European Polymer Journal 103 (2018) 322–334

Contents lists available at ScienceDirect

European Polymer Journal

journal homepage: www.elsevier.com/locate/europolj

New crosslinked sulfonated polytriazoles: Proton exchange properties and microbial fuel cell performance

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ARTICLE INFO

Keywords:
Semifluorinated sulfonated polytriazole
Mechanical property
Proton conductivity
Crosslinked polymer

ABSTRACT

The synthesis, characterization and establishment of the structure-property relationship of a series of new semifluorinated sulfonated polytriazoles (PTCTSH-XX) with varying degrees of sulfonation are described. The polymers were synthesized by the click polymerization reaction of a mixture of two diazide monomers, the non-sulfonated diazide monomer 4,4-bis[3-trifluoromethyl-4(4-azidophenoxy) phenyl]benzene (TAZ) and the sulfonated diazide monomer 4,4′-diazido-2,2′-stilbenedisulfonic acid disodium salt (SAZ), with an equimolar amount of the dialkyne monomer 3,5-bis(prop-2-ynyloxy)benzoic acid (BPBA). The polytriazoles were characterized by ^{1}H and ^{13}C NMR spectroscopy. All the polymers showed good solubility in selected polar aprotic organic solvents along with excellent film forming ability. The TEM micrographs of these polymers exhibited a uniformly phase separated morphology. The polymers showed very high proton conductivity and the values were within the range of 15–67 mS cm^{-1} at 30 °C, 38–163 mS cm^{-1} at 80 °C and 42–176 mS cm^{-1} at 90 °C in hydrated condition. The pristine polymers were crosslinked with poly(vinyl alcohol) and their PEM properties were also investigated. The crosslinked films showed lower water uptake and dimensional swelling and improved oxidative stability in comparison to the pristine membranes. The microbial fuel cell performance of both pristine and crosslinked membranes was also investigated.

1. Introduction

During the last few decades, there has been an increasing demand for alternative clean and sustainable energy sources which has triggered the research in alternative energy technologies. Fuel cells are considered as one of the most promising clean energy sources due to their potential to convert chemical energy into electricity without emitting pollutants [1]. Proton exchange membrane fuel cells (PEMFCs) which employ proton exchange membrane (PEM) have been explored in various application areas as automobiles, residential power sources, and portable devices [2–4]. Recently, the microbial fuel cell (MFC) has gained enormous attention due to its bi-functional advantage as bioelectricity recovery and waste management [5], as, for example, domestic to industrial wastewater treatment [6], solid waste minimization [7], and heavy metal removal [8]. The PEM is the chief element in the fuel cell membrane electrode assembly (MEA) as it simultaneously acts as the proton transport media as well as the separator between the fuel and the oxidant. Nafion® 117 is the most widely used perfluorinated PEM material because of its superior fuel cell properties such as high proton conductivity, and excellent chemical and mechanical stability. However, it has some of the negative aspects such as high production cost, high fuel crossover, low conductivity and loss of mechanical strength at high temperature (> 80 °C) [9,10]. As an alternative to Nafion® 117 for fuel cell application, exhaustive researches have been performed in developing low-cost aromatic semifluorinated sulfonated polymers such as, poly(phenylene)s [11], poly(ether ether ketone)s [12], poly(arylene ether)s [13,14], polyimides [15–17], polybenzimidazoles [18,19] polybenzthiazoles [20] and polytriazoles [21–31].

Usually, PEMs require high proton conductivity in order to be employed in fuel cells. Polymers with a high degree of sulfonation (DS) are generally used to attain high proton conductivity. Furthermore, the mechanical and dimensional integrity should be maintained under humidified conditions for an effective application as PEM. However, polymers with high DS suffer from certain drawbacks such as excessive water uptake and poor chemical-dimensional stability. Moreover, the

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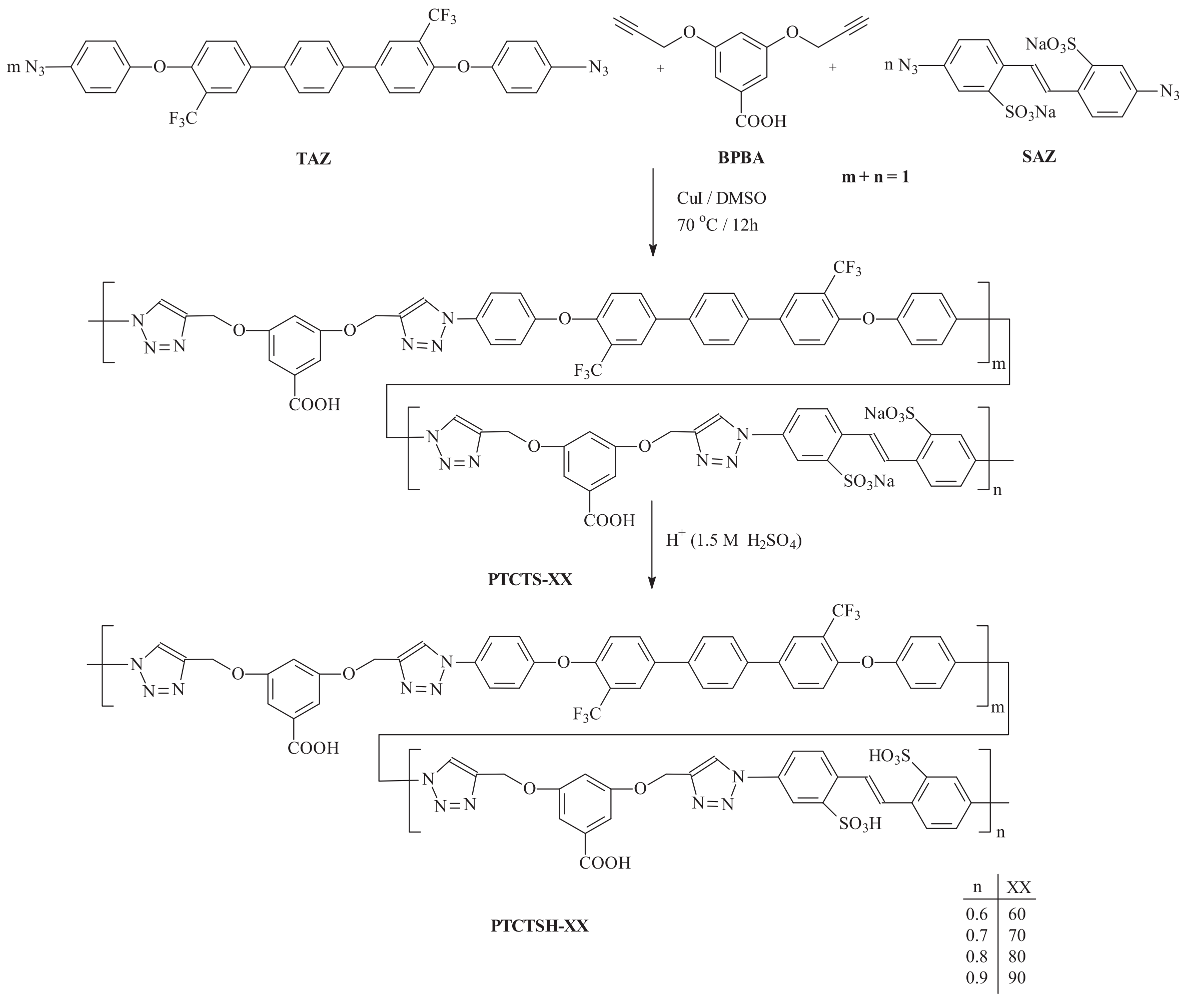
https://doi.org/10.1016/j.eurpolymj.2018.04.023
Received 23 February 2018; Received in revised form 5 April 2018; Accepted 20 April 2018



n	XX
0.6	60
0.7	70
0.8	80
0.9	90

Scheme 1. Schematic presentation of synthesis of PTCTSH-XX copolymer.

mechanical integrity at high DS is also lost, thus restricting their practical utility in PEMFCs. Consequently, various research groups have been working on improving PEMs by suitable approaches to resolve the drawbacks. One of the most promising methodologies is crosslinking that can effectively reduce water uptake and improve dimensional stability [32]. In this regard, crosslinkable groups are often introduced into the polymer and effective crosslinking is achieved either by ionic, covalent or other type of interactions. One of these approaches is crosslinking of carboxylated PEMS through ester linkages via the esterification reaction with hydroxyl containing crosslinking agents. Accordingly, Lee et al. reported crosslinking of carboxylic acid-containing sulfonated polyimide membranes using different diol crosslinkers [33]. Later, Guiver et al. reported crosslinked PEMs from carboxylic acid-containing sulfonated poly(aryl ether ketone) using poly(vinyl alcohol) (PVA) as crosslinking agent [34].

The overall objective of this study is to prepare new sulfonated crosslinkable polytriazoles for fuel cell application. In the present work, a low molar mass carboxylic acid containing dialkyne monomer [3,5-bis(prop-2-ynyloxy)benzoic acid (BPBA)] is used to increase the IEC values of the polymers compared to previously reported polytriazoles prepared from 4,4′-(propane-2,2-diyl)bis(prop-2-ynyloxy)benzene [25]. Further, the carboxylic acid (−COOH) groups of the polytriazoles are used as potential crosslinking sites. Accordingly, a series of sulfonated polytriazoles with different degree of sulfonation were prepared by click polymerization of a mixture of two diazide monomers; 4,4-bis[3-trifluoromethyl-4(4-azidophenoxy) phenyl]benzene (TAZ) and 4,4′-diazido-2,2′-stilbenedisulfonic acid disodium salt (SAZ) with an equimolar amount of BPBA as a dialkyne monomer. The polytriazoles are well characterized by FTIR and NMR spectroscopic techniques. Solution cast membranes are prepared and their PEM properties thoroughly investigated. The pristine polymers are further crosslinked using PVA as crosslinker and PEM properties of the crosslinked membranes are also investigated.

2. Experimental

2.1. Materials

3,5-Bis(prop-2-ynyloxy)benzoic acid (BPBA, dialkyne) and 4,4-bis [3-trifluoromethyl-4(4-azidophenoxy) phenyl]benzene (TAZ, diazide) were synthesized according to the previous reports [20,26]. Tetrabutyl ammonium bromide, tert-butyl nitrite (t-BuONO) and 4,4′-diazido-2,2′-stilbenedisulfonic acid disodium salt (SAZ) were purchased from Aldrich, USA and were used as received without further purification. Poly (vinyl alcohol) (PVA) (M_w ~ 85000, degree of hydrolysis ~86–89%) was purchased from SD Fine Chemicals, India and dried overnight under vacuum at 80 °C prior to use. Copper (I) iodide was purchased from Spectrochem, India and was used as received. Dimethyl sulfoxide (DMSO) was purchased from E. Merck, India. It was kept standing over calcium hydride for 24 h and then the solvent was distilled under reduced pressure. Finally, the distilled solvent was stored over a Type 4A molecular sieve prior to use. Hydroquinone, acetonitrile (CH_3CN), ammonia solution (25%) and concentrated sulfuric acid (95%) were purchased from E. Merck, India. N-Methyl-2-pyrrolidone (NMP), N,N-