.6      |
| PTASH-100     | 549                      | 0                    | 3.38                     | 3.35                     | 3.38                   | 72         | 108         | 215            | 10.2      |
| SPTA1         | 680                      | 0                    | 2.35                     | 2.21                     | 2.28                   | 26         | 30          | 72             | 29        |
| Nafion 117    |                          | 0.91                 |                          |                          |                        | 19         | 20          | 60             | 13.56     |

IECw (wt %) = IECw (dry)/(1 + 0.01WU). WUw (wt %) = [(Wu − Ww)/Wu] × 100. Activation energy determined in the temperature range 30–80 °C and heating rate 1–2 °C min−1. IECw-theo. = (1000/Mw repeat unit) × DS, where DS is calculated theoretically from monomer feed ratio. IECw-NMR = (1000/Mw repeat unit) × DSNMR × 2, where DSNMR calculated from NMR signal intensity.
The swelling ratio (length and thickness) of the PTSQSH-I to IV membranes was measured according to the previous reports. The swelling ratios of the PTSQSH-I to IV membranes show a similar trend to that of water uptake values and depend on the degree of sulfonation as well as fluorine content (Table 3) in the copolymers. The swelling ratio of the copolymers increased with the increase in IECw value and temperature (Table 4), and these values were higher than those of similar type of copolymers due to the higher hydration number (Table 4). Proton Conductivity Measurement. The proton conductivity of the PTSQSH-I to IV copolymers was measured using alternating current impedance spectroscopy. Before the measurement of proton conductivity, all of the copolymers were equilibrated in deionized water for 72 h. The resistance of the copolymers was measured from the Nyquist plot from the higher-frequency intercept of the characteristic semicircle on the real axis. Figure 5 displays a typical Nyquist plot for the PTSQSH-I copolymer at different temperatures, and the resistance of the copolymer regularly decreased with the increase in temperature. Figure 6 displays the proton conductivity values of all copolymers as a function of temperature. The proton conductivity values of all copolymers are presented in Table 3. The proton conductivity values for PTSQSH-I to IV copolymers were in the range of 43–173 mS cm⁻¹ at 30 °C and 132–304 mS cm⁻¹ at 80 °C, and these values were considerably higher in comparison to those of the similar type of copolymers due to their higher IECw values (2.41–3.49 mequiv g⁻¹). The proton conductivity values of PTSQSH-I (IECw = 2.41 mequiv g⁻¹, σ = 132 mS cm⁻¹ at 80 °C) and PTSQSH-III (IECw = 3.10 mequiv g⁻¹, σ = 249 mS cm⁻¹ at 80 °C) were higher than or comparable to those of the analogous copolymers with similar DS values, i.e., PTASH-100 (IECw = 2.86 mequiv g⁻¹, σ = 112 mS cm⁻¹ at 80 °C), PTFSH-100 (IECw = 2.40 mequiv g⁻¹, σ = 136 mS cm⁻¹ at 80 °C), SPTA3 (IECw = 2.86 mequiv g⁻¹, σ = 149 mS cm⁻¹ at 80 °C), PTESH-100 (IECw = 3.38 mequiv g⁻¹, σ = 215 mS cm⁻¹).

Table 4. Swelling Ratio and Hydration Number of the PTSQSH-I to IV Copolymers

| copolymer   | λa [H₂O/SO₃H] | swelling ratio (%) | Δl (%) | Δt (%) | Δv (%) |
|-------------|---------------|--------------------|--------|--------|--------|
| PTSQSH-I    | 4.5           | 30 °C               | 30 °C  | 80 °C  | 30 °C  |
| PTSQSH-II   | 6.2           | 12.3               | 10.5   | 18.4   | 11     |
| PTSQSH-III  | 8.2           | 16.3               | 15.4   | 27.4   | 17     |
| PTSQSH-IV   | 10.2          | 22.5               | 25.5   | 41.7   | 27     |

*λa = WUw (%)/(100 × IECw, theo. × Mw, H₂O), where Mw, H₂O = 18 g mol⁻¹. Δλ (%) = (l_wet − l_dry)/l_dry × 100, Δt (%) = (t_wet − t_dry)/t_dry × 100, Δv (%) = (v_wet − v_dry)/v_dry × 100.
at 80 °C), and Naflon 117 (IECw = 0.91 mequiv g−1, σ = 135 mS cm−1 at 80 °C). The higher fluorine content in the PTSQSH-I (6.85%) and PTSQSH-II (5.68%) copolymers generates polarity difference in the hydrophilic and hydrophobic domains in the polymer, which resulted in better phase-separated morphology and high proton conductivity compared to those for PTASH-100 and many other sulfonated polymers.

The activation energy for proton conduction was calculated from the slopes of the different lines in Figure 8 using the Arrhenius equation. The activation energy values for the PTSQSH-I to IV copolymers were in the range of 9.9−20.9 kJ mol−1, and these values were comparable to those of the analogous copolymers.

Microstructure Analysis. The proton conductivity and water absorbing ability of sulfonated polymers are in relation to the phase separation between the hydrophilic and hydrophobic domains of the sulfonated polymers. The microstructural analysis of the PTSQSH-I to IV copolymers was carried out by scanning transmission electron microscopy (STEM). The STEM micrographs of cross-sectioned lead (Pb2+)−stained membranes are presented in Figure 9. The dark ionic domains in the micrographs represent hydrophilic domains, and these domains are mainly responsible for proton transport. On the other hand, bright regions correspond to the hydrophobic domains, and these regions are responsible for mechanical and dimensional stabilities. The micrographs showed smaller and interconnected ionic clusters (20−45 nm) in the case of PTSQSH-I to III membranes. However, a large number of bigger and interconnected ionic clusters (50−150 nm) were seen in the PTSQSH-IV membrane, which is indicating the presence of very large numbers of aggregated −SO3H groups that formed an extensive hydrophilic domain. The PTSQSH-I to IV membranes showed interconnected ionic channels in all of the cases and therefore the proton conductivity, water uptake, and swelling ratio values were higher in comparison to those of the other type of sulfonated copolytriazoles.

■ CONCLUSIONS

In this work, we have successfully prepared a series of highly sulfonated fluorinated copolytriazoles (PTSQSH-I to IV) by copper-catalyzed click polymerization of equimolar amount of a sulfonated dialkyne (TS) monomer with two different diazide monomers, fluorinated diazide QAZ and sulfonated diazide SAZ. The structural elucidation of the copolymers was performed by FTIR and NMR spectroscopy techniques. The copolymers were thermally stable up to 245 °C with 10% weight loss under synthetic air and showed the ability to form mechanically robust membranes even at very high degree of sulfonation when DMSO was used as a casting solvent. The dry copolymer membranes displayed tensile strength between 30 and 51 MPa and tensile modulus between 1.25 and 2.02 GPa depending on the exact degree of sulfonation. The high IECw values (2.41−3.49 mequiv g−1) of PTSQSH-I to IV copolymers are attributed to their high proton conductivity (135−304 mS cm−1 at 80 °C). Microstructure analysis of the PTSQSH-I to IV copolymers showed well-phase-separated morphology with interconnected hydrophilic domains, contributing to high proton conductivity. Therefore, the incorporation of additional −SO3H groups through the dialkyne monomer helped improve many of the PEM properties of the prepared copolytriazoles. Considering all of the PEM properties, e.g., thermal stability (10% weight loss temperature = 249 °C), mechanical strength (tensile strength = 36 MPa, Young’s modulus = 1.31 GPa), oxidative stability (more than 24 h), and proton conductivity (173 mS cm−1 at 80 °C), PTSQSH-II was the best in the series.
EXPERIMENTAL SECTION

Materials. Propargyl bromide (80 wt % solution in toluene) and 4,4′-diazido-2,2′-stilbene disulfonic acid disodium salt (≥99.0%) (SAZ) were purchased from Sigma-Aldrich, and used as received. Hydroquinone sulfonic acid potassium salt (>98%) was purchased from Alfa Aesar, India. Copper(I) iodide (>99%), acetone, potassium carbonate, and dimethyl sulfoxide (DMSO) were purchased from Spectrochem, India. Potassium carbonate was dried at 120 °C for overnight before use. DMSO and acetone were distilled prior to use. Concentrated sulfuric acid (95%) and ammonia solution were purchased from E. Merck, India. 4,4-Bis[3′-triﬂuoromethyl-4′-(4-azidobenzoxy)benzyl]biphenyl (QAZ) was synthesized according to the earlier reported procedure.30

Synthesis of Potassium 2,5-Bis(2-propyn-1-yloxy)benzenesulfonate (TS). A 250 mL three-necked round bottom ﬂask equipped with a nitrogen inlet, reﬂuxing condenser, and magnetic stirrer was charged with hydroquinone sulfonic acid potassium salt (>98%) was purchased from Alfa Aesar, India. Copper(I) iodide (>99%), acetone, potassium carbonate, and dimethyl sulfoxide (DMSO) were purchased from Spectrochem, India. Potassium carbonate was dried at 120 °C for overnight before use. DMSO and acetone were distilled prior to use. Concentrated sulfuric acid (95%) and ammonia solution were purchased from E. Merck, India. 4,4-Bis[3′-triﬂuoromethyl-4′-(4-azidobenzoxy)benzyl]biphenyl (QAZ) was synthesized according to the earlier reported procedure.30

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Synthesis of Sulfonated Copolytriazoles (PTSQS-I to IV). As an example, the preparation of PTSQS-I is described here: QAZ (0.3973 g, 0.56 mmol), TS (0.3412 g, 1.12 mmol), SAZ (0.3019 g, 0.56 mmol), and 5 mol% CuI (0.010 g, 0.056 mmol) were placed in a 50 mL ﬂame-dried three-necked round bottom ﬂask equipped with a magnetic stirrer, reﬂux condenser, and N2 inlet. DMSO (12 mL) was added to the ﬂask, and the reaction mixture was heated to 70 °C for 12 h. During this period, there was a dramatic increase in the viscosity of the reaction medium. The reaction solution was cooled to room temperature and was precipitated in excess isopropanol. The ﬁbrous precipitate obtained was isolated by ﬁltration and washed several times in 20% ammonia solution followed by deionized water and dried under vacuum at 100 °C for overnight. The yield was 98%. The NMR data of PTSQS-I to IV copolymers in salt form: 1H NMR (DMSO-d6, 30 °C), ppm: 8.91 (H1,7), 8.36 (H5), 8.26 (H17), 8.07 (H12,18), 7.97 (H8), 7.87 (H13,14,15,16), 7.45 (H11), 7.32 (H9,10), 7.17–7.07 (H3,4), 5.29–5.18 (H2,6).

Membrane Preparation and Acidification. The membranes were prepared using the polymer solutions in DMSO at a concentration of 10% w/v. The polymer solutions were ﬁltered and cast in ﬂat-bottom Petri dishes. The Petri dishes were heated at 80 °C inside an oven for overnight for slow removal of the solvent. Afterward, the oven temperature was preset according to the following heating order: 100 °C (4 h), 120 °C (2 h), 140 °C (2 h), and 155 °C (1 h).
membranes were further heated under vacuum at 120 °C for 24 h for removal of any residual solvent. The oven temperature was brought down to room temperature, and the Petri dishes were put into boiling water to remove the membranes. The salt form of the membranes was acidified by putting them in 1.5 M H2SO4 solution for 24 h. The acidified membranes were washed a number of times with deionized water to ensure complete removal of any surface-absorbed acid (H2SO4).

Finally, the membranes were dried at 100 °C for 24 h under vacuum and yellow membranes of thickness between 55 and 65 μm were obtained.

**Measurements and Characterization.** A 600 MHz NMR instrument, Bruker instrument (Switzerland), was used to record the 1H NMR spectra of the monomers and polymers. Deuterated DMSO-d6 or CDCl3 and tetramethylsilane were used as solvents and internal standard, respectively. Fourier transform infrared (FTIR) spectra were recorded using a NEXUS 870 FTIR instrument, Thermo Nicolet. The molecular weight of the copolymers (salt form) was determined via gel permeation chromatography using DMAc with 3 g L−1 LiCl as an eluent. The apparatus consists of an Agilent 1200 series high-performance liquid chromatography pump (Agilent Technologies), a PolarGel-M column, and a refractive index K2301 (Knauer, Germany) detector. Linear poly(methyl methacrylate) with molecular weight between 500 and 1 000 000 Da was used for calibration purpose. Thermal stability of the membranes was studied using a TGA instrument, TGA Q50 (TA Instruments). The experiments were conducted in a synthetic air mixture atmosphere (N2/O2 = 80:20) at a heating rate of 10 K min−1. Differential scanning calorimetry (DSC) measurements were carried out using a DSC Q20 instrument (TA Instruments) at a heating rate of 10 K min−1 under nitrogen. A FEI-TECNAI G2 20 S-TWIN transmission electron microscope (TEM) was used to obtain the TEM micrographs of the lead-stained membranes operated at an accelerating voltage of 120 kV. The mechanical behavior of the dry acidified membranes was checked using a tensile testing machine manufactured by Tinius Olsen, U.K., model no. HSKS. The test specimens of width 10 mm, length 63 mm, and thickness 50−65 μm were used, and the measurements were performed in tension mode at a test speed of 5 mm min−1 at ambient temperature (∼32 °C). Water uptake, dimensional change, and oxidative stability of the polymer membranes were checked according to the reported procedure.30,34 The ion exchange capacity (IECw) was calculated from the following formula: IECw = (1000/Mw) × DS × 2, where Mw and DS are the molecular weight of the repeat unit and degree of sulfonation, respectively, which was experimentally determined by the titrimetric method.35 The DS values were determined from 1H NMR signal integrals and were also used to calculate the IECw of the copolymers.36 Volume-based ion exchange capacity (IECV) values were calculated in the dry state of the copolymers by multiplying the corresponding IECw values with their densities. Similarly, IEC values of the wet state were calculated from the water uptake values of the corresponding copolymers.30,40 Proton conductivity (in-plane) of the hydrated membranes (10 mm × 20 mm × 55−65 μm) was determined using the following equation: \[ \sigma = \frac{l \times R}{A} \times \sigma_0 \] where \( \sigma \), \( l \), \( R \), and \( A \) are the in-plane proton conductivity, distance between the two electrodes, resistance, and area of the sample, respectively. A GAMRY reference 3000, impedance analyzer was used to measure the R values of the copolymer membranes over the frequency range of 100 Hz to 1 MHz. A four-probe conductivity cell was used to hold the membranes.

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**Notes**

The authors declare no competing financial interest.

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