

Original Article

Preparation and Characterizations of Triptycene Integrated Poly (Arylene Ether Sulfone) Based Block and Random Copolymers

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Abstract - The present study aims to synthesize porous poly (arylene ether sulfone) (PAES) copolymers infused with triptycene monomer, prepared via two synthesis methods: block and random copolymerization. The morphologies and properties of both synthesized PAES copolymers were further studied and compared. Obtained results showed that all the procured triptycene monomers, oligomers, and PAES copolymers were successfully synthesized and verified through proton nuclear magnetic resonance (¹HNMR) and Fourier-Transform Infrared Spectroscopy (FTIR) analyses. Gel Permeation Chromatography (GPC) showed that the obtained random PAES copolymer exhibited higher molecular weight than block PAES copolymer. At the same time, the thermogravimetric analysis demonstrated that the triptycene-integrated block PAES copolymer was slightly more thermally stable than the random PAES copolymer. After the membrane preparation, Field Emission Scanning Electron Microscopy (FESEM) and porosity studies documented that the block PAES copolymer membrane exhibited larger pore size with increased porosity compared to the random PAES copolymer membrane. The current study also found that both pore size and porosity could improve water uptake and the ion exchange capacity of the PEMs. The block PAES membrane also recorded superior proton conductivity compared to the random PAES copolymer membrane. The membrane procured in this study displayed workability in the PEMFC test at an operating temperature of 80°C and 60% RH. It is shown that the morphology and properties of the synthesized polymer varied when different synthesis methods were applied.

Keywords - Block copolymer, Random copolymer, Morphology, Triptycene, Poly (arylene ether sulfone).

1. Introduction

One of the most fascinating topics in supramolecular and materials chemistry is the search for new and effective building motifs for building artificial supramolecular acceptors and functional materials [1]. Being one of such materials, triptycenes' unique shape-persistent characteristics encourage novel concepts in the design of the available materials [2]. Triptycene, a basic form of triptycene, is an aromatic compound with three benzene rings. Triptycene's three-dimensional rigid, propeller-like structures and three open electron-rich cavities make it useful in host-guest chemistry, supramolecular devices, and materials science [1].

Attempts to explore its usage in the design of Polymer Electrolyte Membranes (PEMs) have also recently gained a lot of interest among researchers for the application of fuel cells. Polymer Electrolyte Membranes (PEMs) transport protons from anodes to cathodes [3,4]. Among the aromatic hydrocarbon-based PEMs, poly (arylene ether sulfone) (PAES) has gained significant attention as the polymer produces high-temperature plastics with excellent mechanical and dielectric properties, flame retardancy, and heat resistance with ease of synthesis and more affordable. Furthermore, PAES membranes possess superior dimensional and chemical stability, especially at high temperatures and humidity [5].



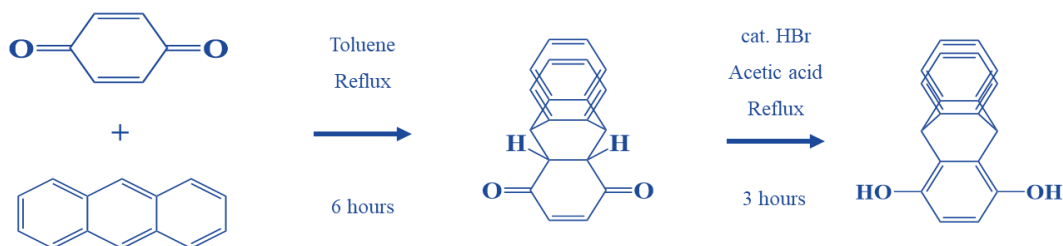


Fig. 1 Synthesis of triptycene hydroquinone

To further enhance the PAES membrane's porosity, recent research has focused on integrating bulky and space-occupying molecules, such as triptycene, into the polymer backbones [6-10]. Additionally, triptycene group-containing polymers demonstrated high thermal and chemical stabilities, mechanical enhancement, and low water absorption [6,7]. Moreover, the strong and stacked triptycene structures are more conducive to forming channels between chains to transport the proton and stimulate strong and durable supramolecular strengthening through chain threading and interlocking mechanisms [7,11]. It is generally acknowledged that polymers prepared using different synthesis methods would produce varied physical and chemical properties. Previously, efforts to improve PEMs, including forming phase-separated block morphology membranes that could alter their physical properties and elevate the proton conductivity for fuel cell applications, were investigated [12]. Hence, the current study aims to analyze the physical and chemical properties of triptycene integrated-PAES polymers prepared using different polymer synthesis methods (via random and block copolymerization). To verify their chemical structures, the prepared PAES polymers will be characterized through proton nuclear magnetic resonance (¹HNMR) and gel permeation chromatography (GPC). Furthermore, the porosity of the prepared PAES membranes will be further evaluated.

2. Experimental

2.1. Materials

All purchased chemicals were at least reagent grade; no further purification was required. The current study utilized anthracene (97.0%), 1,4-benzoquinone (98.0%), bis (4-chlorophenyl) sulfone (BCPS) (98.0%), 4,4'-biphenol (BP) (97.0%), potassium carbonate (K₂CO₃) (99.995%), calcium carbonate (CaCO₃) (≥99.0%), hydrochloric acid (HCl) (37.0%), and sodium chloride (NaCl) (≥99.0%), which were purchased from Sigma-Aldrich Chemie, GmbH, Germany to synthesize the membranes. Glacial acid (100%) and hydrobromic (HBr) (47%) acids, N, N-dimethylacetamide (DMAc) (99%), toluene (≥99.9%), isopropyl alcohol (IPA) (≥99.8%) and methanol (≥99.9%) were purchased from Merck Co., Germany. All chemicals were employed without further purification.

2.2. Synthesising Triptycene Hydroquinone

The illustration of the triptycene hydroquinone synthesis pathway adapted in the present study [9] (See Figure 1).

Firstly, anthracene and 1,4-benzoquinone in toluene were heated under reflux for six hours before being cooled to room temperature. Subsequently, the precipitated benzoquinone triptycene was filtered, rinsed with toluene, and dried in a vacuum oven overnight at 75°C. Triptycene benzoquinone was then added to glacial acetic acid and heated under reflux. The HBr was gradually added to the reaction, stirred for three hours under reflux, and left to cool at room temperature. Next, the precipitated triptycene hydroquinone was filtered and dried overnight at 75°C in a vacuum oven to produce a 77% yield. ¹HNMR (DMSO-d₆): 8.82 (2H, s), 7.41 (4H, m), 6.99 (4H, m), 6.31 (2H, s), 5.80 (2H, s); Fourier transform infrared (FTIR) (cm⁻¹): 3256 (–OH).

2.3. Synthesising The Block Copolymer

2.3.1. The Telechelic Oligomer A

A 100 mL round-bottom flask was filled with BCPS (4.51 g, 15.7 mmol), triptycene hydroquinone (3.61 g, 12.6 mmol), potassium carbonate (2.90 g, 21 mmol), DMAc (32 mL), and toluene (16 mL). The reaction mixture was heated with a Dean-Stark trap at 145°C for three hours. Subsequently, the reaction temperature was increased to 170°C and left for three hours to produce a viscous solution. The solution was then cooled to 25°C to obtain a dark brown paste residue, which was dropped gently into 500 mL of IPA in a beaker. The substance was then dissolved in water and distilled for one hour to procure the oligomer, which was evaporated and vacuum oven-dried at 100°C. The telechelic oligomer A was produced at a 75% yield [13]. Fourier transform infrared (FTIR) (cm⁻¹): 1322, 1293, 1068 (O=S=O), 1227 (C-O); Mw = 4.09 kDa, PDI = 1.18.

2.3.2. The Telechelic Oligomer B

The toluene (16 mL), BCPS (4.51 g, 15.7 mmol), BP (3.11 g, 16.7 mmol), potassium carbonate (4.62 g, 33.4 mmol), and DMAc (32 mL) were mixed in a 100 mL round-bottom flask and heated with a Dean-Stark trap at 145°C for two hours before the reaction temperature was elevated to 170°C for another two hours [13]. The mixture collected was diluted with 20 mL of DMAc to reduce its viscosity and poured into 1 L of deionized water to obtain a white substance. After curing, the component was washed multiple times with methanol and dried in a vacuum oven to procure telechelic oligomer B at 80% yield [13]. Fourier transform infrared (FTIR) (cm⁻¹): 1322, 1293, 1068 (O=S=O), 1227 (C-O), 3300 (–OH); Mw = 9.93 kDa, PDI = 2.08.

2.4. Synthesising Triptycene Integrated Block PAES Copolymer

The present study synthesized a block copolymer of telechelic oligomers A and B at a 1:2 ratio. The illustration of the synthesis and structure of the telechelic oligomers and triptycene integrated block PAES copolymer (see Figure 2). First, the synthesized telechelic oligomers A (0.04 g, 0.047 mmol) and B (0.06 g, 0.093 mmol), potassium carbonate (0.03 g, 0.21 mmol), calcium carbonate (0.07 g, 0.7 mmol), DMSO (4 mL), and toluene (1 mL) were poured in a 100 mL round-bottom flask, stirred vigorously with a magnetic bar, and cooked for 20 h at 145°C.

After the polymerization, the reaction temperature decreased to room temperature with a limited amount of DMAc incorporated into the mixture to minimize viscosity [13]. The polymer solution was poured into a beaker of 1 M HCl. The light brown fiber was then washed with 3 M NaCl solution to adjust the sorting form before being scrubbed again with DI water to eliminate residual NaCl. An 89% block copolymer was obtained after the vacuum oven-dried solution [13]. Fourier transform infrared (FTIR) (cm⁻¹): 1322, 1290, 1073 (O=S=O), 1227 (C-O); Mw = 36.15 kDa, PDI = 1.86.

2.5. The Triptycene Integrated Random PAES Copolymer Synthesis

The random copolymer synthesis pathway manufactured in the current study is demonstrated (see Figure 3). A 100 mL round-bottom flask was filled with BCPS (5.74 g, 20 mmol), triptycene hydroquinone (1.91 g, 6.67 mmol), BP (2.48 g, 13.33 mmol), potassium carbonate (3.32 g, 24 mmol), calcium carbonate (0.07 g, 0.7 mmol), DMAc (60 mL), and toluene (30 mL) before being stirred vigorously with a magnetic bar for 20 h at 145°C [13].

After the polymerization was achieved, the temperature was lowered to room temperature, and a small amount of DMAc was added to the solution, which was essential in minimizing the viscosity of the solution. The polymer solution was transferred into a beaker of 1 M HCl. Next, the resultant light brown substance was washed with 3 M NaCl solution to adjust the sorting form and washed again with DI water to remove residual NaCl. A random copolymer at a 95% yield was procured after the substance was vacuum oven-dried. Fourier transform infrared (FTIR) (cm⁻¹): 1322, 1290, 1073 (O=S=O), 1227 (C-O); Mw = 71.46 kDa, PDI = 1.98.

2.6. Preparation of the Membranes

The study dissolved 0.1 g of each synthesized copolymer into 10 ml DMAc solvent. Although the block copolymer was dissolved at room temperature with moderate stirring speed, the random copolymer was only dissolved when heated to 40–60°C. The membranes were cast on a glass plate before being dried in a vacuum oven at 60°C for 2 hours and then at 80°C for 4 hours.

The membranes were then peeled with limited DI water and dried again to assess their thickness. Finally, the membranes were acidified by boiling them in an aqueous solution of 1 M sulphuric acid (H₂SO₄) and washed numerous times with deionized water [13]. The prepared membranes recorded thicknesses that ranged from 75 to 100 µm.

2.7. Characterization of the Monomer, Polymers and PAES Membrane

The chemical structures of triptycene were analyzed with Proton Nuclear Magnetic Resonance (¹HNMR). The membrane samples were dissolved in dimethyl sulfoxide-d₆ (DMSO-d₆) with tetramethylsilane (TMS) as the internal reference. The analysis was performed with a 300 MHz Fourier 300 spectrometer (Bruker, Germany). The synthesized polymers' Fourier transform infrared (FTIR) spectra were measured on a Cary FTIR spectrometer within the 4000–650 cm⁻¹ range to identify chemical bonds present. The oligomers and PAES polymers' molecular weight and molecular weight distributions were evaluated with gel permeation chromatography (GPC) (1260 Infinity). THF was employed as the eluent at a 1 mL min⁻¹ flow rate. The acquired values were then compared to the polystyrene standard set. The thermal stability of the polymers was evaluated using thermogravimetric analysis (TGA) (STA6000) with a heating rate of 10°C/min.

The FEI Quanta 400 Field emission scanning electron microscope (FESEM) cross-section micrographs were employed to examine the internal membrane morphologies of the samples acquired in the current study. The membranes were briefly immersed in liquid nitrogen to freeze them before breaking them to procure sample pieces for the assessment. The procedure was performed without causing any damage to the interior structure of the membranes.

Geometric information, such as size distribution and the number of pores in a cross-section membrane, was obtained with the Image J® software. The membrane water uptake in the present study was evaluated in their dry and wet conditions [13]. The membranes were dried overnight in a vacuum oven at 90°C before they were weighed. Subsequently, the membranes were immersed in water at room temperature (25°C) for 24 h and were considered after wiping the water off the surfaces with filter papers. Water uptake percentages of the samples were determined with Equation 1 [13]. The assessment was repeated at 80°C. Four samples were evaluated for each membrane, where the average water uptakes at 25 and 80°C were determined.

$$\text{Water uptake, WU (\%)} = \frac{M_{\text{wet}} - M_{\text{dry}}}{M_{\text{dry}}} \times 100\% \quad (1)$$

Where M_{wet} represents the mass of the membrane after 24 h of immersion in water, while M_{dry} denotes the mass of the dry membrane [13].

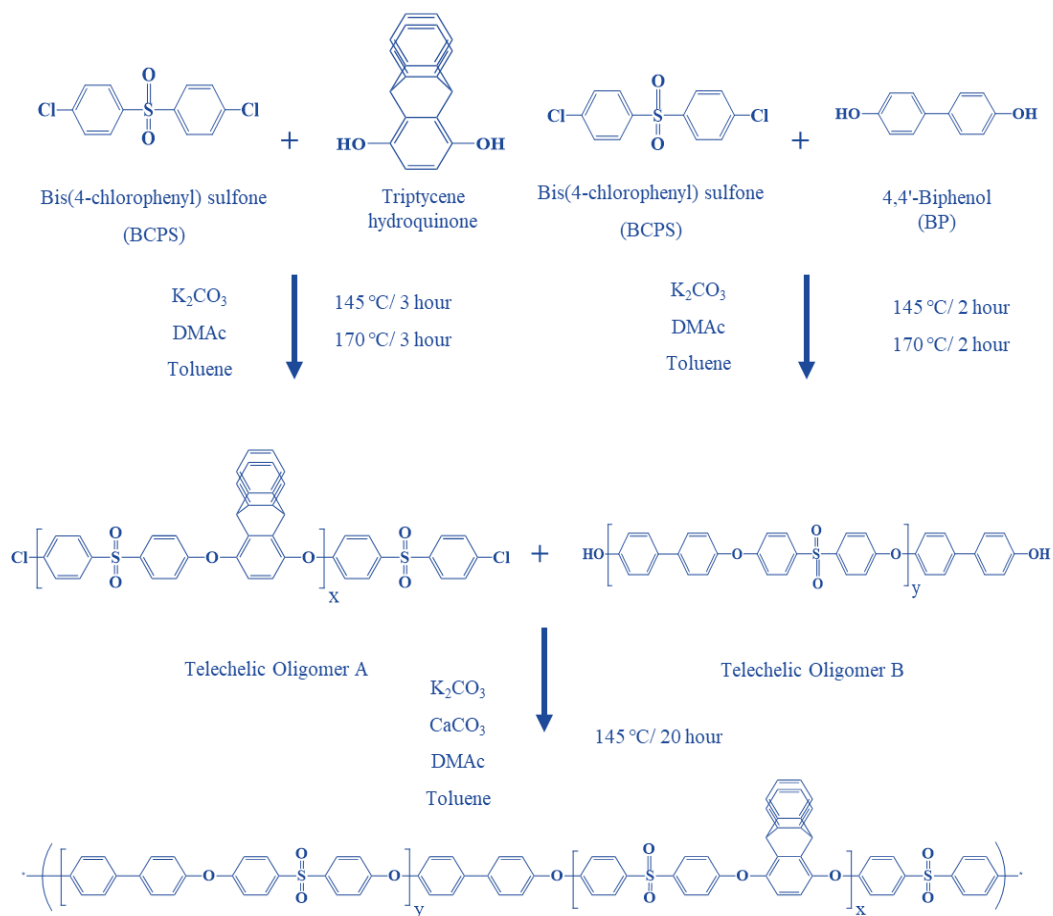
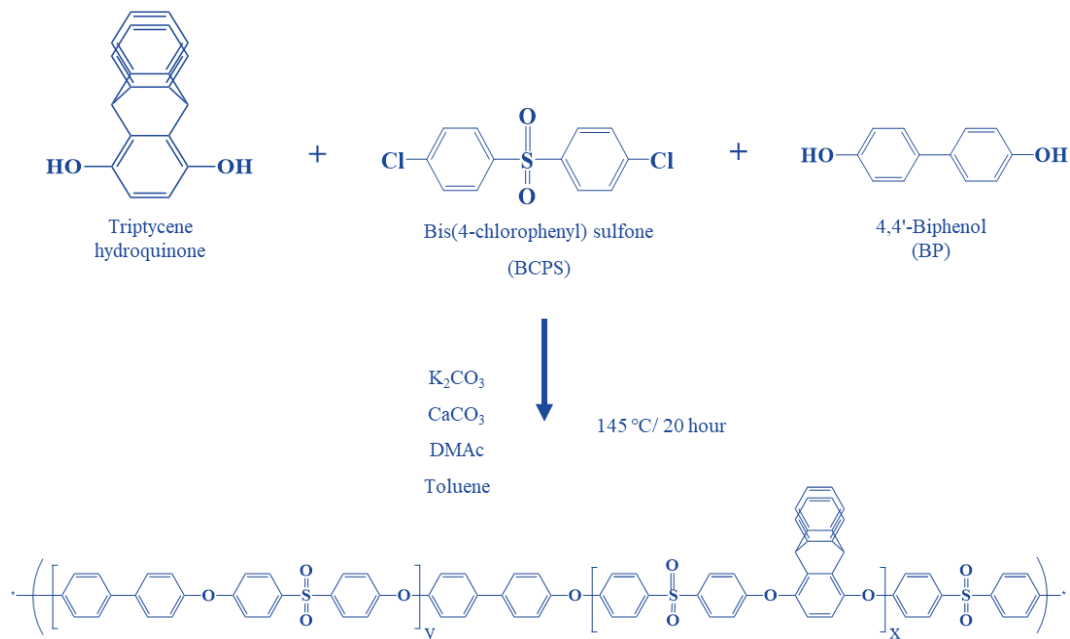


Fig. 2 Triptycene integrated block poly (Arylene Ether Sulfone)



Triptycene integrated random poly (arylene ether sulfone)

Fig. 3 Triptycene integrated random poly (Arylene Ether Sulfone)

The IEC of the membrane samples acquired in this study were determined through titration. An excess of 5 M NaCl aqueous solution in a large conical flask was employed to equilibrate a piece of the membrane for three days [14]. Subsequently, the solution was titrated with 0.01 M NaOH [13]. The IEC of each sample was calculated according to Equation 2.

$$\text{IEC} = \frac{V_{\text{NaOH}} - C_{\text{NaOH}}}{w_{\text{dry}}} \quad (2)$$

Where V_{NaOH} is the volume of NaOH added at the point of equivalence (mL), C_{NaOH} denotes the concentration of NaOH (M), and w_{dry} corresponds to the dry membrane weight [13]. Impedance spectroscopy [Solartron 1260 Gain phase Analyser, AMETEK, Inc., United Kingdom (UK)] was employed to examine the transverse proton conductivities of the sample membranes over the 1–107 Hz frequency and 50–500 mV oscillating voltage ranges. The hydrated membranes were sandwiched between two stainless steel electrodes to evaluate their proton conductivities at room temperature. Next, the specimens' transverse conductivities (σ) were determined from the impedance measurements according to Equation 3.

$$\text{Transverse conductivity, } \sigma = \frac{d}{RA} \quad (3)$$

The sample's thickness and surface area are represented by d and A , respectively, and R was determined from the low intersection of the high-frequency semi-circle on a complex impedance plane with the $\text{Re}(Z)$ axis.

The present study recorded the cell voltage versus current density data on a fuel cell test system (850e) with hydrogen (100 mL/min) and oxygen (100 mL/min) lines, with 40% Pt on carbon paper as electrodes and platinum ruthenium 0.5 mg/cm² 60% as catalyst to evaluate the performance of the acquired membranes.

Carbon papers were used as a gas diffusion layer. Before the evaluations, the membranes were cut into 3 × 3 cm squares, while the anodes and cathodes were 1.5 × 1.5 cm squares. The membranes were then sandwiched between the electrodes and hot pressed at 80°C and 4 bar for 3 minutes. Next, the membrane electrode assemblies were placed inside the cell before all gas tubes were connected. Finally, the temperature was set to 80°C and 60% relative humidity (RH).

3. Results and Discussion

3.1. Thermal Properties of Block and Random PAES Polymers

Thermal stability is an imperative parameter defining the ideal characteristics and a critical standard of PEMs [3]. Figure 4 represents the TGA results of the membranes. Both PAES copolymers are observed to undergo two stages of degradation. The first stage occurred within the 200–270°C

temperature range, possibly due to the loss of water molecules and tightly bound water molecules. The trend supported the results reported by previous studies, where the first stage of degradation was referred to as the dehydration step and occurred within the 25–220°C range [16]. One such study reported the loss of tightly bound water molecules at temperatures up to 300°C [17].

Nonetheless, the copolymers synthesized in the current study recorded minimal weight loss during the first degradation stage. Consequently, the block PAES polymer lost less weight than the random PAES polymer. The second stage is known as the polymer backbone degradation stage. Generally, this is the last stage of weight loss for polymers.

The results demonstrated that the thermal degradation of the samples analyzed occurred at temperatures over 500°C. The block PAES membrane exhibited polymer backbone degradation at approximately 585°C, while the random PAES membrane documented the second stage polymer degradation at around 580°C.

3.2. Morphology of Block and Random PAES Membranes

FESEM was conducted to identify the morphology of the block and random PAES copolymers after the membrane preparation. Figure 5 demonstrates the FESEM cross-sectional images of block and spontaneous PAES copolymer membranes. The images revealed the presence of pores and voids in both PAES copolymer membranes, where the triptycene possesses a unique feature that enables it to form porosity within polymer matrixes. Subsequently, the pore size and the probability density function of the pore size were determined with the image J® software.

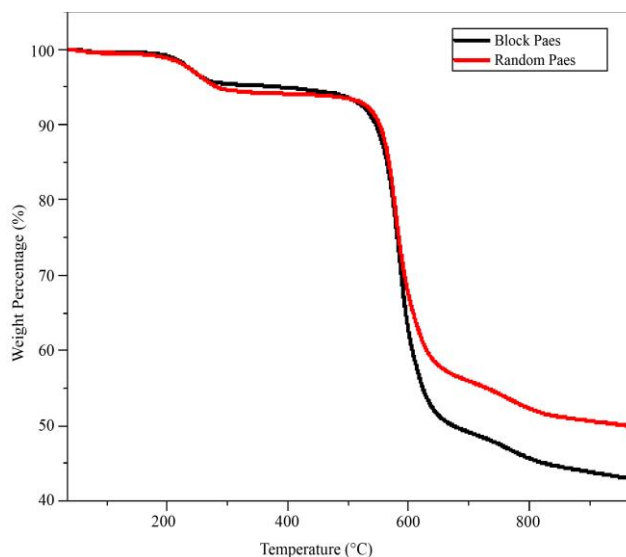


Fig. 4 The TGA of the block and random PAES copolymer membranes

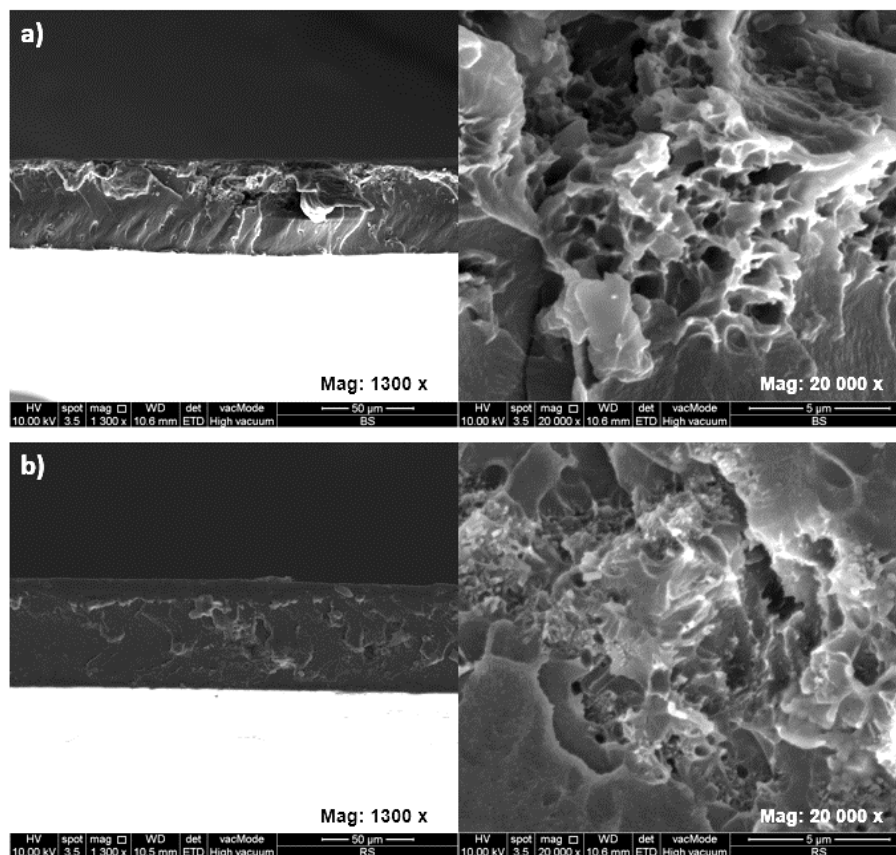


Fig. 5 The cross-section images of the (a) block PAES and (b) random PAES copolymer membranes at different magnifications

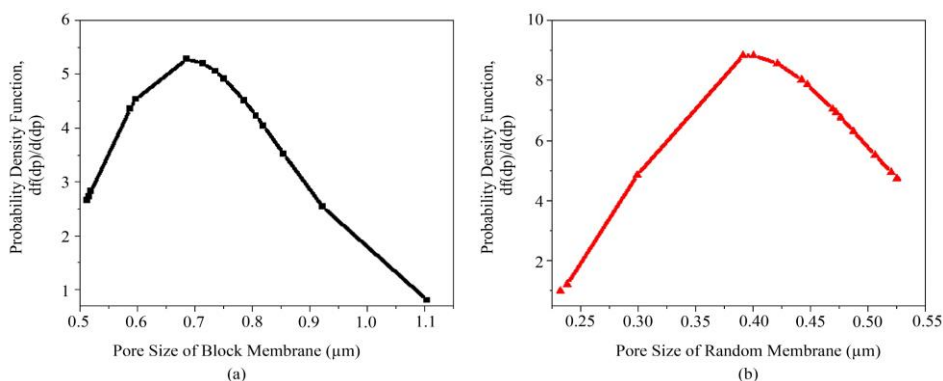


Fig. 6 The probability density function of pore sizes of the (a) block PAES and (b) random PAES copolymer membranes

Figure 6 depicts the probability density function of the pore sizes of both copolymer membranes. The graphs indicated that the block PAES copolymer membrane possessed a higher probability density function and larger pore sizes than the random PAES copolymer membrane, revealing the influence of the molecular weight of the prepared polymers. It was previously reported that membranes produced from higher molecular weight polymers exhibited small inter-connected structures, whereas membranes prepared with lower molecular weight polymers demonstrated more broad pore structures [18]. Therefore, the block PAES copolymer membrane's pore size is slightly larger than that of

random PAES copolymer membranes due to the lower molecular weight of the produced block PAES copolymer.

Moreover, a parameter that defines the core property of porous membranes is porosity, a measure of the void spaces in materials. Hence, the dry-wet method determined the porosity of both PAES copolymer membranes [19]. It is identified that the block PAES membrane was more porous, at 5.12% than that of the random PAES membrane, which was documented at 2.45%. This is probably due to the larger pores in the block PAES copolymer membrane, verified with the FESEM study.

Table 1. The water uptake, ion exchange capacity, and proton conductivity values of the block and random PAES copolymer membrane samples

Membrane	Water uptake (%)		IEC (mmol/g)	Proton conductivity (mS/cm)
	25°C	80°C		
Block PAES	5.13	7.9	1	2.00 (25°C)
Random PAES	2.24	3.21	0.76	0.30 (25°C)

3.3. Water Uptake and Ion Exchange Capacity of Block and Random PAES Membranes

Water uptake is a crucial factor that determines the performance of PEMs. Water molecules are necessary for the development of charge carriers and the mobility of ions in PEMs [20]. Ion exchange capability, fractional free volume, hydrophobicity, and intra- and intermolecular interactions, such as π - π stacking, are interplaying parameters that influence water uptake and swelling behaviours of copolymer membranes [8]. It was previously reported that the membranes with higher water uptake exhibited better proton conductivity [11]. Moreover, porous PEMs are only conductive when immersed in water and could swell to approximately 20–30% by weight [21].

Table 1 lists the block's water uptake, ion exchange capacity, proton conductivity values, and random PAES copolymer membrane samples.

The block PAES copolymer membrane recorded higher water uptake than the PAES copolymer membrane. The observations were mainly due to processing, which significantly improved the phase separation of the block copolymers. Furthermore, larger pores might also be attributed to the findings as water uptake directly correlates with the pore size of membranes [22].

Interestingly, the water uptake trends of the membranes analyzed in the present study demonstrated increment at approximately 80°C. Therefore, the results demonstrated that the membranes performed effectively at high temperatures since improved water uptake results in enhanced IEC. Furthermore, the pores enable the hydronium ions to pass through the membranes, which boosts the transport of protons, particularly in a humidified environment. Hence, the IEC of the membranes is greatly improved [23]. Consequently, the phase separation performed in the present study affected the properties of the synthesized membranes in terms of water uptake and ion exchange capacity.

Proton conductivity is a significant parameter that verifies the performance of PEMs. The results in Table 1 revealed that the block PAES membrane exhibited better conductivity at two mS/cm. The random PAES membrane only recorded 0.3 mS/cm when operated at room temperature. The findings could be attributed to triptycene, which induces pore formations within polymer matrixes. The pores would facilitate proton transports, especially in a humidified state, due to more accessible hydronium ions transfers through the membranes [23].

The porous morphology of membranes reportedly aids proton transport [15]. The block PAES membrane procured in the current study allowed a significant proton amount to pass through as it recorded larger pores and porosity. Moreover, the lack of ionic groups indicated that proton conductivity occurred via the vehicle mechanism. The results follow block and random membranes' water uptake and IEC trend.

3.4. Fuel Cell Performance of Block and Random PAES Membrane

It is vital to validate the applicability of the procured membranes for PEMFC, where the current and power densities are determined, by assessing their fuel cell performance. Figure 7 illustrates the current density-voltage and the power-current density curves of the electrode assembly of the membranes in single cells operated at 80°C and 60% RH. The block PAES membrane performed well, exhibiting maximum current and power densities of 239.92 mA/cm² and 99 mW/cm². In contrast, the random PAES membrane fulfilled inferiorly, recording maximum current and power densities of 175 mA/cm² and 73 mW/cm².

The results revealed that the block PAES membrane possessed the lowest degradation for MEA applications compared to the random PAES membrane. The superior performance documented by the block PAES sample might be attributed to its excellent proton conductivity and water uptake since fuel cell performance peaks when its proton conductivity is at the highest value.

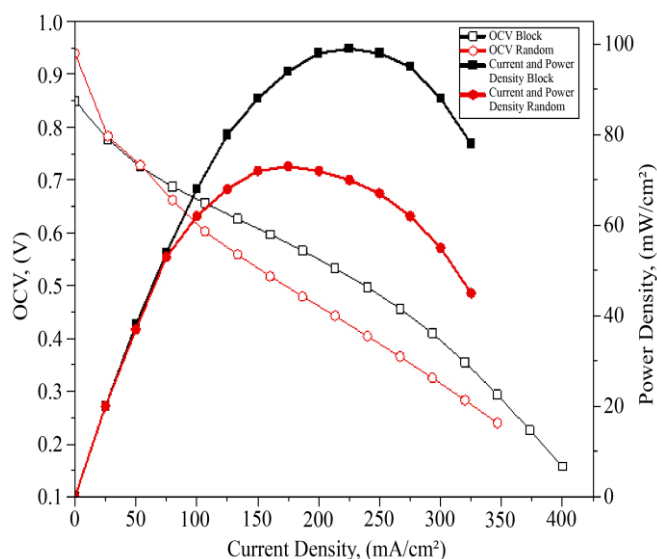


Fig. 7 Fuel cell performance of block and random PAES membranes at 80°C and 60% RH

4. Conclusion

The present study successfully synthesized triptycene-integrated, block, and random PAES copolymers, and the properties of both copolymers were further analyzed. The structural analyses of the synthesized monomer, oligomers, and polymers were conducted using ¹HNMR, FTIR, and GPC. It was found that the random PAES copolymer produced higher molecular weight compared to the block PAES copolymer.

The FESEM images demonstrated that the block PAES membrane consisted of larger pores and was more porous than the random PAES membrane, mainly attributed to the lower molecular weight of the produced block PAES copolymer. Furthermore, the random PAES polymer, which made higher molecular weight, was observed to have small interconnected membrane pore structures. The thermogravimetric analysis also demonstrated that the triptycene-integrated block PAES copolymer membrane was more thermally stable than a random PAES copolymer membrane.

Adding triptycene monomers to the polymer backbones increased the porosity of the synthesized membranes. The current study also found that pore size and porosity facilitated

water uptake, ion exchange capacity, and proton conductivity of the PEMs. The membrane procured in this study passed the PEMFC test at an operating temperature of 80°C and 60% RH.

Hence, this study showed that the morphology and properties of the synthesized polymer varied when different synthesis methods were applied. Additionally, selecting the monomer and the synthesis method is essential in designing the polymer with the desired properties.

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