Supporting information

A Highly Stable Aliphatic Backbone from Visible Light-induced RAFT Polymerization for Anion Exchange Membranes

Qianqian Ge,[1] Guangzu Wang,[2] Xiang Zhu,[1] Weisheng Yu,[2] Jiahui Zhou,[2] Bin Wu,[1] Yahua Liu,[2] Zhengzhi Zheng,[1] Zhengjin Yang,[2,]* Jiasheng Qian[1,]*

[1] Key Laboratory of Environment-Friendly Polymeric Materials of Anhui Province, School of Chemistry & Chemical Engineering, Anhui University, Hefei 230601, P.R. China

[2] Department of Applied Chemistry, School of Chemistry and Materials Science, University of Science and Technology of China, Hefei 230026, P.R. China

*Correspondence: yangzj09@ustc.edu.cn; 89022@ahu.edu.cn

1. General analytical information

1.1 Nuclear magnetic resonance (NMR) and Fourier transform infrared (FTIR) spectroscopy

NMR spectra were recorded on an AVANCEII 400 MHz or a Bruker Ascend™ 400 MHz instrument at room temperature using chloroform-D ($CDCl_3$) or methyl sulfoxide-d_6 (DMSO-d_6) as a solvent. For PQEVE membrane, the solid state nuclear magnetic resonance (NMR) was performed on a 600 MHz WB solid-state nuclear magnetic resonance spectrometer. Attenuated total reflection-Fourier transform infrared (ATR-FTIR) spectroscopy analysis of the membrane samples was performed with a ThermoFisher Nicolet FT-IR spectrometer (Germany) under ambient conditions with a resolution of 5 cm^{-1} and a wide spectral range of 4000-400 cm^{-1}.

1.2 Gel permeation chromatography (GPC)

The molecular weight and polydispersity (PDI= M_w/M_n) of PCEVE were determined by GPC using a PL 120 Plus (Agilent Technologies Co., Ltd, China) equipped with a differential refractive index detector. The detection system was calibrated with narrow molecular weight distribution polystyrene standards (2 mg mL^{-1}) with molecular weights of 550 to 6.03×10^6 g mol^{-1}. Samples were freshly prepared in THF (HPLC) and filtered with a 0.45 μm polytetrafluoroethylene syringe filter prior to injection, and THF containing 0.03 wt% LiCl was used as the eluent at a flow rate of 1.0 mL min^{-1}. The PL Gel Mixed Carbon 18 SEC column was maintained at 40 °C to achieve separation.

1.3 Transmission electron microscopy (TEM)

The TEM samples were stained by soaking the membrane in a 1 mol L^{-1} potassium iodide aqueous solution for 48 h, washed with distilled water for two days, and dried under vacuum at 50 °C. The stained membrane was sectioned using a Leica Ultracut EM (UC7FC7, China) to yield slices with thicknesses of 60-100 nm and coated on a copper grid. The electron micrograph was acquired with a JEM-2100 (Japan) transmission electron microscope operated at 20 kV.

1.4 Small-angle X-ray scattering (SAXS)

SAXS of membrane PQEVE in Cl^- form was measured after drying the membrane sample at 50 °C under vacuum for 24 h by employing a Saxesess mc2 (Anton Paar, Austria). The characteristic separation length (d) was calculated using Bragg's law below:

$$d = {}^{2\pi}/_{q_{max}}$$

1.5 Ion exchange capacity (IEC)

The IEC was measured by Mohr's method. For a typical procedure, the membrane sample was first immersed in 1 mol L^{-1} NaCl aqueous solution for 24 h and washed with distilled water to convert the membrane into the Cl^- form. The membrane was then dried to a constant weight, denoted as W_{dry}. Finally, the membrane was soaked in 0.5 mol L^{-1} Na_2SO_4 aqueous solution for 24 h to exchange Cl^- with SO_4^{2-}. The Cl^- ions released from the membrane were then titrated with a standard 0.05 mol L^{-1} $AgNO_3$ aqueous solution using K_2CrO_4 as the colorimetric indicator. The IEC value could therefore be calculated from the amount of consumed $AgNO_3$ and the weight of the dry membrane in Cl^- form (W_{dry}), as shown in the following equation.

$$IEC = V(AgNO_3) \times C(AgNO_3)/W_{dry}$$

1.6 Water uptake (WU) and linear swelling ratio (LSR)

The membrane in chloride form was first cut into 1 cm × 4 cm samples and immersed in deionized water at a predetermined temperature for 24 h. The fully hydrated membrane samples were then removed, and the membrane surface was quickly wiped dry with tissue paper. The corresponding weight and length were recorded as W_{wet} and L_{wet}. The samples were finally dried under vacuum at 60 °C, and the weight and length of the dry samples were also recorded and denoted as W_{dry} and L_{dry}. The water uptake and LSR of the membranes were accordingly calculated from the equations as follows.

$$WU = (W_{wet} - W_{dry})/W_{dry} \times 100\%$$

$$LSR = (L_{wet} - L_{dry})/L_{dry} \times 100\%$$

where W_{dry} and L_{dry} are the weight and length of dry membranes, respectively, while W_{wet} and L_{wet} are those of the wet membranes.

1.7 Hydroxide conductivity and chloride conductivity

The ionic conductivity of the membrane was evaluated on an Autolab PGSTAT 302N (Eco Chemie, Netherland) using a standard four-point probe technique. The Teflon measuring cell has 2 current-collecting electrodes and 2 potential-sensing electrodes. Prior to the measurement, the membrane sample was fully hydrated by immersed in distilled water at a given temperature, followed by mounted onto the home made cell. The impedance was determined in galvanostatic mode at an ac current amplitude of 0.1 mA over a frequency range of 1 MHz to 100 Hz. Using a Bode-type plot, a constant value of the impedance over the frequency region was determined, and the corresponding resistance was obtained from a Nyquist plot. The conductivity can be calculated according to the following equation:

$$\sigma = L/RWd$$

where L is the distance between two potential-sensing electrodes (here 1 cm), R is the absolute ohmic resistance of the membrane sample, and W (here 1 cm) and d are the width and thickness of the sample, respectively.

1.8 Membrane mechanical property

The mechanical properties, including tensile strength (TS) and elongation at break (Eb), of the membrane in the fully dry state and hydrated state at room temperature were recorded on an Instron 5967 at a stretch rate of 0.5 N min^{-1}.

1.9 Thermogravimetric analysis (TGA)

The thermal degradation behaviour of the PQEVE membrane was evaluated with a Labsys Evo analyser (France) from 30 to 700 °C at a heating rate of 10 °C min^{-1} in a nitrogen atmosphere.

1.10 X-ray photoelectron spectroscopy (XPS)

The presence of quaternary ammonium groups (QAs) within PQEVE membrane was identified by XPS on a KRATOS, AXIS SUPRA+ XPS system using Al Kα radiator and analyzed by the XPSPEAK4.1 software.

1.11 Differential scanning calorimetry (DSC)

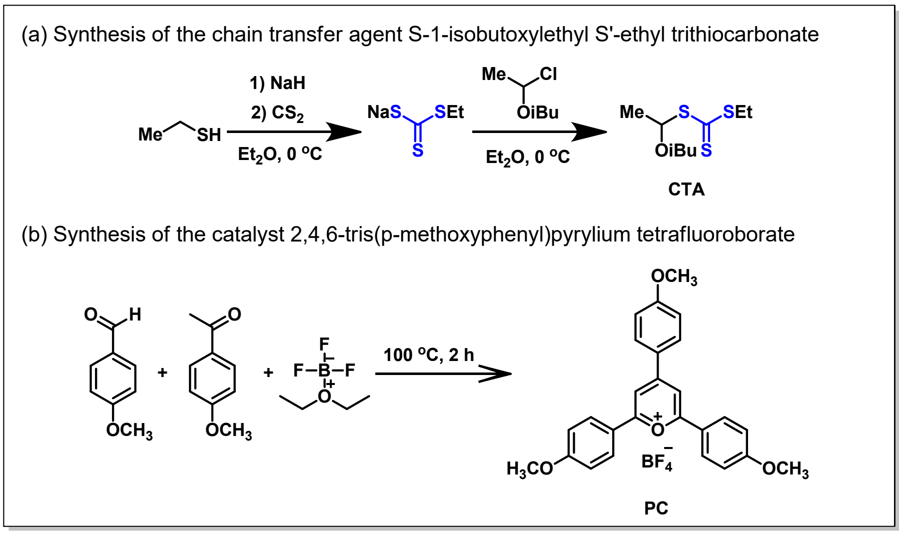
DSC was tested on a DSC 214 Polyma (Netzsch, Germany) and heated from -20 °C to 200 °C at a heating rate of 10 °C/min under nitrogen atmosphere.

1.12 Alkaline stability

In this study, both the alkaline stability of the PCEVE polymer backbone and PQEVE membrane were assessed. For the PCEVE backbone, the polymer was directly immersed in 4 mol L^{-1} NaOH aqueous solutions within a sealed bottle at 60 °C for 10 days. A portion of the polymer sample was periodically removed, thoroughly washed with distilled water and dried in a vacuum oven for the ^{1}H NMR and GPC measurements. For membrane alkaline stability, membrane samples were soaked in 1 mol L^{-1} NaOH aqueous solutions at 60 °C for 10 days. Several membrane samples were taken out every two days and washed with distilled water for measuring the IEC values and ionic conductivity. The chloride conductivity was determined and compared in case of atmospheric CO_2 contamination.

1.13 H_2/O_2 fuel cell performance

The ionomer quaternized poly(2,6-dimethyl-1,4-phenylene oxide) (QPPO) was first dissolved in isopropanol to form a homogenous solution and then mixed with the catalyst (PtRu/C for anode, Pt/C for cathode, 60 wt% in metal content) under ultrasonication to yield the catalyst ink (20 wt% QPPO and 80 wt% catalyst). The resulting catalyst inks were sprayed on carbon papers (Toray TGP-H-060) to form gas diffusion electrodes with a catalyst loading of 0.5 mg cm^{-2} on both electrodes. The electrode area was of 12.25 cm^2. The prepared catalyst-coated electrode (CCE) and the PQEVE membrane with a thickness of approximately 85 μm were then converted into OH^- form by immersion in an aqueous NaOH solution (1 mol L^{-1}) for 12 h, followed by thoroughly washing with distilled water. Finally, the PQEVE membrane was sandwiched between two CCEs to form a membrane electrode assembly (MEA). The MEA was placed in a graphite single fuel cell, and the cell fixture was tightened to ensure intimate contact among the layers in the test cell. The single cell was tested on an 890E Multi Range fuel cell test station (Scribner Associates, USA) in galvanic mode. Pure H_2 and O_2 gases were fully humidified at 60 °C and fed at a rate of 1000 mL min^{-1} with a symmetric back pressure of 0 MPa. The cell voltage at each current density was recorded after the power output stabilized.



Scheme S1. The synthesis of the chain transfer agent (CTA) S-1-isobutoxylethyl S′-ethyl trithiocarbonate (a) and the photocatalyst (PC) 2,4,6-tris-(p-methoxyphenyl)pyrylium tetrafluoroborate (b).

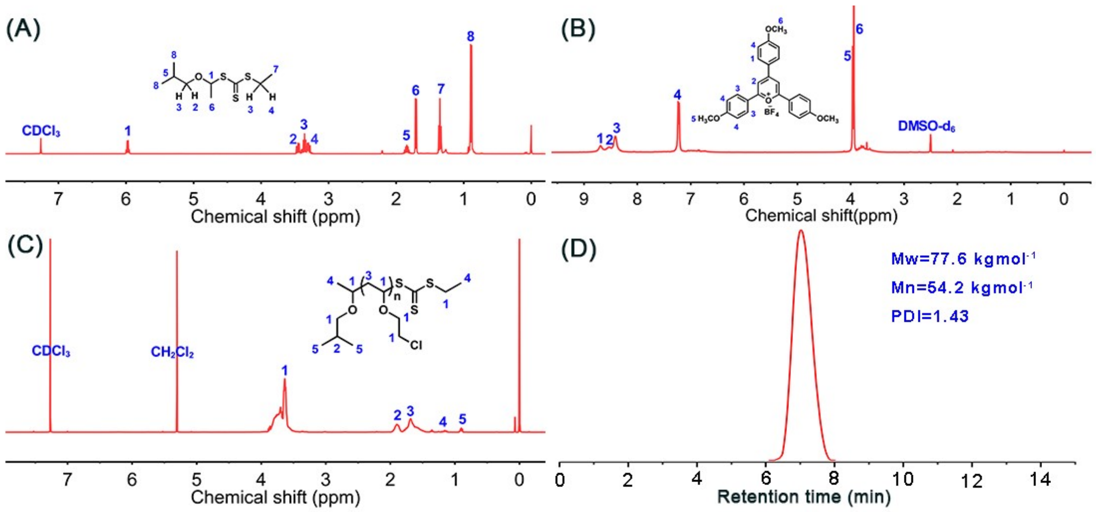


Fig. S1 ^{1}H NMR spectra of the chain transfer agent (CTA) S-1-isobutoxylethyl S′-ethyl trithiocarbonate (A), the photocatalyst (PC) 2,4,6-tris(p-methoxyphenyl)pyrylium tetrafluoroborate (B), the polymer PCEVE (C) and the GPC trace of PCEVE (D).

Table S1 Optimal polymerization condition for synthesis of polymeric backbone PCEVE.

Monomer CEVE (mL)	Solvent DCM (mL)	Photocatalyst (mg)	CTA (mg)	n(CEVE):n(CTA): n(photocatalyst)	Temperature (°C)	Exposure time (h)
5.0	6.5	2.4	19.5	600:1:0.06	25	12

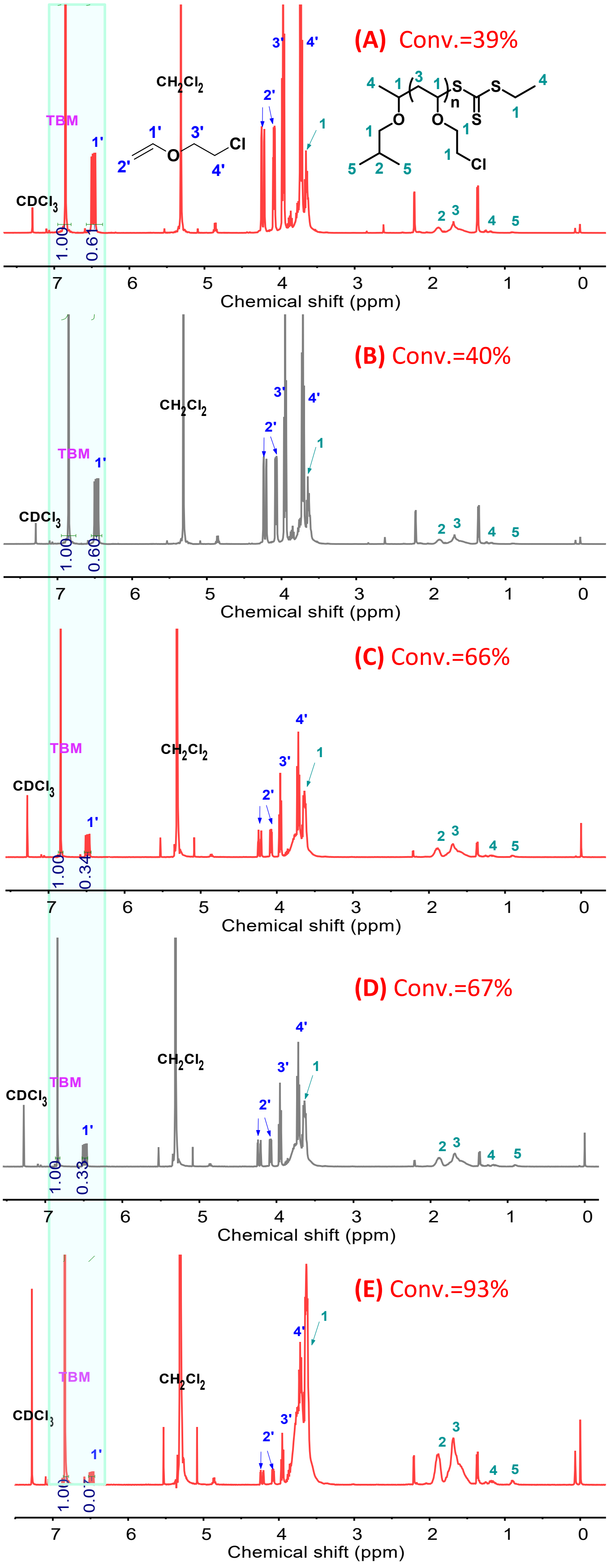


Fig. S2 The monomer conversion determined by ^{1}H NMR at point A, B, C, D and E shown in Fig. 1B, with an equimolar amount of tribromomethane (TBM) to that of the feeding monomer as an internal standard. ^{1}H NMR spectra for (A) the reaction mixture after exposed to blue LEDs for 1 h; (B) the reaction mixture followed by being stirred for another 1 h in the dark after process A; (C) the reaction mixture followed by being re-exposed to blue LEDs for 1 h after process B; (D) the reaction mixture followed by being stirred for another 1 h in the dark after process C; (E) the reaction mixture followed by re-exposed to blue LEDs for 10 h after process D.

[a] The monomer conversion is 39%, 40%, 66%, 67% and 93%, respectively, which is calculated by the integration area ratio of protons from TBM to those of 1' from monomer CEVE, as highlighted in shadow.

[b] The feeding ratio is listed in Table S1 shown below.

[c] The other unmarked peaks are probably attributed to protons from intermediates.

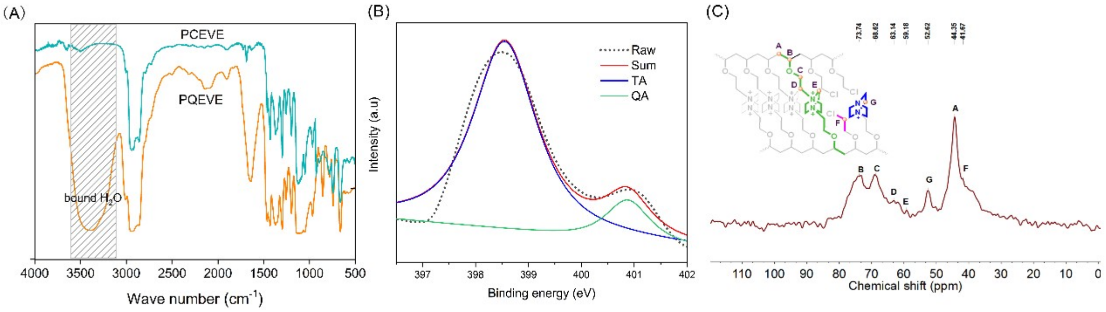


Fig. S3 Characterization of successful quaternization of PCEVE to yield PQEVE membrane. **(A)** IR spectra of PCEVE and PQEVE in attenuated total reflection-Fourier mode on polymer or membrane samples; (B) XPS signals for N 1s electron in PQEVE membrane; (C) Solid state ^{13}C NMR spectrum of PQEVE membrane.

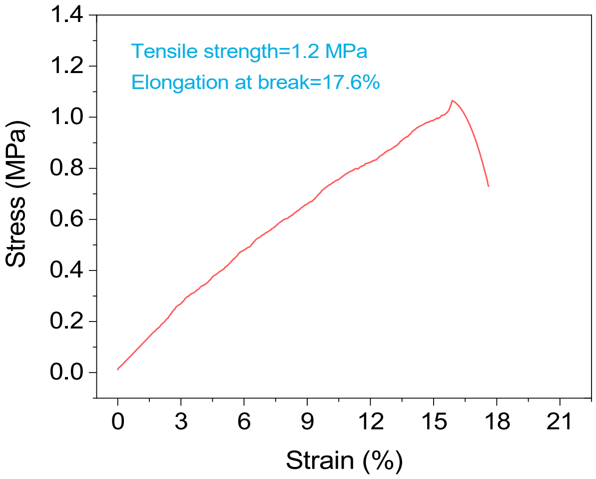


Fig. S4 Mechanical property for the membrane at fully dry state prepared from PCEVE with a low molecular weight of 23.1 kg mol^{-1}.

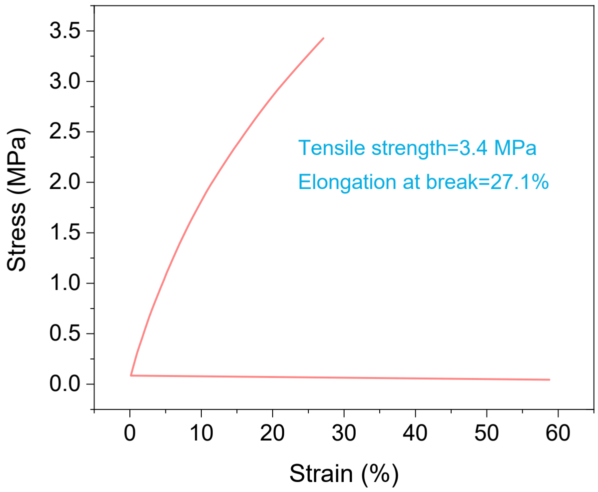


Fig. S5 Mechanical property for PQEVE membrane tested at fully dry state.

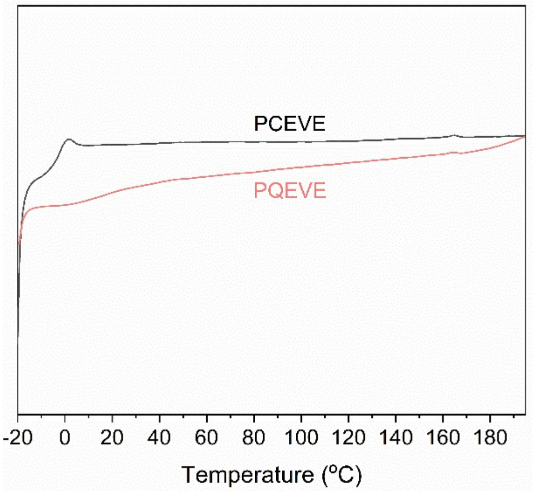


Fig. S6 DSC curves of PCEVE polymer backbone and PQEVE membrane.

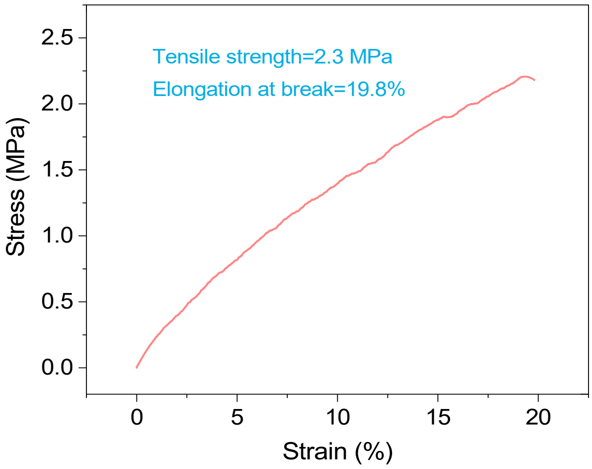


Fig. S7 Mechanical property for PQEVE membrane tested at fully dry state after alkaline treatment in 1 mol L^{-1} NaOH aqueous solutions at 60 °C for 10 days.