Electronic Supporting Information

Ionic Nanoporous Membranes from Self Assembled Liquid Crystalline Brush-like Imidazolium Triblock Copolymers

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1. Materials

Grubbs catalyst second generation, norbornene-2-carboxylic acid (a mixture of endo and exo, 98%), 1-methylimidazole, 4-dimethylaminopyridine and bis(trifluoromethylsulfonyl)amine lithium salt (TFSI 99%) are purchased from Sigma-Aldrich and used without further purification. Modified Grubbs catalyst second-generation (H2IMes)(pyr)2(Cl)2RuCHPh (mG2)[1] is synthesized. The following chemicals: Dry methylene chloride (CH_2Cl_2, 99.8%), acetonitrile, anhydrous tetrahydrofuran (THF, 99.9%), anhydrous dimethylformamide (DMF), oxalyl chloride (98%), ethyl vinyl ether (EVE, 99%) and pentane (99%) are purchased from Acros Organics while 12-bromo-1-dodecanol and 6-bromo-1-hexanol (98%) are obtained from TCI America.

2. Characterization

^{1}H NMR spectroscopy is conducted on Bruker DMX 500 MHz NMR spectrometer with $CDCl_3$ as the lock solvent at room temperature. ^{1}H NMR chemical shifts are presented in ppm downfield from TMS. The molecular weight of NBPLA is determined by gel permeation chromatography (GPC) using a Waters 1515 coupled with a PL-ELS1000 evaporative light scattering (ELS) detector and a Waters 2487 dual-wavelength absorbance UV-Vis detector with tetrahydrofuran (THF) as eluent and polystyrene (PS) standards for constructing a standard calibration curve. Differential scanning calorimetry (DSC) is conducted on the TA-2920 instrument (Q-200 series) calibrated with an Indium standard. The amount of sample used is 5-10 mg, and the scanning rate is 10 °C/min. Phase transition temperatures are determined by the first cooling cycle using Universal Analysis software. Thermogravimetric analysis is performed using 5-10 mg of the sample on a TGA Q500 1732 for review of thermal properties at 20° C/min under Nitrogen. Attenuated infrared (ATIR) spectra are recorded on a diamond ATIR spectrometer. Scanning electron microscope (SEM) images of all samples are recorded using an FEI Teneo LVSEM equipped with an ETD detector with an accelerating voltage of 15 kV. The film samples are prepared by compression molding and sputter-coated with a thin gold conductive layer before imaging. The ion exchange capacity (IEC) is measured using a precise glass pH electrode as well as spectroscopic data obtained from Perkin Elmer lambda 1050 UV/VIS/NIR spectrometer as described in later sections. Small angle X-ray scattering (SAXS) is carried out on a pin-hole collimated Rigaku SMAX3000 instrument configured with CuKα radiation (1.542 Å) produced by a micro-focus source. The beam diameter on the sample plane is 1 mm, and the scattered intensity is recorded on a gas-wire electronic area (2D) detector. The area detector has a resolution

of 1024 × 1024 pixels, located at ~80 cm from the sample center, permitting access of scattering vectors ranging from 0.015 to 0.35 Å^{-1}. Silver behenate (d-spacing=58.38 Å) is used to calibrate the SAXS diffraction patterns.

Dynamic Mechanical Analysis (DMA).

Tensile test: The non-crosslinked and crosslinked copolymer films are tested in the extension mode using DMA Q850 (TA instruments). The film's thickness was between 0.2- 0.3 mm, width of 5 - 6 mm and size/length of 12 – 15mm. The films were stretched at a constant tensile/strain rate of 0.1mm/s at room temperature.

Viscoelastic Properties: The mechanical properties and the glass transition temperature was measured using DMA Q 850 at a constant frequency (1 Hz), 10 μm amplitude, and 0.1N initial static force in a temperature range of - 60 °C to 100 °C, with a heating rate of 3 °C/min, and application of 0.2 % strain.

Electrical conductivity measurement by Four-Point probe

Ossila four-point probe system (UK) instrument was used to measure the sheet resistance, resistivity, and conductivity of the CNT films. The 4-point probe has a space distance of 1.27 mm between each probe. Initially the 4-probe instrument calibrated by using the ITO glass (2*1.5 cm, 100 nm thickness) substrate, which having the resistance of 18 Ω/sq, resistivity of 1.8 μΩ/sq and conductivity of 554.6 kS/m. The *I–V* curve and data was directly obtained from the instrument, then the sheet resistance (R), resistivity and conductivity values were obtained from the Ossila software by applying the sample and probe parameters. The thickness of ionic gels is measured through the micrometer vernier caliper. Resistance, resistivity, and the conductivity of the sheet were calculated using the following formulas.

$$R_s = 4.5323 \frac{\Delta V}{I} \qquad \rho = R_s * t \qquad \sigma = \frac{1}{\rho}$$

Where ΔV is change in voltage measured between the inner probes, I is the current applied between the outer probes, R_s is the resistance of the sheet (Ω/squ), ρ is the resistivity (Ω.m), σ is the conductivity (S/m) and *t* is the film thickness (μm) measured from micrometer vernier caliper. The

thickness of each gel varied from one sample to another sample. To get accurate data, the measurements are taken from the center of the sample or sheet with triplicates.
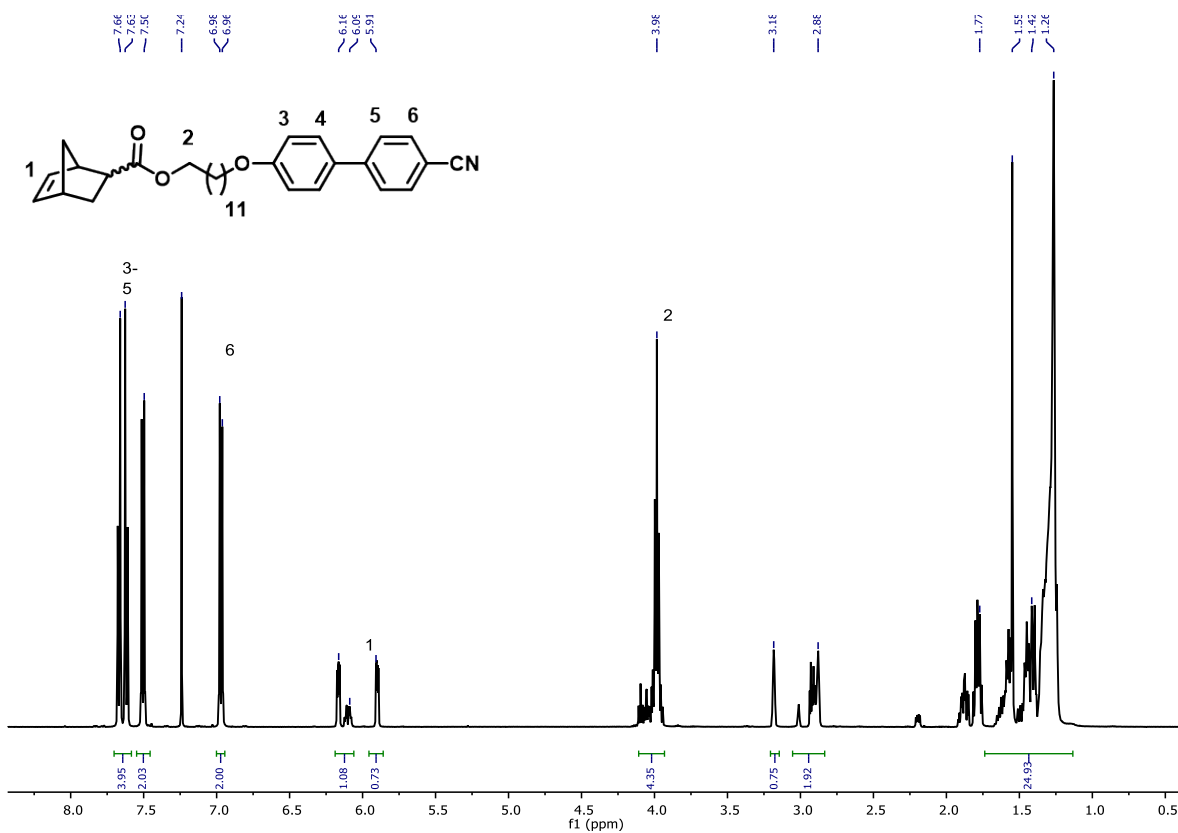
Characterization of monomers

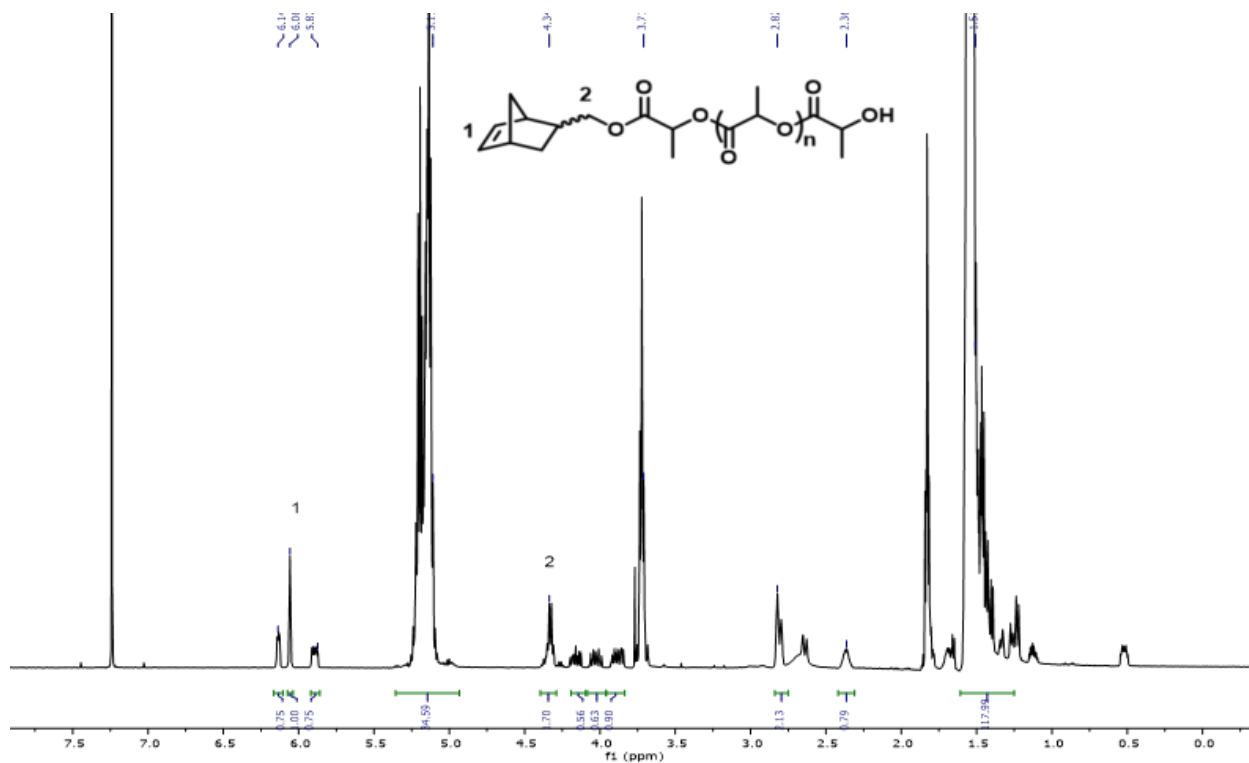**Figure S1:** Representative [1] HNMR of NBCB12 in CDCl$_3$ at room temperature.

Figure S2: Representative ^{1}HNMR of NBPLA2K in CDCl$_3$ at room temperature.
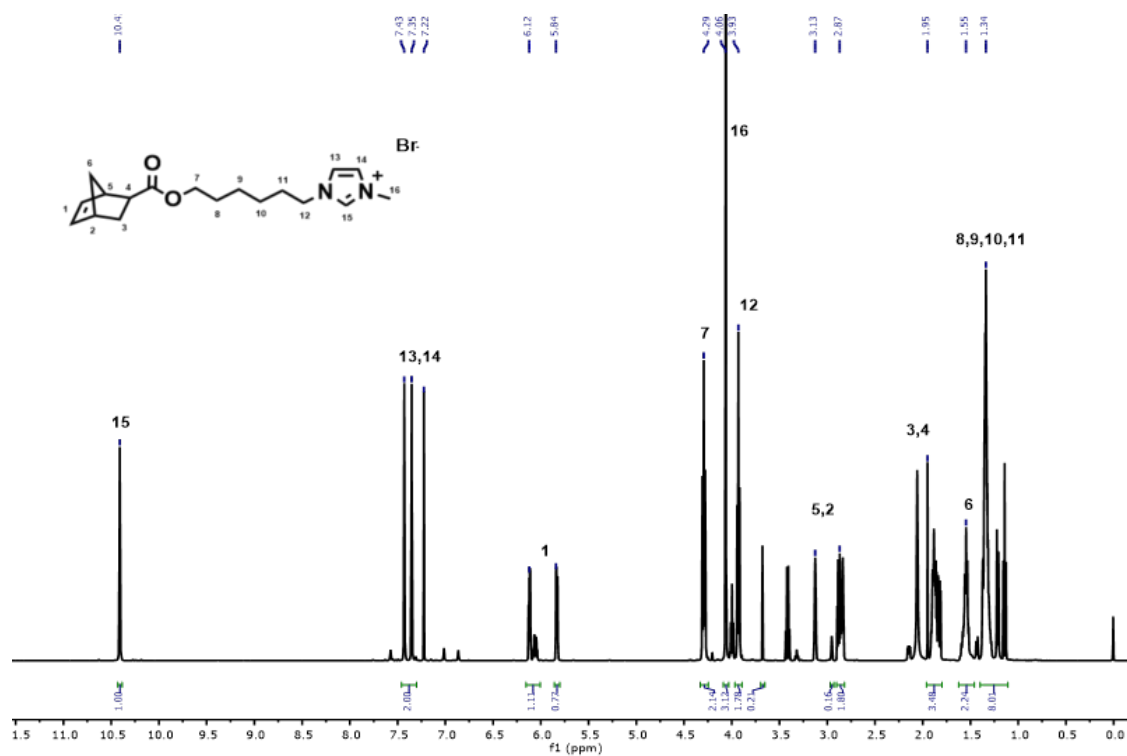

Figure S3: Representative ^{1}HNMR of NBIm$_6$Br monomer in CDCl$_3$ at room temperature.
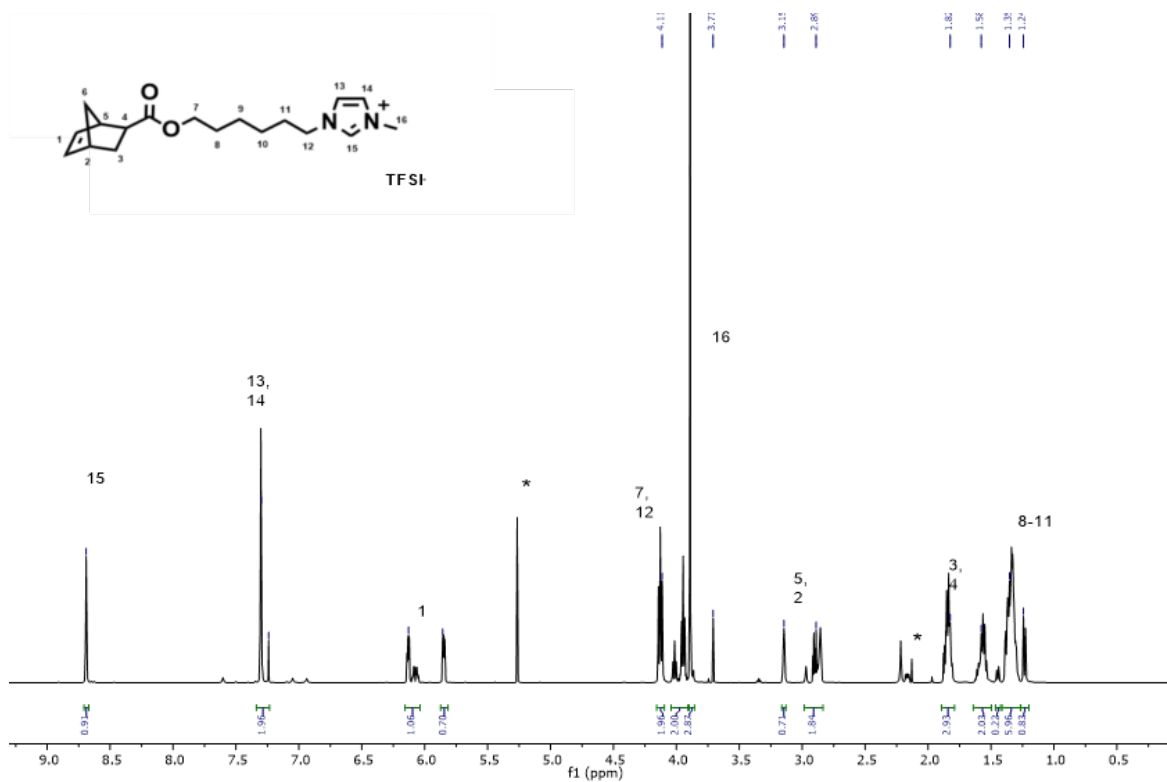
Figure S4: Representative ^{1}HNMR of NBIm$_6$Fs monomer in CDCl$_3$ at room temperature.
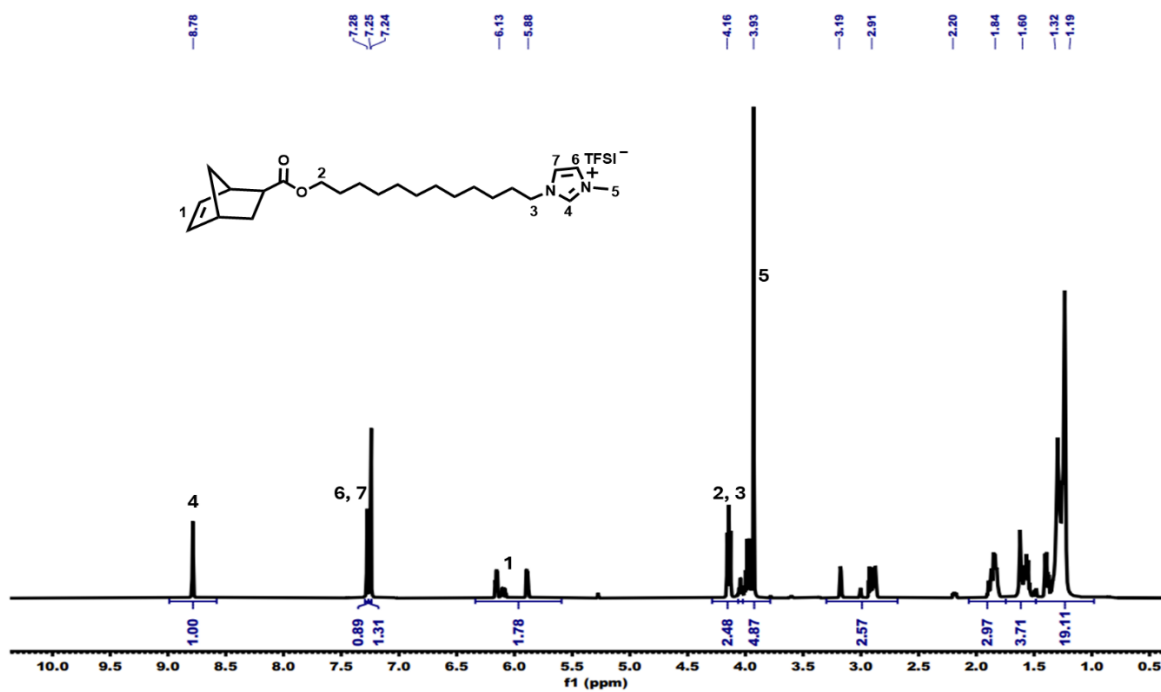

Figure S5: Representative ^{1}HNMR of NBIm$_{12}$Fs monomer in CDCl$_3$ at room temperature.
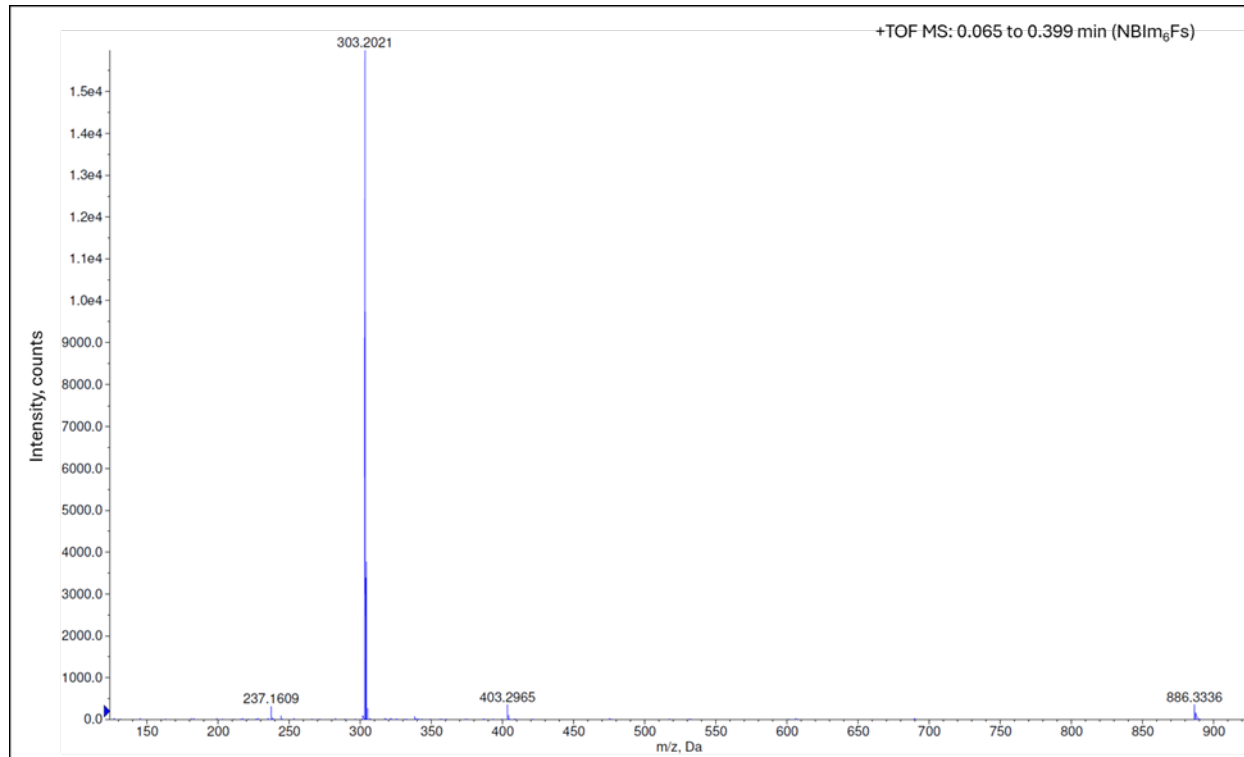
Figure S6: High resolution mass spectrometry (HRMS) of 5-norbornene-2-carboxylate-1-hexyl-3-methyl-imidazolium (NBIm$_6$Fs).
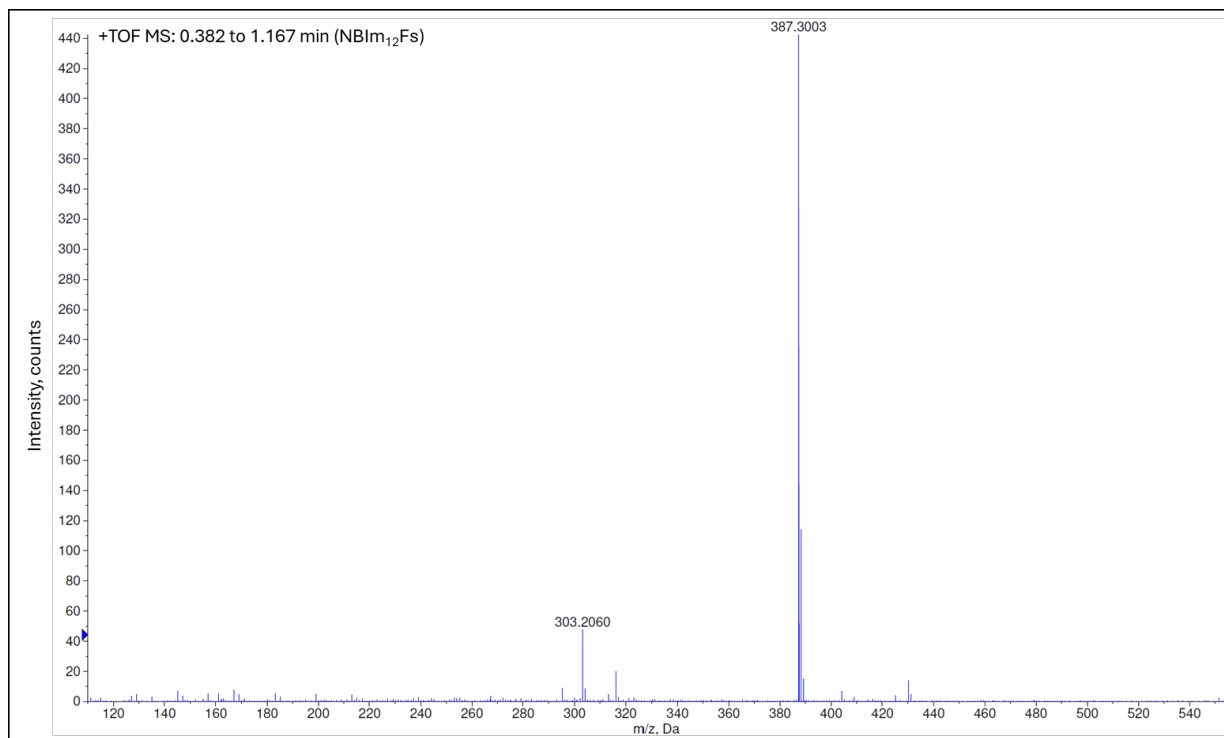
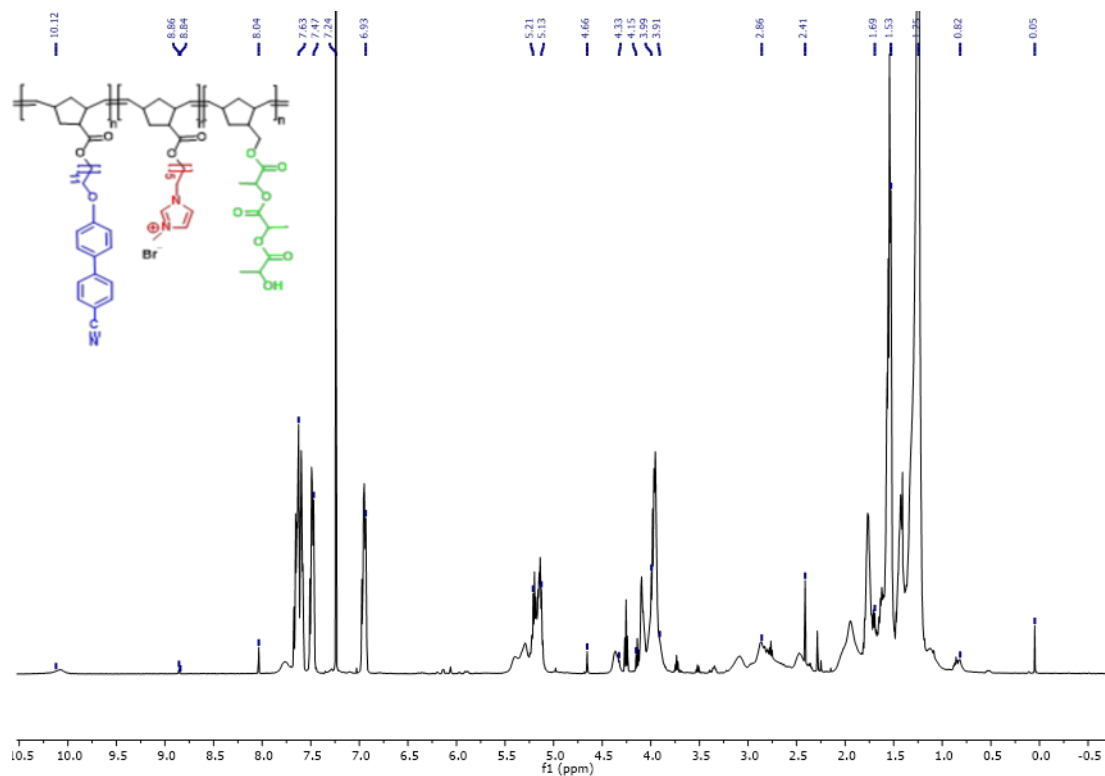**Figure S7:** High resolution mass spectrometry (HRMS) of 5-norbornene-2-carboxylate-1-dodecyl-3-methyl-imidazolium (NBIm$_{12}$Fs).

Figure S8: ^{1}H NMR of the triblock copolymer TBIm$_6$Br in CDCl$_3$ at room temperature.
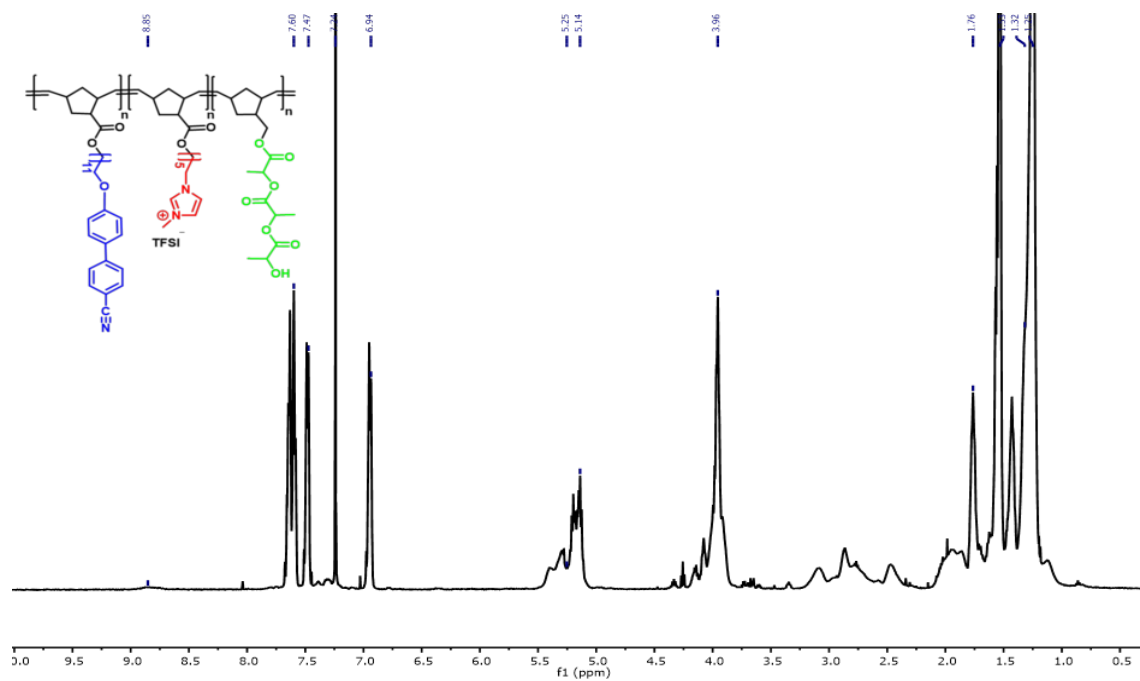

Figure S9: ^{1}H NMR of the triblock copolymer TBIm$_6$Fs in CDCl$_3$ at room temperature.
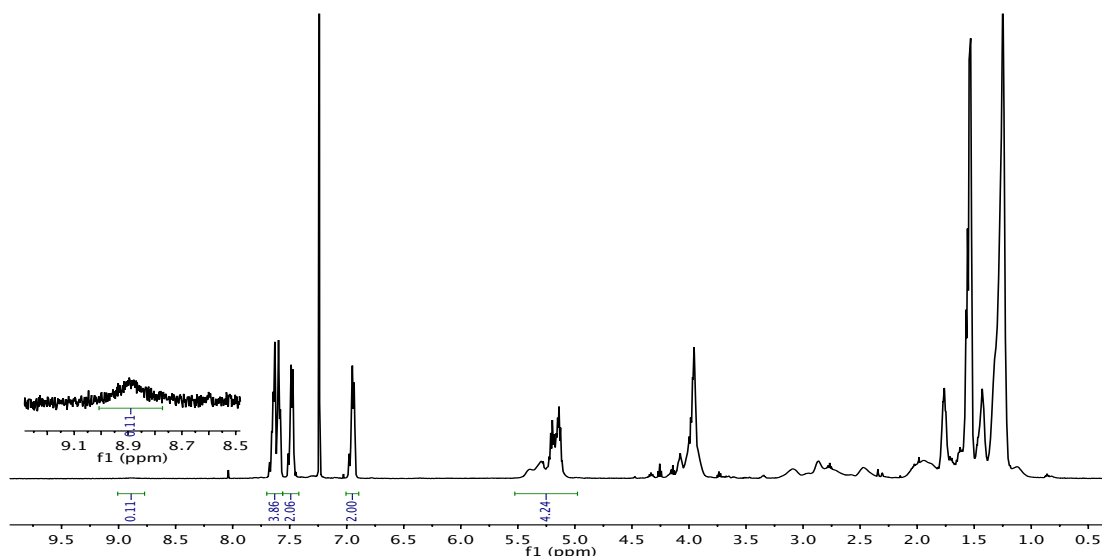
Figure S10: ^{1}H NMR of the triblock copolymer TBIm$_6$Fs in CDCl$_3$ at room temperature.

3.Preparation of nanoporous thin films

A. *Representative procedure for crosslinking of the triblock copolymer*

200 mg of the triblock copolymer (TBImBr), 5 mg of 2-hydroxy-4′-(2-hydroxyethoxy)-2-methylpropiophenone, and 12 mg of 1,10-decanedithiol are weighed in separate vials covered in aluminum foil. 1 mL of THF is added to the bottles to dissolve the contents and are mixed thoroughly. The solvent is then entirely evaporated by purging with Nitrogen for a few minutes and vacuum drying the sample overnight. A thin film of the sample is produced by compression molding at 82°C and quenched to room temperature, followed by UV crosslinking for 3 hours resulting in a crosslinked film. The gel fraction of a crosslinked sample in THF is determined to be ~42 %.

B. *Etching of crosslinked films to remove PLA.*

 The crosslinked film sample is immersed in a solution of 0.5M NaOH prepared in 6:4 water: methanol mixture and maintained at 50 ºC for five days. The nanoporous membrane is

subsequently washed thoroughly with distilled water to remove any residue left after etching. It is then vacuum dried overnight and characterized using FTIR.

4. Determination of ion exchange capacity (IEC)

Thin films are pre-treated to activate the membrane before taking IEC measurements as described here. The activation procedure consists of the alternating conversion of the membrane from OH^- to H^+. The dry weight of 1 cm * 1 cm membrane specimens is recorded and then immersed in distilled water for 24 hours. Then the membranes are exposed to a solution of 0.1 M NaOH solution for 2 hours. After thorough washing with distilled water, the membranes are then immersed in a 0.1 M HCl solution overnight, washed with water again, and immersed in a 0.1 M NaOH for 4 hours and finally immersed in distilled water for 24 hours. Both potentiometric and spectroscopic methods measure the ion exchange capacity of the thin films, and the IEC value is calculated as follows:

$$IEC = \frac{no. \, of \, moles \, of \, ions \, exchanged \, (mmol)}{dry \, weight \, of \, the \, membrane \, (g)}$$

Potentiometric method for IEC determination

The pre-treated membrane samples are converted into the OH^- form by exposing the membranes in a solution of 1M NaOH for 12 hours. The membranes are washed with distilled water to remove excess OH^- ions and immersed in a 0.1 M NaCl solution in the presence of Ar gas. The excess OH^- ions are replaced with Cl^- ions. The change in the solution pH is measured using a glass pH electrode, and the exchanged moles of OH^- are determined using a calibration curve.

The calibration curve is acquired by first stabilizing the glass pH electrode in a 0.1M NaCl solution. Once the electrode signal has stabilized, 0.05 mL aliquots of 0.01 M NaOH are added, and the pH after each dose is recorded.
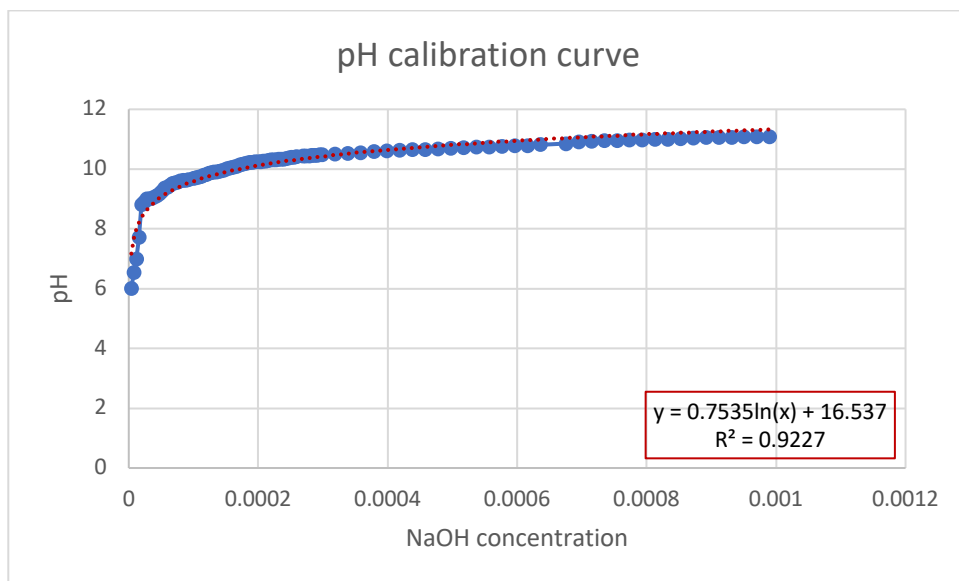

Figure S11: Calibration curve for potentiometry.

Table S1: IEC calculation from potentiometric data

| Thin film	pH	cNaOH/ moldm^{-3}	Mmol	Mass of the film/ g	IEC mmol/g
TBIm$_6$Br	9.58	0.00005	0.0005	0.0401	0.013 ± 0.001
TBIm$_6$Br-E	9.87	0.00008	0.0008	0.0361	0.022 ± 0.001
TBIm$_6$Br-XL	9.68	0.00006	0.0006	0.0384	0.015 ± 0.001
TBIm$_6$Br-XLE	9.52	0.00007	0.0007	0.0256	0.027 ± 0.003
TBIm$_{12}$Br	9.72	0.00008	0.0008	0.0375	0.021 ± 0.002
TBIm$_{12}$Br-E	9.98	0.00010	0.0010	0.0245	0.041 ± 0.003
TBIm$_{12}$Br-XL	9.65	0.00009	0.0009	0.0347	0.026 ± 0.002
TBIm$_{12}$Br-XLE	9.63	0.00010	0.0010	0.0330	0.030 ± 0.002
TBIm$_6$Fs	10.47	0.00012	0.0012	0.0205	0.058 ± 0.004
TBIm$_6$Fs-E	11.08	0. 00015	0.0015	0.0168	0.089 ± 0.005
TBIm$_6$Fs-XL	10.89	0. 00013	0.0013	0.0172	0.076 ± 0.005
TBIm$_6$Fs-XLE	11.02	0. 00014	0.0014	0.0161	0.0870 ± 0.005
TBIm$_{12}$Fs	10.37	0. 00012	0.0012	0.0197	0.061 ± 0.004
TBIm$_{12}$Fs-E	11.56	0. 00017	0.0017	0.0152	0.112 ± 0.006
TBIm$_{12}$Fs-XL	10.42	0. 00012	0.0012	0.0183	0.0656 ± 0.006
TBIm$_{12}$Fs-XLE	11.24	0. 00016	0.0016	0.0171	0.0936 ± 0.0016
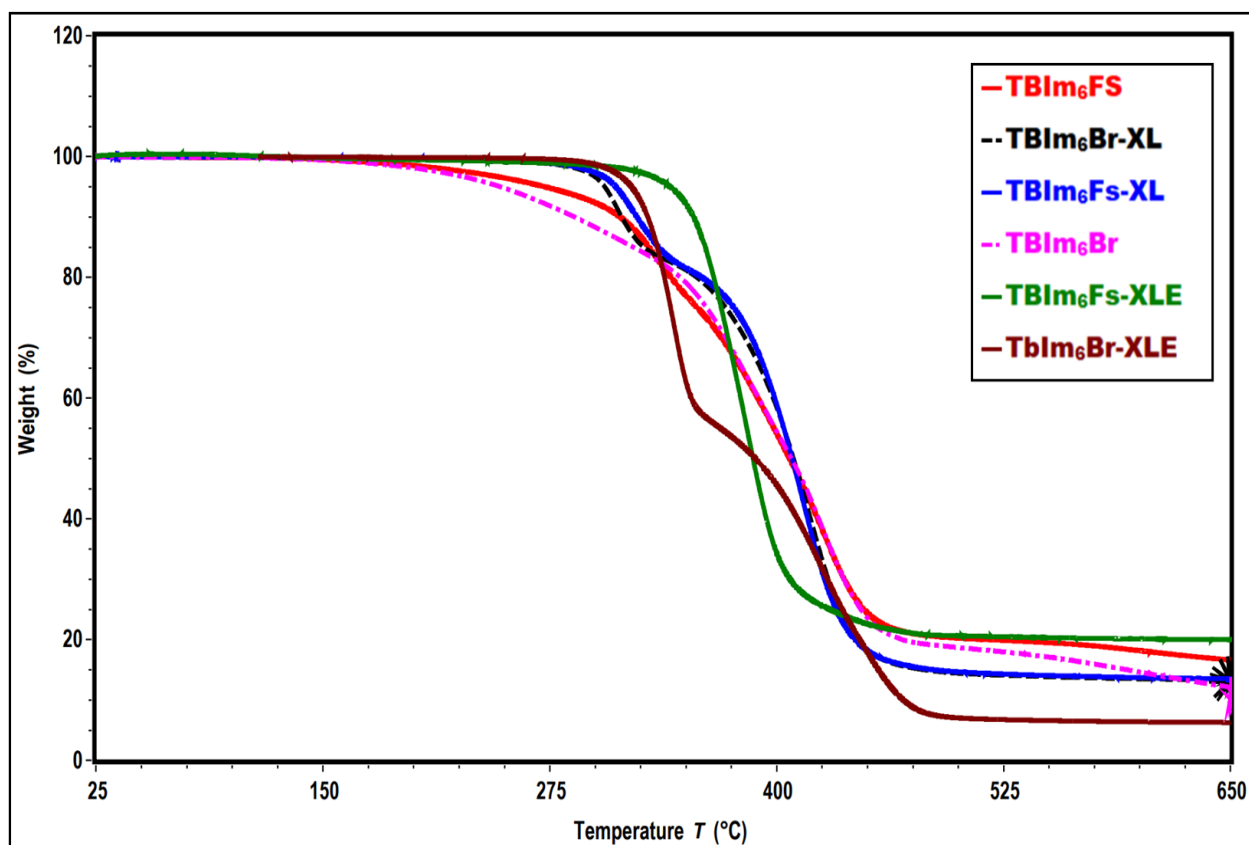
Figure S12: Thermogravimetric analysis of triblock copolymers before (TBIm$_6$Br and TBIm$_6$Fs), after crosslinking (TBIm$_6$Br-XL and TBIm$_6$Fs-XL), and after PLA etching (TBIm$_6$Br-XLE and TBIm$_6$Fs-XLE) respectively.

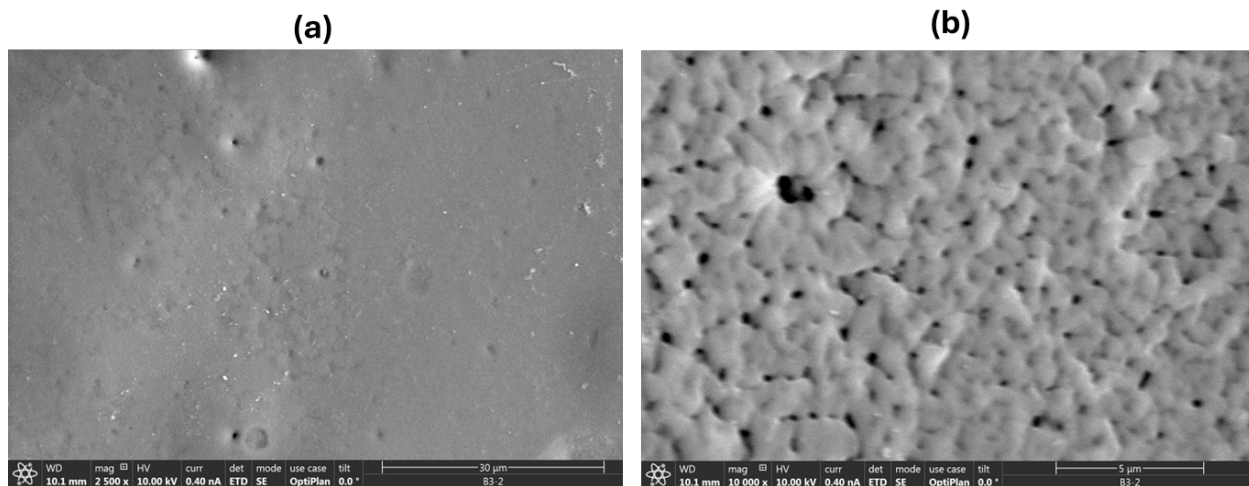**(a)**   **(b)**

Figure S13: Comparative SEM images of the gold sputter coated protected triblock copolymer, (a) TBIm$_{12}$Fs and (b) the corresponding TBIm$_{12}$Fs-XLE nanoporous membrane under both low and high magnifications. The membrane image in (b) shows the porous nature of the nanoporous membrane.
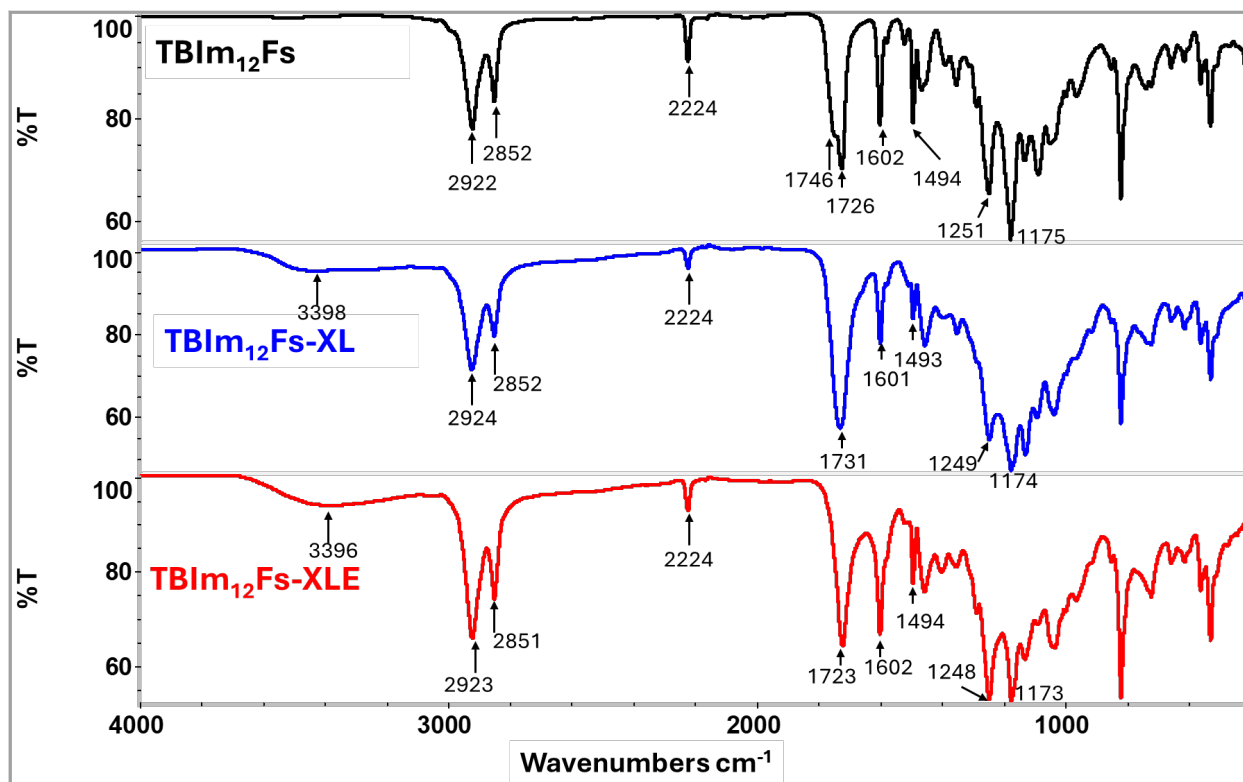
Figure S14: FTIR spectrum of TBIm$_{12}$Fs triblock copolymer before crosslinking, after crosslinking, and etching of crosslinked nanoporous samples.
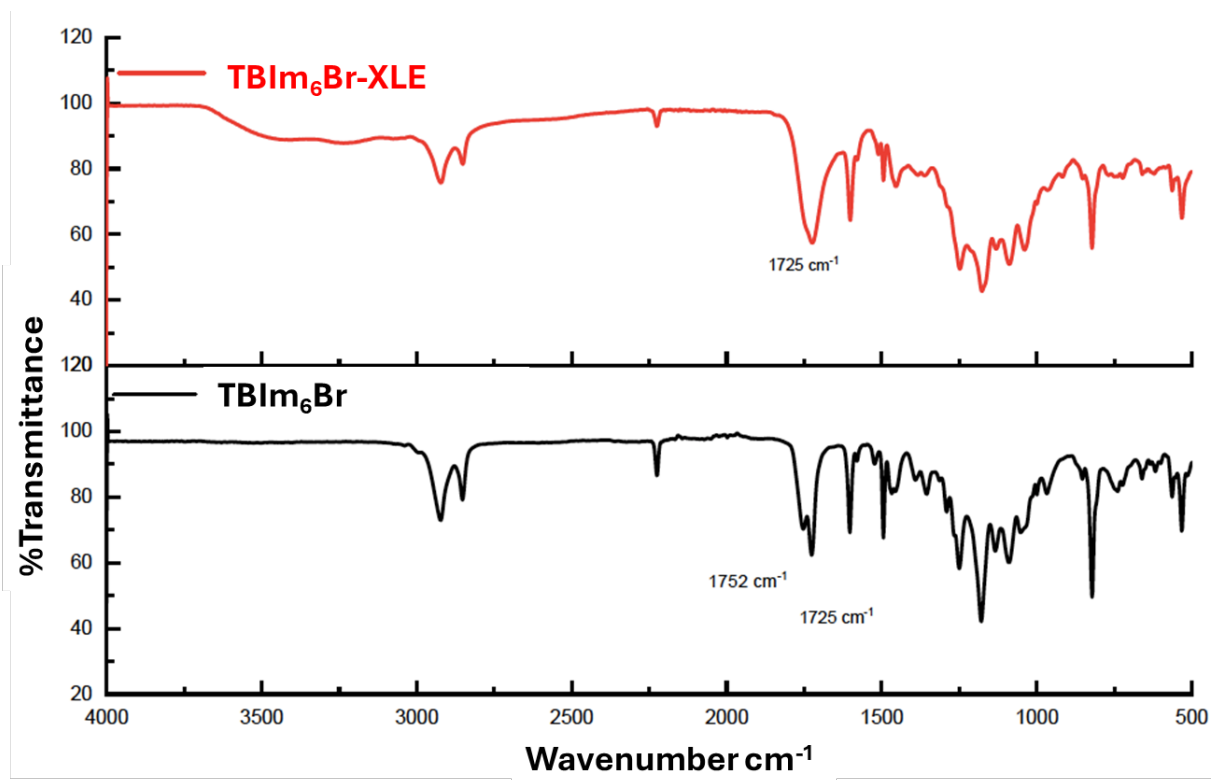
Figure S15: FTIR spectrum of triblock copolymer before etching (TBIm$_6$Br) and triblock copolymer nanoporous membrane after crosslinking and etching (TBIm6Br-XLE).
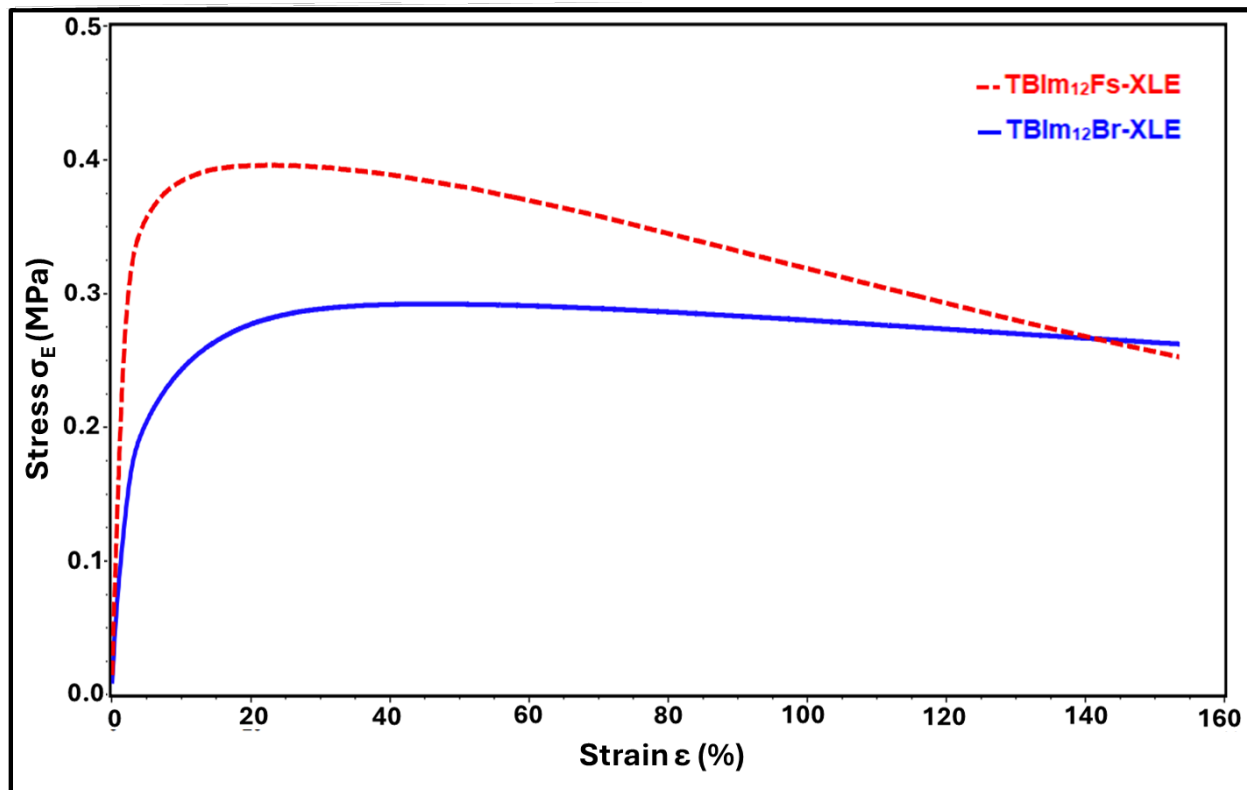
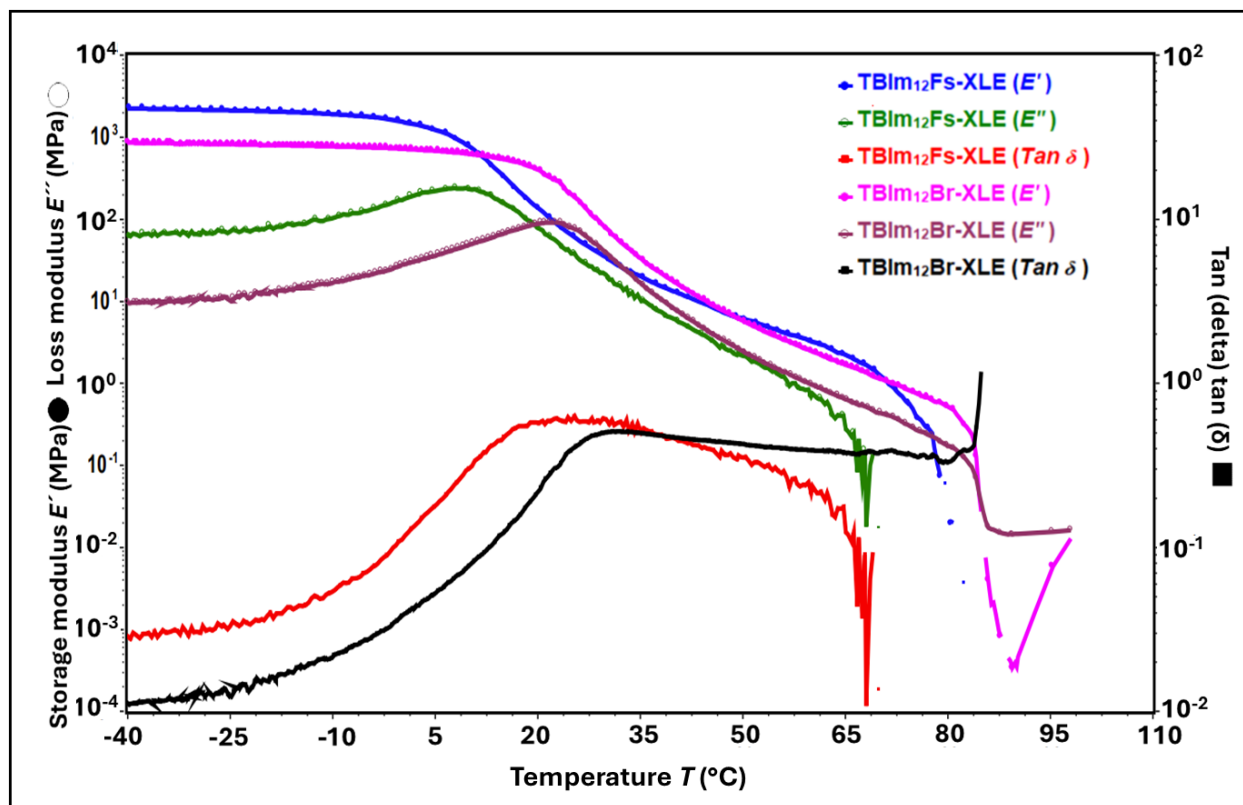**Figure S16.** Stress-strain curves for TBIm$_{12}$Fs-XLE and TBIm$_{12}$Br-XLE samples.

Figure S17. Variation of storage modulus, loss modulus, and tan with temperature for TBIm$_{12}$Fs-XLE and TBIm$_{12}$Br-XLE samples.