

Preparation and properties of UV-crosslinked imidazole functionalized poly(aryl ether sulfone) anion exchange membrane

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In this study, poly(aryl ether sulfone) with a 200% degree of chloromethylation was sequentially grafted with 4-hydroxychalcone and *p*-hydroxybenzyl alcohol (HBA), followed by chlorination (SOCl₂) and quaternization with 1,2,4,5-tetramethylimidazole, yielding the target polymer QPSPSF60-TMIm140. ¹H NMR confirmed a side-chain composition of 30% chalcone and 70% imidazolium units. Photochemical reactions of QPSPSF60-TMIm140 were carried out under UV irradiation to form cross-linked structures. Two types of anion exchange membranes with different degrees of photocrosslinking (cQPSPSF60-TMIm140-xmin) were prepared by UV irradiation with different crosslinking times. At 80 °C, the uncrosslinked membrane exhibited a water uptake (WU) of 440.4%, a swelling ratio (SR) of 77.3%, and an ionic conductivity (σ) of 120.5 mS·cm⁻¹. After 6 min of UV crosslinking, cQPSPSF60-TMIm140-6min showed reductions in WU and SR of 31.8% and 22.5%, respectively, while σ remained high at 110.1 mS·cm⁻¹ (only an 8.6% decrease). The crosslinked membrane also demonstrated excellent alkaline stability: after 20 days in 1 mol·L⁻¹ NaOH at 60 °C, it retained 90.4% of its initial ion exchange capacity and 90.0% of its original conductivity. Moreover, photocrosslinking improved the thermal and mechanical properties: the initial decomposition temperature increased by 7 °C and the tensile strength rose by 8.1 MPa compared with the uncrosslinked counterpart. These results indicate that the photo-induced crosslinking strategy effectively enhances dimensional stability and alkaline resistance without significantly compromising ionic conductivity, offering a promising route to high-performance AEMs for fuel cell applications.

Photocrosslinking; side-chain-type; 1,2,4,5-tetramethylimidazole; anion exchange membrane

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1. Introduction

Anion exchange membrane fuel cells (AEMFCs) are a rapidly developing class of fuel cells that offer several advantages, including fast oxygen reduction reaction kinetics, low fuel permeability, and the ability to use non-precious metals as electrode catalysts^[1-2]. As such, they represent a promising clean energy conversion technology capable of replacing proton exchange membrane fuel cells^[3-5]. Anion exchange membranes (AEMs), as key components of AEMFCs^[6-8], serve to separate the anode and cathode,

transport OH⁻, and support catalysts, which directly determining the performance and service life of the fuel cells^[9]. Despite recent advances, existing AEMs still face the challenge of balancing ionic conductivity, dimensional stability, and alkali resistance, which limits the widespread adoption of AEMFCs. Consequently, the development of AEMs that simultaneously achieve high ionic conductivity and excellent alkaline stability has become a major research focus^[10-12].

Ionic conductivity in polymer membranes is typically enhanced by increasing the ion exchange capacity (IEC). However, excessively high IEC often leads to increased water uptake and swelling ratio, compromising dimensional stability and mechanical strength, and potentially causing membrane rupture. To address this issue, researchers have

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focused on tailoring the molecular architecture of AEMs and optimizing the hydrophilic-hydrophobic balance to induce well-defined microphase-separated morphologies. Such structures facilitate the formation of interconnected hydrophilic domains that serve as efficient ion-conducting pathways, enabling high ionic conductivity even at moderately low IEC levels^[13-14]. Current strategies to promote microphase separation include the design and synthesis of side-chain-type^[15], ion-cluster-type^[16], and block-type^[17] AEMs. Nevertheless, when the IEC of these membranes is raised too high, they remain susceptible to excessive water uptake, increased swelling, and reduced alkaline stability.

Crosslinking represents a key strategy to balance ionic conductivity, dimensional stability, and alkaline resistance in AEMs^[18-20]. The introduction of a three-dimensional cross-linked network tightly connects polymer chains, effectively suppressing excessive water uptake and swelling, thereby enhancing dimensional stability. Moreover, such a network can act as a physical barrier that hinders the attack of hydroxide ions (OH^-) on both the polymer backbone and cationic functional groups, slowing membrane degradation in alkaline environments and improving overall alkaline stability^[21].

In this study, poly(aryl ether sulfone) with excellent thermal, chemical, and dimensional stability was selected as the polymer backbone. The backbone was chemically modified to introduce chalcone and anisole moieties into the side chains, followed by functionalization with 1,2,4,5-tetramethylimidazole, a cation with high alkaline stability^[22-24]. A UV-crosslinkable imidazole-functionalized AEM was then prepared by UV irradiation for different durations. On one hand, the anisole-containing side chains promote the formation of a microphase-separated morphology within the membrane, enhancing ion transport and thus ionic conductivity. On the other hand, these side chains spatially separate the cationic groups from the polymer backbone, mitigating OH^- -induced degradation of the ether linkages and improving alkaline stability. Meanwhile, the chalcone units undergo a [2+2] cycloaddition reaction under UV light, forming a crosslinked network between polymer chains. Notably, this crosslinking process can be conducted at room temperature in the swollen state without any photoinitiator, helping to preserve the pre-formed ion-conducting channels during network formation. As a result, the adverse effect of crosslinking on ionic conductivity is minimized, while the mechanical properties and alkaline resistance of the AEMs are simultaneously enhanced.

2. Experiment section

2.1 Chemical reagents

Poly(aryl ether sulfone) with a chloromethylation degree of 200% (CMPSF200) and 4-hydroxychalcone (4-HC) were synthesized according to Ref.[25]. All reagents were of analytical grade and obtained from the following sources:

CHCl_3 , ZnCl_2 , tetrahydrofuran (THF), *N*-methylpyrrolidone (NMP), CH_3OH , K_2CO_3 , *p*-hydroxybenzyl alcohol (HBA), NaOH, *N,N*-dimethylformamide (DMF), and thionyl chloride (SOCl_2) were purchased from Sinopharm Chemical Reagent Co., Ltd.; tetrabutylammonium bromide (TBAB), was purchased from Aladdin Biochemical Technology Co., Ltd.; and 1,2,4,5-Tetramethylimidazole (TMIm) was purchased from Shanghai Macklin Biochemical Technology Co., Ltd.

2.2 Preparation of AEMs

CMPSF200 (2 g) and DMF (60 mL) were added to a 100 mL single-necked flask and stirred until completely dissolved. Subsequently, 4-HC (0.7 g), TBAB (1.68 g), and K_2CO_3 (0.72 g) were added sequentially, and the mixture was reacted in a water bath at 35 °C for 40 min. After the reaction, the crude product was precipitated by pouring the mixture into deionized water, then filtered and dried. The dried crude product was dissolved in THF, reprecipitated in CH_3OH , collected by suction filtration, and dried again to afford photosensitive poly(aryl ether sulfone) (PSPSF60) in a yield exceeding 95%.

Next, 2 g of PSPSF60 and 60 mL of DMF were added to a 100 mL single-necked flask and stirred until dissolved. Subsequently, 2.96 g of HBA, 3.74 g of TBAB, and 1.70 g of K_2CO_3 were added sequentially, and the mixture was reacted in a water bath at 40 °C for 3.5 h. After the reaction, the product was obtained as a white flocculent polymer (PSPSF60-HBA140) by precipitation with deionized water, followed by suction filtration and drying in an oven. The yield exceeded 95%.

Then, PSPSF60-HBA140 (2 g) and DMF (60 mL) were added to a 100 mL single-necked flask and stirred until completely dissolved. SOCl_2 (1.8 mL) was added dropwise to the solution, and the reaction mixture was stirred in an ice bath for 30 min. After the reaction, the product was precipitated in CH_3OH , collected by suction filtration, and dried under vacuum to afford side-chain-type photosensitive chloromethylated poly(aryl ether sulfone) (PSPSF60-CM140) as a white, fine flocculent solid in over 95% yield.

For the preparation of the UV-crosslinkable membrane, PSPSF60-CM140 (0.5 g) was dissolved in NMP (8 mL) in a 25 mL single-necked flask with stirring to obtain a homogeneous solution. An equimolar amount of TMIm was then added, and the reaction mixture was stirred at 60 °C for 2 h. After the reaction was complete, the solution was filtered and cast onto a smooth glass plate (8 cm × 8 cm). The cast film was first dried on a hot plate at 60 °C for 3 h under a N_2 atmosphere, followed by further drying in an oven at 80 °C until complete removal of the solvent. The resulting membrane was peeled off, immersed in a 1 mol·L⁻¹ NaOH aqueous solution for 48 h to complete the alkalinization process, and finally rinsed thoroughly with distilled water prior to use. This gave the UV-crosslinkable side-chain-type imidazole-functionalized anion exchange

membrane (QPSPSF60-TMIm140).

To obtain UV-crosslinked membranes, the QPSPSF60-TMIm140 membrane was immersed in deionized water for 24 h to reach a fully hydrated state. It was then irradiated with UV light under a N₂ atmosphere for 3 and 6 min, respectively, to yield two membranes with different degrees of photocrosslinking, designated as cQPSPSF60-TMIm140-*x*min (*x* = 3, 6). The entire process is illustrated in Figure 1.

2.3 Characterization and properties

2.3.1 Characterization

¹H NMR spectra were recorded on a Bruker AVANCE III 400 MHz fully digital nuclear magnetic resonance spectro-

meter (Germany), using tetramethylsilane (TMS) as the internal standard and CDCl₃ or DMSO-d₆ as the solvent. UV-Vis absorption spectra were measured on a Shimadzu UV-2450 spectrophotometer (Japan) over a wavelength range of 200 to 800 nm. Thermogravimetric analysis was performed on a NETZSCH TG209 F3 instrument (Germany). The AEM samples were heated from 30 to 600 °C at a rate of 10 °C·min⁻¹ under a N₂ atmosphere with a flow rate of 30 mL·min⁻¹. Tensile tests were conducted using an INSTRON AI-7000M servo-controlled computer system tensile testing machine (USA). Specimens with dimensions of 10 mm × 70 mm were tested at a crosshead speed of 5 mm·min⁻¹.

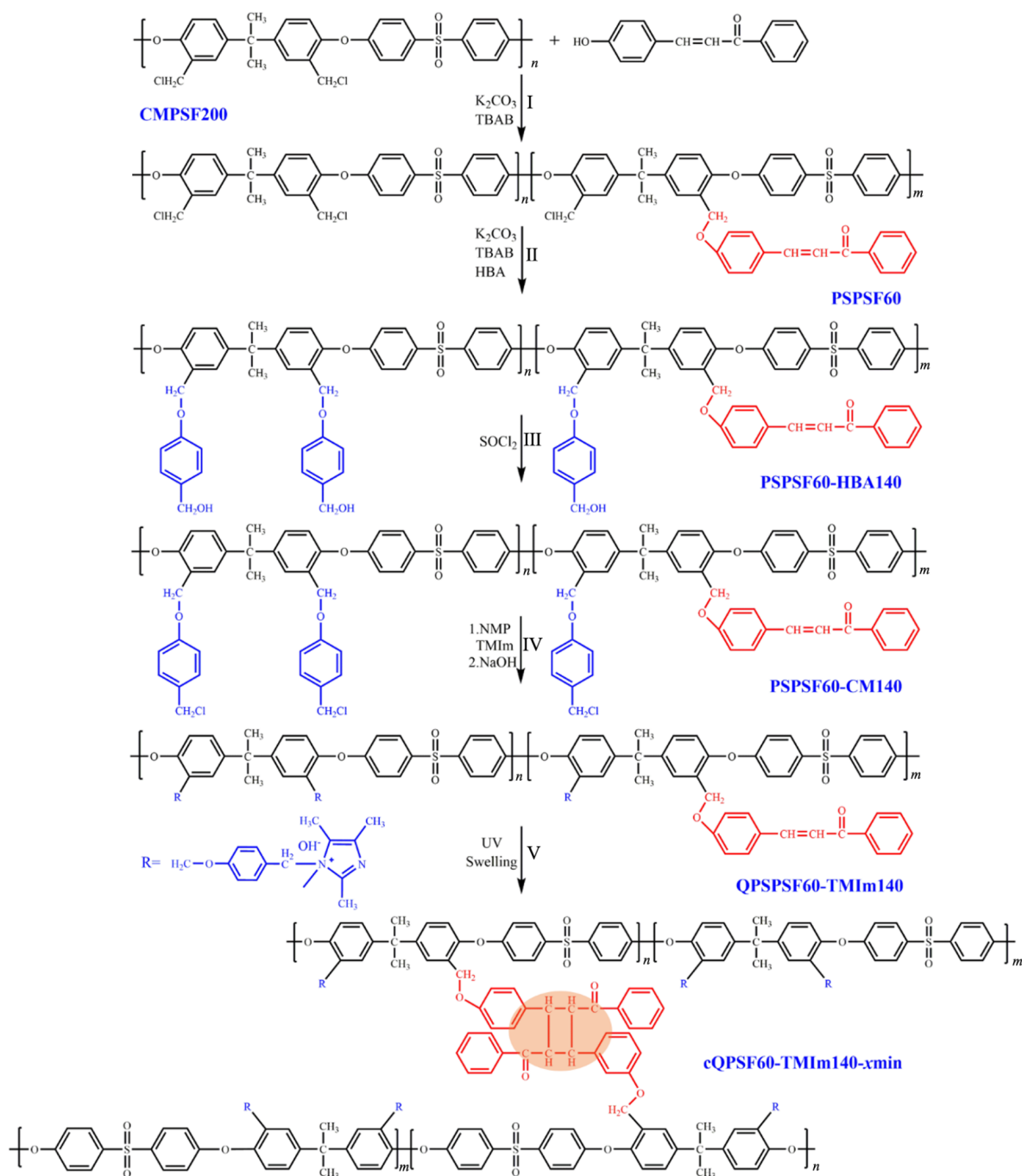


Figure 1 Synthetic route of AEMs

2.3.2 Photosensitivity

Dissolve QPSPSF60-TMIm140 in *N,N*-dimethylacetamide (DMAC) to prepare a solution with a mass fraction of 0.1%. Coat the solution on the surface of a cuvette and dry to form a film. Use a Newport Model 9119X UV exposure instrument (USA) to irradiate the polymer membrane with UV light in the wavelength range of 320 to 450 nm for different durations. Test the UV-Vis spectra of the polymer with varying irradiation time using a UV-Vis spectrometer. The crosslinking degree (ρ) of the polymer is calculated by Equation (1),

$$\rho = \frac{A_0 - A_t}{A_0} \times 100\%, \quad (1)$$

where A_0 and A_t represent the absorbance of the polymer film at the maximum absorption peak for irradiation times (s) of 0 and t , respectively.

2.3.3 Ion exchange capacity

The ion exchange capacity (IEC, C_{IE}) of AEMs was tested by back titration. Weigh the dry membrane (m), soak the membrane in a certain volume of $0.05 \text{ mol} \cdot \text{L}^{-1}$ HCl (V_{HCl}) solution for 48 h. Using phenolphthalein as an indicator, titrate with $0.01 \text{ mol} \cdot \text{L}^{-1}$ NaOH solution, and accurately record the volume of NaOH solution used (V_{NaOH}). The IEC of AEMs is calculated by Equation (2).

$$C_{IE} = \frac{c_{\text{HCl}} \times V_{\text{HCl}} - c_{\text{NaOH}} \times V_{\text{NaOH}}}{m} \times 1000. \quad (2)$$

2.3.4 Water uptake and swelling ratio

Weigh the dry AEM (m_{dry}) and measure its length (l_{dry}). Then soak the dry membrane in deionized water at different temperatures for 48 h to reach water absorption equilibrium. Take out the membrane, quickly wipe off the water on the membrane surface with filter paper, weigh the wet membrane (m_{wet}) and measure its length (l_{wet}). The water uptake (WU, R_W) and swelling ratio (SR, R_S) of the membrane are calculated by Equations (3) and (4).

$$R_W = \frac{m_{\text{wet}} - m_{\text{dry}}}{m_{\text{dry}}} \times 100\%, \quad (3)$$

$$R_S = \frac{l_{\text{wet}} - l_{\text{dry}}}{l_{\text{dry}}} \times 100\%. \quad (4)$$

2.3.5 Ionic conductivity

The AEM was first immersed in a $1 \text{ mol} \cdot \text{L}^{-1}$ NaOH solution for 48 h to complete alkalization. Subsequently, the membrane was taken out and thoroughly rinsed with distilled water to remove residual alkali. Then, a membrane sample ($1 \text{ cm} \times 1.5 \text{ cm}$) was then mounted between two platinum electrodes and placed in a constant temperature and humidity chamber. The electrodes were connected to an Autolab AUT87128 electrochemical workstation to measure the membrane resistance (R) at various temperatures. The ionic conductivity (σ) of the AEM was calculated using Equation (5), where L is the distance between the electrodes,

and A is the effective cross sectional area of the membrane.

$$\sigma = \frac{L}{A \times R}. \quad (5)$$

2.3.6 Alkaline stability

The crosslinked and uncrosslinked AEMs were immersed in a $1 \text{ mol} \cdot \text{L}^{-1}$ NaOH solution at 60°C for 20 days. At pre-determined time intervals, membrane samples were retrieved, thoroughly rinsed with deionized water to remove surface alkali, and then characterized. The temporal evolution of both IEC and the σ was monitored to evaluate the alkaline stability.

3 Results and discussion

3.1 Preparation and characterization of QPSPSF60-TMIm140

First, CMPSF200 with a chloromethylation degree of 200% was functionalized with chalcone to afford the photosensitive polymer PSPSF60, which has a chalcone grafting degree of 30%. Subsequently, the remaining chloromethyl groups in PSPSF60 were fully substituted by HBA to yield PSPSF60-HBA140. The $-\text{OH}$ of the incorporated HBA units were then chlorinated using SOCl_2 , giving PSPSF60-CM140. Finally, quaternization was performed with TMIm, followed by alkalization, to obtain the target membrane material QPSPSF60-TMIm140, which contains 30% chalcone and 70% imidazolium side chains.

The chemical structure of each intermediate and the final polymer was confirmed by ^1H NMR spectroscopy (See Figure 2). In the ^1H NMR spectrum of PSPSF60, the characteristic signal of the chloromethyl protons at 4.65 decreased significantly after chalcone grafting. Concurrently, new resonances emerged at 5.02 and in the region of 7.45 to 7.98, which are assigned to the methylene protons adjacent to the chalcone moiety and the aromatic protons of chalcone, respectively. These changes confirm the successful introduction of chalcone. The grafting degree (30%) was determined by integrating the relative peak areas of these

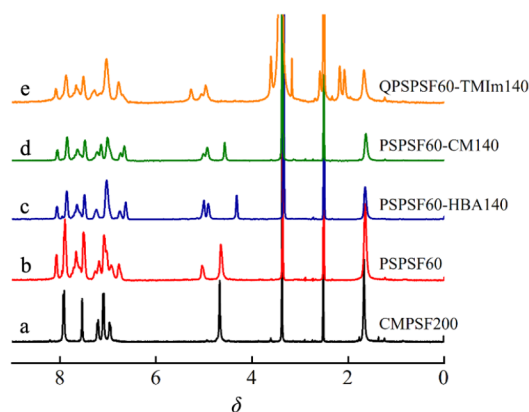


Figure 2 ^1H NMR spectra of polymers

newly appeared methylene protons and the remaining chloromethyl protons. After substitution with HBA, the chloromethyl signal at 4.55 disappeared completely. New peaks appeared at 4.33 (methylene protons adjacent to the hydroxyl group), 4.92 (methylene protons of the benzyl ether linkage), and 6.63 (aromatic protons ortho to the hydroxymethyl group). These features verify the complete conversion of the residual chloromethyl groups to HBA-substituted units, yielding PPSF60-HBA140.

After chlorination of the —OH groups in the side chain of PPSF60, the original methylene peak adjacent to the alcohol hydroxyl group at 4.33 completely disappeared. Meanwhile, a new proton absorption peak corresponding to the chloromethyl group on the side chain appeared at 4.59, indicating that —OH was fully substituted by —Cl and confirming the successful synthesis of PPSF60-CM140. Finally, the spectrum of the quaternized polymer QPSPSF60-TMIm140 shows the disappearance of the chloromethyl peak at 4.58. A new signal at 5.47 corresponds to the methylene protons linked to the imidazolium cation. Additionally, four distinct methyl proton signals from TMIm are observed at 3.69, 2.53, 2.14, and 2.12. These results collectively confirm the successful formation of the imidazolium salt and the synthesis of the target ionomer.

3.2 Photosensitivity of QPSPSF60-TMIm140 and preparation of cQPSPF60-TMIm140-xmin

The photosensitivity of QPSPSF60-TMIm140 was evaluated by ultraviolet irradiation in the wavelength range of 350 to 450 nm. The UV-Vis spectra and the conversion rate of the —CH=CH— group in the chalcone units as a function of UV irradiation time are shown in Figure 3. As illustrated in Figure 3a, QPSPSF60-TMIm140 exhibits excellent photosensitivity. The maximum absorption peak (λ_{max}) of the —CH=CH— group in the chalcone structure appears at 340 nm. With increasing UV irradiation time, the intensity of this peak gradually decreases. This decrease is attributed to the [2+2] photoaddition reaction of the —CH=CH— group

in the chalcone side chains of QPSPSF60-TMIm140, which forms a crosslinked structure and progressively consumes the —CH=CH— group. This observation also confirms that the photosensitive chalcone groups were successfully grafted onto the polymer side chains. The UV-Vis spectra qualitatively illustrate the crosslinking process of the —CH=CH— group. The degree of crosslinking was quantitatively calculated using Equation (1). Figure 3b presents the reaction rate curve, plotting the photocrosslinking degree against irradiation time. The reaction rate was rapid during the initial stage of photocrosslinking. After 100 s of irradiation, the photocrosslinking degree reached 49%, after which the photoreaction slowed down. This deceleration is attributed to the isolation effect of the chalcone groups and the restriction imposed by the already formed crosslinked network on further photocrosslinking of the remaining —CH=CH— group. The experimental results showed that the maximum photocrosslinking degree attained was 73%^[26-27]. Based on the photocrosslinking degrees shown in Figure 3b, two irradiation times of 3 and 6 min were selected. QPSPSF60-TMIm140 was irradiated with UV light at room temperature in the swollen state under N_2 protection to prepare cQPSPF60-TMIm140-3min and cQPSPF60-TMIm140-6min, two membranes with different crosslinking degrees, in order to investigate the effect of the photocrosslinking degree on the properties of the AEMs.

3.3 Surface morphology of QPSPSF60-TMIm140 and cQPSPF60-TMIm140-xmin

Figure 4 shows the AFM phase images of QPSPSF60-TMIm140 and cQPSPF60-TMIm140-xmin. Both membranes exhibit clear phase-separated structures with alternating bright and dark regions. The anisole side chain structure promotes the aggregation of cationic groups away from the main chain into clusters, inducing the formation of hydrophilic/hydrophobic microphase-separated morphologies and constructing continuous ion transport channels, which is beneficial for OH^- transport. Notably, the size of the ion

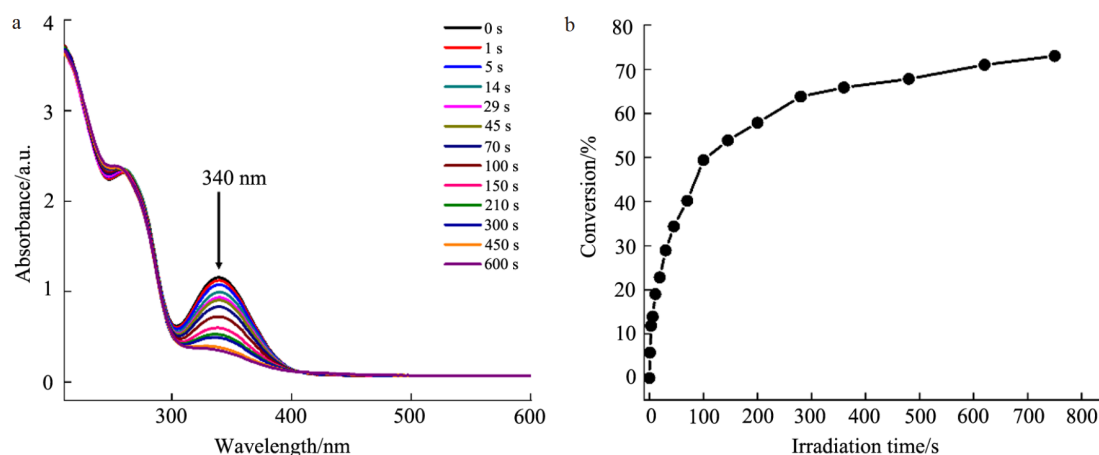


Figure 3 UV-Vis spectra (a) and conversion rate (b) of QPSPSF60-TMIm140 under different UV irradiation times

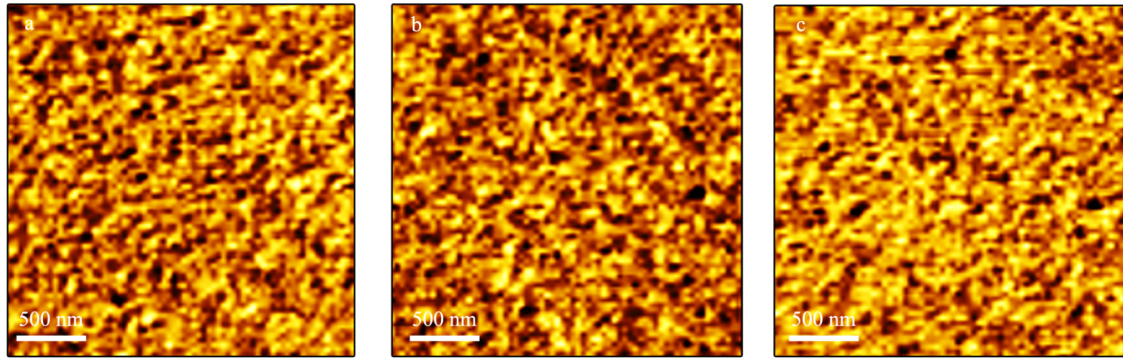


Figure 4 AFM images of uncrosslinked membrane QPSPSF60-TMIm140(a), cQPSPF60-TMIm140-3min (b), and cQPSPF60-TMIm140-6min (c)

clusters remains almost unchanged before and after photocrosslinking, indicating that the crosslinking process has little effect on the internal ion channels and ionic conductivity of the membrane.

3.4 Properties of QPSPSF60-TMIm140 and cQPSPF60-TMIm140-xmin

The IEC is defined as the millimoles of ion exchange groups per gram of dry membrane ($\text{mmol} \cdot \text{g}^{-1}$), significantly influences the water uptake, swelling ratio, and ionic conductivity of AEMs, and is therefore a key indicator for evaluating AEM performance. Table 1 lists the theoretical and actual IEC values, as well as the water uptake and swelling ratio of QPSPSF60-TMIm140 and cQPSPF60-TMIm140-xmin. For QPSPSF60-TMIm140, the theoretical and actual IEC values were 1.47 and $1.36 \text{ mmol} \cdot \text{g}^{-1}$, respectively. The actual IEC was slightly lower than the theoretical value, mainly due to incomplete replacement of OH^- and Cl^- . The actual IEC values of cQPSPF60-TMIm140-xmin were lower than that of QPSPSF60-TMIm140, and a higher crosslinking degree led to a greater decrease in IEC. This is attributed to the crosslinked network structure hindering ion exchange to some extent. For cQPSPF60-TMIm140-6min, which has a high crosslinking degree, the IEC decreased by only 8.1% compared with QPSPSF60-TMIm140, indicating that the photocrosslinking method employed in this study has little effect on IEC.

Moderate water uptake and swelling ratio can promote hydration of cationic groups, accelerate ion dissociation, and facilitate rapid ion conduction, all of which are crucial for AEMs. However, excessive water uptake dilutes the hydroxide ion concentration, leading to reduced ionic conductivity, and may even cause membrane deformation or

rupture, thereby limiting practical applications. As shown in Table 1, the water uptake and swelling ratio of both QPSPSF60-TMIm140 and cQPSPF60-TMIm140-xmin increased with increasing temperature. This is likely because higher temperatures accelerate polymer chain mobility, increasing the free volume within the membrane and allowing more water molecules to be stored. At 80°C , the water uptake and swelling ratio of QPSPSF60-TMIm140 were 440.4% and 77.3%, respectively. After 6 min of UV irradiation, the water uptake and swelling ratio of the crosslinked membrane decreased by 31.8% and 22.5%, respectively. This reduction is due to the crosslinked network restricting molecular chain movement, thereby reducing water uptake and improving dimensional stability.

3.5 Ionic conductivity of QPSPSF60-TMIm140 and cQPSPF60-TMIm140-xmin

Ionic conductivity is a decisive parameter for the performance of AEMFCs, making the hydroxide ion conductivity of AEMs a primary metric for membrane evaluation. The temperature-dependent OH^- conductivities of the uncrosslinked membrane QPSPSF60-TMIm140 and the photocrosslinked membranes cQPSPF60-TMIm140-xmin are presented in Figure 5. As expected, the ionic conductivity of all membranes increased with rising temperature. This trend is attributed to the enhanced mobility of water molecules and polymer chain segments at elevated temperatures, which facilitates ion transport. Furthermore, the flexible side-chain architecture endows the cationic groups with high local mobility, thereby contributing to the overall conductivity.

As summarized in Figure 5 and Table 1, cQPSPF60-TMIm140-3min and cQPSPF60-TMIm140-6min exhibited high conductivities of 114.3 and $110.1 \text{ mS} \cdot \text{cm}^{-1}$, respec-

Table 1 IEC, water uptake, swelling ratio, and ionic conductivity of AEMs

AEM	IEC/($\text{mmol} \cdot \text{g}^{-1}$)		WU/%		SR/%		$\sigma/(\text{mS} \cdot \text{cm}^{-1})$	
	Theor ^a	Exp ^b	20 $^\circ\text{C}$	80 $^\circ\text{C}$	20 $^\circ\text{C}$	80 $^\circ\text{C}$	20 $^\circ\text{C}$	80 $^\circ\text{C}$
QPSPSF60-TMIm140	1.47	1.36	29.9	440.4	9.8	77.3	44.0	120.5
cQPSPF60-TMIm140-3min	-	1.30	28.8	325.8	9.6	66.8	40.7	114.3
cQPSPF60-TMIm140-6min	-	1.25	27.0	300.2	9.5	59.9	38.1	110.1

a: calculated by ^1H NMR; b: tested by back titration.

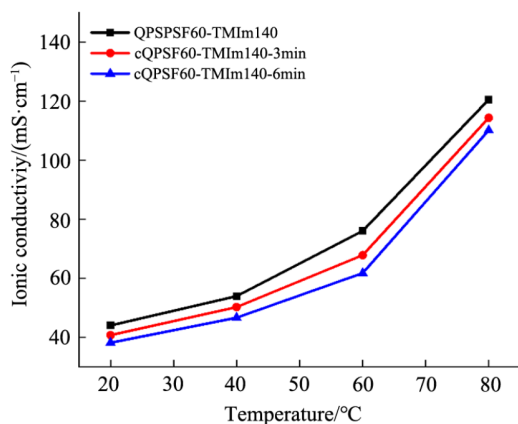


Figure 5 Ionic conductivity of QSPSF60-TMIm140 and cQPSF60-TMIm140-xmin at different temperatures

tively, at 80 °C. Compared to the value of the uncrosslinked reference membrane QSPSF60-TMIm140 ($120.5 \text{ mS}\cdot\text{cm}^{-1}$), these represent modest reductions of only 5.1% and 8.6%. This result indicates that UV-induced crosslinking effectively suppresses excessive water uptake and swelling while imposing a minimal penalty on ionic conductivity.

A comparison of the overall membrane performance between this work and recently reported AEMs is provided in Figure 6. Notably, although cQPSF60-TMIm140-6min possesses a lower IEC than several other membranes, it achieves a higher ionic conductivity. This favorable compromise between IEC and conductivity underscores its superior overall performance^[20,28-33].

Considering the water uptake, swelling ratio, and ionic conductivity of the membranes comprehensively, the performance of cQPSF60-TMIm140-6min was better than that of cQPSF60-TMIm140-3min. Therefore, the subsequent investigations into mechanical properties, thermal stability, and alkaline stability were focused primarily on QSPSF60-TMIm140 and the optimally crosslinked membrane cQPSF60-TMIm140-6min.

3.6 Alkaline stability of QSPSF60-TMIm140 and cQPSF60-TMIm140-6min

Alkaline stability is a critical factor determining the long-term durability of AEMs in fuel cell applications. To evaluate this property, QSPSF60-TMIm140 and cQPSF60-TMIm140-6min were subjected to an accelerated aging test in $1 \text{ mol}\cdot\text{L}^{-1}$ NaOH at 60 °C. The temporal evolution of their IEC and σ was monitored, and the results are shown in Figure 7. After 20 days of aging, QSPSF60-TMIm140 experienced reductions of 14.3% in IEC and 12.7% in conductivity. In contrast, cQPSF60-TMIm140-6min showed superior retention, with decreases of only 9.6% in IEC and 10.0% in conductivity. These results clearly demonstrate that the three-dimensional crosslinked network effectively shields the polymer backbone (particularly the ether linkages) and the cationic functional groups from hydroxide ion attack, thereby significantly enhancing the alkaline stability of the membrane.

3.7 Thermal stability and mechanical properties of QSPSF60-TMIm140 and cQPSF60-TMIm140-6min

The TGA results are shown in Table 2 and Figure 8a. The decomposition of QSPSF60-TMIm140 and cQPSF60-TMIm140-6min mainly occurred in three stages. The first stage started at about 239 °C, primarily due to the decomposition of imidazole groups; the second stage began near 322 °C, corresponding to the degradation of the chalcone side chain units; the final decomposition stage above 425 °C is associated with the cleavage of the polymer backbone. Notably, cQPSF60-TMIm140-6min exhibited higher onset temperatures in each degradation step compared to its uncrosslinked counterpart, confirming that the photo-induced crosslinked network enhances the thermal stability of the material. Since the typical operating temperature of AEMFCs is around 80 °C, the thermal performance of cQPSF60-TMIm140-6min is fully adequate for practical applications.

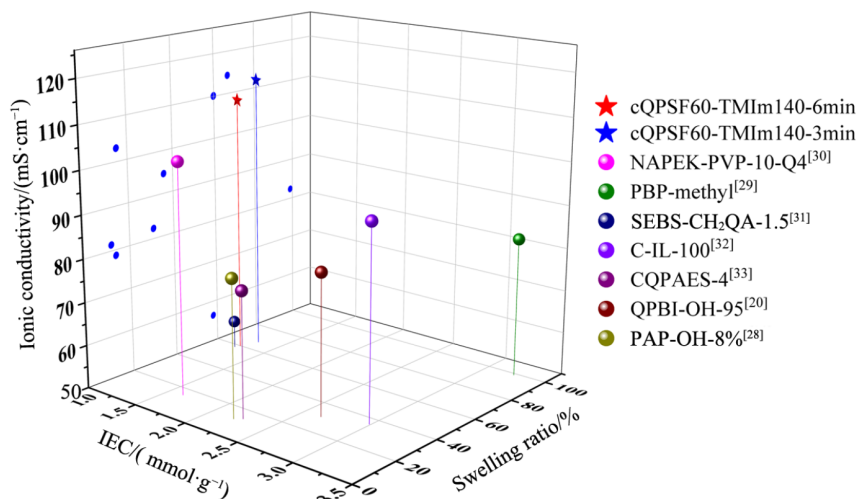


Figure 6 Performance comparison of AEMs in previous reports and this study

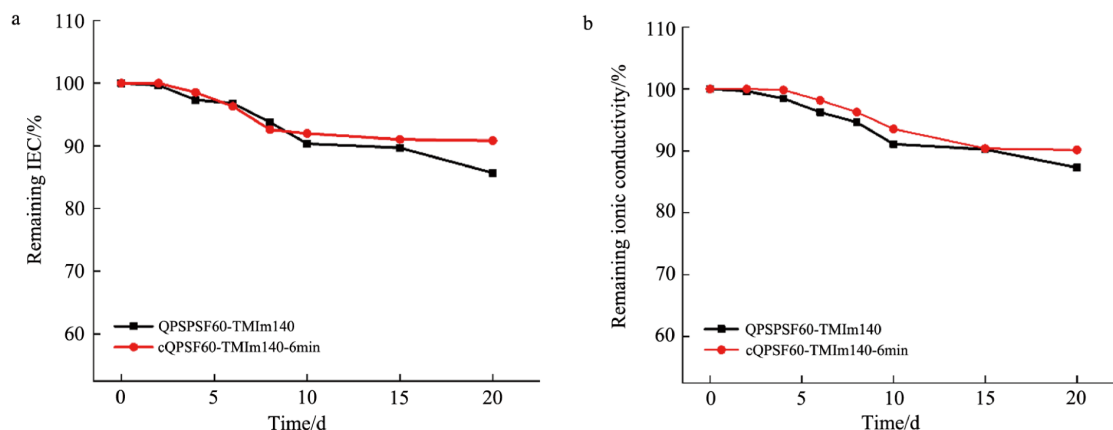


Figure 7 IEC retention(a) and ionic conductivity retention(b) of QPSPSF60-TMIm140 and cQPSPF60-TMIm140-6min with time

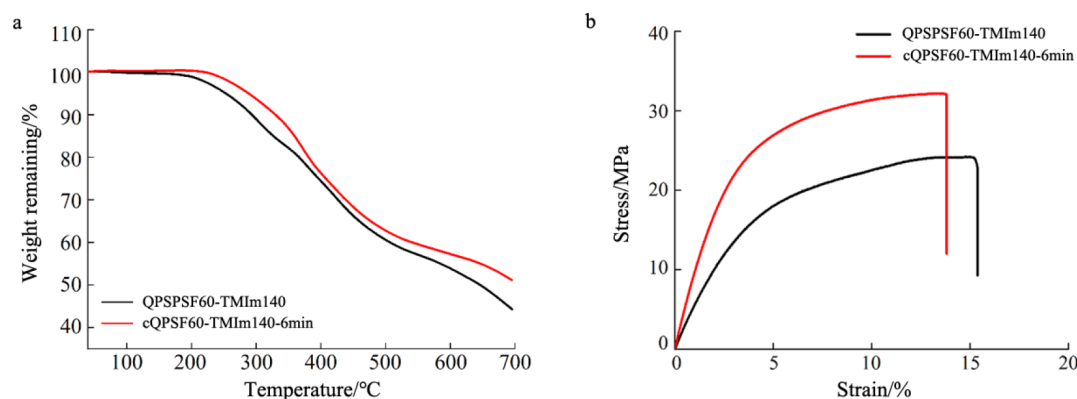


Figure 8 TGA thermogram (a) and stress-strain curves (b) of QPSPSF60-TMIm140 and cQPSPF60-TMIm140-6min

Table 2 Thermal properties of QPSPSF60-TMIm140 and cQPSPF60-TMIm140-6min

AEM	$t_{d1}/^{\circ}\text{C}$	$t_{d2}/^{\circ}\text{C}$	$t_{d3}/^{\circ}\text{C}$
QPSPSF60-TMIm140	239	322	425
cQPSPF60-TMIm140-6min	246	329	429

t_{d1} , t_{d2} , and t_{d3} represent the first, second, and third weight loss temperatures, respectively.

The mechanical properties were investigated by tensile testing, and the stress-strain curves are presented in Figure 8b. The uncrosslinked membrane QPSPSF60-TMIm140 showed a tensile strength of 24.2 MPa and an elongation at break of 15.4%. After crosslinking, cQPSPF60-TMIm140-6min exhibited a 25.1% increase in tensile strength (32.3 MPa), while the elongation at break decreased by 11.0% (to 13.7%). This improvement in strength, accompanied by a moderate reduction in ductility, is a direct result of the crosslinked network, which restricts chain mobility and enhances intermolecular interactions, thereby increasing stiffness while maintaining sufficient toughness for membrane handling and operation.

4 Conclusion

In this study, a photo-crosslinkable anion-exchange mem-

brane was successfully developed through the sequential functionalization of a highly chloromethylated poly(aryl ether sulfone). The target polymer, QPSPSF60-TMIm140, featuring side chains containing 30% chalcone and 70% imidazolium units, was synthesized and confirmed by ^1H NMR. Upon UV irradiation, the chalcone groups underwent a [2+2] photocycloaddition, forming a crosslinked network with a maximum crosslinking degree of 73%. Two crosslinked membranes, cQPSPF60-TMIm140-3min and cQPSPF60-TMIm140-6min, were fabricated by varying the irradiation time.

The photocrosslinking strategy effectively improved the overall membrane performance. Compared with the uncrosslinked membrane, cQPSPF60-TMIm140-6min exhibited significantly reduced water uptake (by 31.8%) and swelling ratio (by 22.5%) while maintaining high ionic conductivity ($110.1 \text{ mS}\cdot\text{cm}^{-1}$, only an 8.6% reduction). Moreover, after 20 days of accelerated aging in $1 \text{ mol}\cdot\text{L}^{-1}$ NaOH at 60°C , the crosslinked membrane retained 90.4% of its initial ion-exchange capacity and 90.0% of its original conductivity, demonstrating excellent alkaline stability. The crosslinked network also enhanced the thermal and mechanical properties, raising the initial decomposition temperature by 7°C and increasing the tensile strength by 8.1 MPa.

These results confirm that photo-induced crosslinking

provides an effective and practical approach to balancing the often-conflicting requirements of high ionic conductivity, dimensional stability, and alkaline resistance in anion-exchange membranes. The developed membrane system therefore exhibits strong potential for application in durable, high-performance anion-exchange membrane fuel cells.

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UV可交联的咪唑功能化聚芳醚砜阴离子交换膜的制备与性能

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摘要 以氯甲基化率为200%的聚芳醚砜为聚合物骨架, 通过侧链改性与功能化, 成功制备出一种侧链含30%查尔酮结构的UV可交联咪唑功能化聚芳醚砜阴离子交换膜(QPSPSF60-TMIm140)。采用¹H NMR和UV-Vis对聚合物的结构进行了表征。结果表明, QPSPSF60-TMIm140具有良好的光敏性, 在UV光照射下可发生光化学反应形成交联结构。通过控制UV光照时间, 制备了2种不同光交联度的阴离子交换膜(cQPSPSF60-TMIm140-xmin)。在80 °C时, QPSPSF60-TMIm140的吸水率和溶胀率分别达到440.4%和77.3%, 离子传导率为120.5 mS·cm⁻¹。经UV交联后, cQPSPSF60-TMIm140-6min的吸水率和溶胀率分别下降了31.8%和22.5%, 而离子传导率仍保持在110.1 mS·cm⁻¹以上。在60 °C的1 mol·L⁻¹ NaOH溶液中浸泡20 d后, cQPSPSF60-TMIm140-6min的离子交换容量和离子传导率分别保留初始值的90.4%和90.0%。此外, 光交联还显著提升了膜的热稳定性和机械性能。研究表明, 光交联策略有效改善了阴离子交换膜在高吸水条件下的尺寸稳定性与耐碱性, 所制备的膜材料在相关领域展现出良好的应用潜力。

关键词 光交联; 侧链型; 1,2,4,5-四甲基咪唑; 阴离子交换膜