Supporting Information for

Thermoplastic Solid-State Polymer Electrolytes Based on Linear B-A-B Tri-block Copolymers

Xiaohang Wang,[a,b] Yingxue Wang,[b] Shengxiao Zhang,[a]* Zhengfeng Ma,[b,c]* and Keling Hu[b,c]*

[a] School of Chemistry and Chemical Engineering, Ludong University, Yantai 264025, China.

[b] Shandong Laboratory of Advanced Materials and Green Manufacturing at Yantai, Yantai, Shandong 264006, P. R. China.

[c] State Key Laboratory of Solid Lubrication, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou, Gansu 730000, P. R. China.

E-mail: hukeling@amgm.ac.cn; lduzsx@ldu.edu.cn; mazhf@licp.cas.cn

Experimental Section

Materials. Poly(ethylene glycol) methyl ether methacrylate (PEGMA, average M_n = 300 g mol^{-1}) was purchased from Sigma-Aldrich (Shanghai, China). Ethylene glycol bis(2-iodo-2-phenylacetate) (EPh-II) was customer-made and used as received. S-Butyrylthiocholine iodide (S-BChI, 98%) was supplied by Bidepharm (Shanghai, China). 2,2'-Azobis(2,4-dimethylvaleronitrile) (V65, 98%) and lithium bis(trifluoromethanesulfonyl)imide (LiTFSI, 99%) was purchased from Aladdin (Shanghai, China). Methyl methacrylate (MMA, ≥99.5%, containing 30 ppm MEHQ as stabilizer) and neutral alumina (100-200 mesh) was purchased from Macklin (Shanghai, China). Tetrabutylammonium iodide (BNI, 98%) was provided by TCI (Shanghai, China). Ethanolamine (99%) was purchased from Energy Chemical (Beijing, China). Sodium thiosulfate (≥97%) was supplied by Leyan (Shanghai, China). Anhydrous ethanol (analytical grade), tetrahydrofuran (THF, analytical grade), *n*-hexane (analytical grade), methyl tert-butyl ether (analytical grade), acetone (analytical grade), and other common solvents were obtained from Hushi Reagent (Yantai, China).

Synthesis of the PPEGMA-II macroinitiator. PEGMA (30 g, 200 mmol), EPh-II (0.55 g, 2 mmol), S-BChI (0.32 g, 2 mmol), and V65 (0.37 g, 3 mmol) were mixed in a 250 mL round-bottom flask equipped with a magnetic stir bar. The solution was degassed with high-purity nitrogen for 30 minutes to remove dissolved oxygen. The reaction system was then stirred at 50 °C in an oil bath for 0.5-1.5 hours under light protection to prevent photodegradation of the terminal iodide groups. After completion of the reaction, the mixture was cooled to room temperature and diluted with ethanol (10 mL). The polymer solution was then precipitated in a mixed solvent of *n*-hexane/methyl tert-butyl ether (v/v = 1:1, 200 mL) to remove unreacted monomers and small-molecule by-products. The product was collected by decantation and dried under vacuum to obtain PPEGMA-II with different number-average molecular weights (M_n) as listed in **Table S1**.

Table S1. Synthesis of the macroinitiator PPEGMA-II

Entry	Monomer	Initiator	Time (h)	T (°C)	$M_{n,GPC}$	$Đ$
a	PEGMA	EPh-II	1	50	6300	1.19
b	PEGMA	EPh-II	1.25	50	10000	1.17
c	PEGMA	EPh-II	1.5	50	15300	1.19

Synthesis of linear PMMA$_n$-b-PPEGMA$_m$-b-PMMA$_n$ Tri-block Copolymers. The linear tri-block copolymer, PMMA$_n$-PPEGMA$_m$-PMMA$_n$, was synthesized by the reversible complexation-mediated polymerization (RCMP) using PPEGMA-II as the macroinitiator. In a typical procedure, PPEGMA-II (2.89 g, 1 mmol), MMA (13.56 g,

800 mmol), and BNI (0.12 g, 2 mmol) were mixed in a round-bottom flask at a molar ratio of 800: 2: 1. The reaction mixture was stirred at 60 °C under an argon atmosphere in an oil bath. After the reaction, the mixture was cooled to room temperature and diluted with tetrahydrofuran (THF, 10 mL). The polymer was then precipitated in a mixed solvent of *n*-hexane/methyl tert-butyl ether (v/v = 1:1, 200 mL) to remove unreacted monomers and low-molecular-weight by-products. The product was collected by decantation and dried under vacuum, yielding the tri-block copolymer with varying number-average molecular weights as listed in **Table S2**.

Table S2. PPEGMA-II initiated block copolymerization with MMA.

Entry	Macroinitiator	Monomer	Time (h)	T (^{o}C)	$M_{n,GPC}$	$M_{n,NMR}$	$Đ$	f_{hard} (%)
S1	PPEGMA-II [a)]	MMA	5	60	11700	12000	1.19	48.7
S2	PPEGMA-II [a)]	MMA	6	60	12900	14000	1.17	55.7
S3	PPEGMA-II [b)]	MMA	5	60	19300	21000	1.25	52.4
S4	PPEGMA-II [b)]	MMA	6	60	21000	22000	1.23	53.6
S5	PPEGMA-II [c)]	MMA	3	60	22700	28800	1.34	46.8
S6	PPEGMA-II [c)]	MMA	5	60	27900	32700	1.25	53.3
S7	PPEGMA-II [c)]	MMA	4	60	26800	35000	1.28	56.2

[a] PPEGMA-II (Table S1, entry a, $M_{n,GPC}$ = 6300 $Đ$ = 1.19); [b] PPEGMA-II (Table S1, entry b, $M_{n,GPC}$ = 11000, $Đ$ = 1.17); [c] PPEGMA-II (Table S1, entry c, $M_{n,GPC}$ = 15300, $Đ$ = 1.19).

Preparation of Solid Polymer Electrolyte (SPE) Membranes

Deiodination Process. The $PMMA_n$-$PPEGMA_m$-$PMMA_n$ tri-block copolymer was dissolved in 30 mL of acetone. After complete dissolution, ethanolamine (10-fold molar excess relative to the terminal iodine groups) was added, and the solution was stirred at room temperature in the dark for 24 h. Subsequently, 0.5 g of sodium thiosulfate and 0.5 g of Al_2O_3 were introduced, followed by additional stirring for 3 h. The solution was then filtered, concentrated by rotary evaporation, and precipitated in a mixed solvent of *n*-hexane/methyl tert-butyl ether (v/v = 1:1). The product was washed three times, collected by decantation, and dried under vacuum to yield the deiodinated polymer.

Solution Casting Method. The de-iodinated polymer was dissolved in 30 mL of THF within an argon-filled glove box. Lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) was added at an EO/Li molar ratio of 10:1, and the mixture was homogenized by stirring. After filtration, the solution was cast into a polytetrafluoroethylene (PTFE) mold. A glass cover was placed over the mold to allow controlled solvent evaporation, resulting in the formation of uniform SPE membranes.

Thermal Annealing Treatment. The SPE membranes on PTFE substrates were

transferred to a temperature-controlled oven at 60 ℃ for 48 h to induce microphase separation. Following annealing, the membranes were carefully peeled off from the PTFE substrates for subsequent characterization.

Characterization

Nuclear Magnetic Resonance (NMR) Spectroscopy. ^{1}H NMR spectra were acquired using a Bruker AV400 NMR spectrometer (400 MHz) with $CDCl_3$ as the solvent. Chemical shifts were recorded in parts per million (ppm).

Fourier Transform Infrared (FTIR) Spectroscopy. FTIR measurements were performed on a Shimadzu IRTracer-100 spectrometer equipped with an attenuated total reflectance (ATR) accessory. The block copolymer $PMMA_n$-b-$PPEGMA_m$-b-$PMMA_n$ was scanned in the range of 500-4000 cm^{-1} at a resolution of 4 cm^{-1}. Each spectrum was obtained by averaging 32 scans to ensure sufficient signal-to-noise ratio.

Differential Scanning Calorimetry (DSC). Thermal properties were analyzed using a NETZSCH DSC 3500 instrument under nitrogen atmosphere (flow rate: 20 mL/min). Samples (10-20 mg) were sealed in aluminum crucibles and subjected to the following temperature program: (1) heating to 200 °C at 10 °C/min, (2) isothermal holding at 200 °C for 10 min, (3) cooling to room temperature at 10 °C/min, and (4) reheating to 200°C at 10 °C/min. The glass transition temperature (T_g) was determined from the middle point of the heat capacity change in the second heating scan.

Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy (EDS). Morphological characterization was conducted using a TESCAN CLARA GHM field-emission scanning electron microscope. Prior to imaging, samples were sputter-coated with a gold layer using a Quorum Q150T ES sputter coater (30 mA, 120 s). Elemental analysis was performed with an Oxford Instruments X-MaxN 80 EDS detector at an accelerating voltage of 15 kV.

X-ray Diffraction (XRD). XRD patterns were collected on a Bruker D8 ADVANCE diffractometer with Cu Kα radiation (λ = 1.5406 Å) operating at 40 kV and 40 mA. The scanning range was 5-80° (2θ).

Gel Permeation Chromatography (GPC). Molecular weight and molecular weight distribution were determined using a Shimadzu GPC system equipped with a refractive index detector. THF (HPLC grade, Aladdin) was used as the eluent at a flow rate of 0.8 mL/min through two PLgel Mixed-C columns (7.5 × 300 mm, 40 °C). The system was calibrated with narrow polystyrene standards (M_w = 100-3,000,000 g/mol).

Mechanical Property Testing. Tensile tests were carried out on a Shimadzu AGS-X 500N universal testing machine at a crosshead speed of 20 mm/min. The dumbbell-shaped specimens (20 × 5 mm^2) were prepared from the membranes and tested at room temperature. Five replicates were measured for each sample to ensure reproducibility.

Atomic Force Microscopy. The measurements were performed using a Bruker Dimension Icon atomic force microscope in ScanAsyst in Air mode, with a Bruker RTESPA-75 probe (nominal spring constant: 3 N/m; scan rate: 1.99 Hz).

Thermogravimetric Analysis (TGA). The measurements were performed on a Linseis PT1000 thermobalance under a nitrogen atmosphere (flow rate: 20 mL/min). The sample (15-20 mg) was heated from room temperature to 600 °C at a heating rate of 10 °C/min.

Electrochemical Impedance Spectroscopy (EIS). The measurements were performed using a Solartron Analytical ENERGYLAB XM potentiostat in the frequency range of 100 kHz to 10 mHz with a 10 mV AC perturbation. Impedance spectra were analyzed from Nyquist plots to obtain the bulk resistance of the electrolyte. Measurements were conducted at 20 °C, 30 °C, 40 °C, 50 °C, 60 °C, and70 °C. The membrane thickness was determined using a digital micrometer (±1 μm) by averaging five readings, and the electrode area was calculated from the measured electrode diameter. Ionic conductivity was then determined from these parameters using the method described in the main text.

$$\sigma = \frac{d}{AR_b}$$

where *d* is thickness, A is electrode area, and R_b is bulk resistance extracted from Nyquist plots.

Electrochemical stability (LSV). The electrochemical stability window of the SPE was evaluated by linear sweep voltammetry (LSV) using a Li | SPE | stainless-steel (SS) cell. The scan was conducted at 70 °C with a scan rate of 0.5 $mV \cdot s^{-1}$ over the voltage range of 3–6 V (vs Li/Li^+). Current densities were normalized by the electrode area.

Temperature-dependent ionic conductivity analysis. The temperature dependence of ionic conductivity was analyzed using both Arrhenius and Vogel–Tammann–Fulcher (VTF) models.

The Arrhenius equation is expressed as:

$$\sigma_{(T)} = \sigma_0 \exp\left(-\frac{E_a}{RT}\right)$$

where E_a is the activation energy and R is the gas constant.

For polymer electrolytes exhibiting non-Arrhenius behavior, the VTF model was applied:

$$\sigma_{(T)} = \sigma_0 \exp\left[-\frac{B}{T - T_0}\right]$$

where σ_0 is the pre-exponential factor, $B$is a pseudo-activation parameter, and T_0 is the Vogel temperature associated with the onset of segmental freezing.

The apparent activation energy at a given temperature was calculated from the VTF parameters according to:

$$E_{a(T)} = RB\,\frac{T^2}{(T-T_0)^2}$$

Nonlinear fitting was performed using Origin software.

Table S3. Temperature-dependent ionic conductivity and VTF fitting parameters.

Sample	$\sigma_{(25\,°C)}$ (S·cm^{-1})	$\sigma_{(70\,°C)}$ (S·cm^{-1})	σ_0 (S·cm^{-1})	B (K)	T_0 (K)	$E_{a\,(70\,°C)}$ (kJ·mol^{-1})
S1	1.91×10^{-7}	6.08×10^{-6}	2.48×10^{-4}	322.8	253.1	39.0
S2	8.91×10^{-8}	4.94×10^{-6}	2.61×10^{-4}	324.9	257.5	43.3
S3	2.84×10^{-8}	1.82×10^{-6}	3.79×10^{-1}	2431.2	150.0	63.8
S4	9.98×10^{-8}	4.15×10^{-6}	1.77×10^{-4}	357.6	250.4	40.7
S5	1.64×10^{-7}	4.47×10^{-6}	1.82×10^{-5}	111.1	274.6	23.1
S6	1.04×10^{-7}	1.89×10^{-6}	3.60×10^{-5}	251.2	255.2	31.8
S7	8.42×10^{-8}	9.54×10^{-7}	6.73×10^{-6}	155.0	262.8	23.5

$\sigma_{(70°C)}$ values were taken from the experimental low-frequency plateau conductivities, while $\sigma_{(25°C)}$ values were obtained from VTF fitting due to the absence of direct measurement at 25 °C.

The VTF parameters are used here primarily as empirical descriptors within the investigated temperature window.

The block ratio of $PMMA_n$-b-$PPEGMA_m$-b-$PMMA_n$ was obtained quantitatively from the integrations of the non-overlapping peaks at 3.62 ppm (PMMA, –COOC***H*****$_3$**) and 4.08 ppm (PPEGMA, –COOC***H*****$_2$**–).

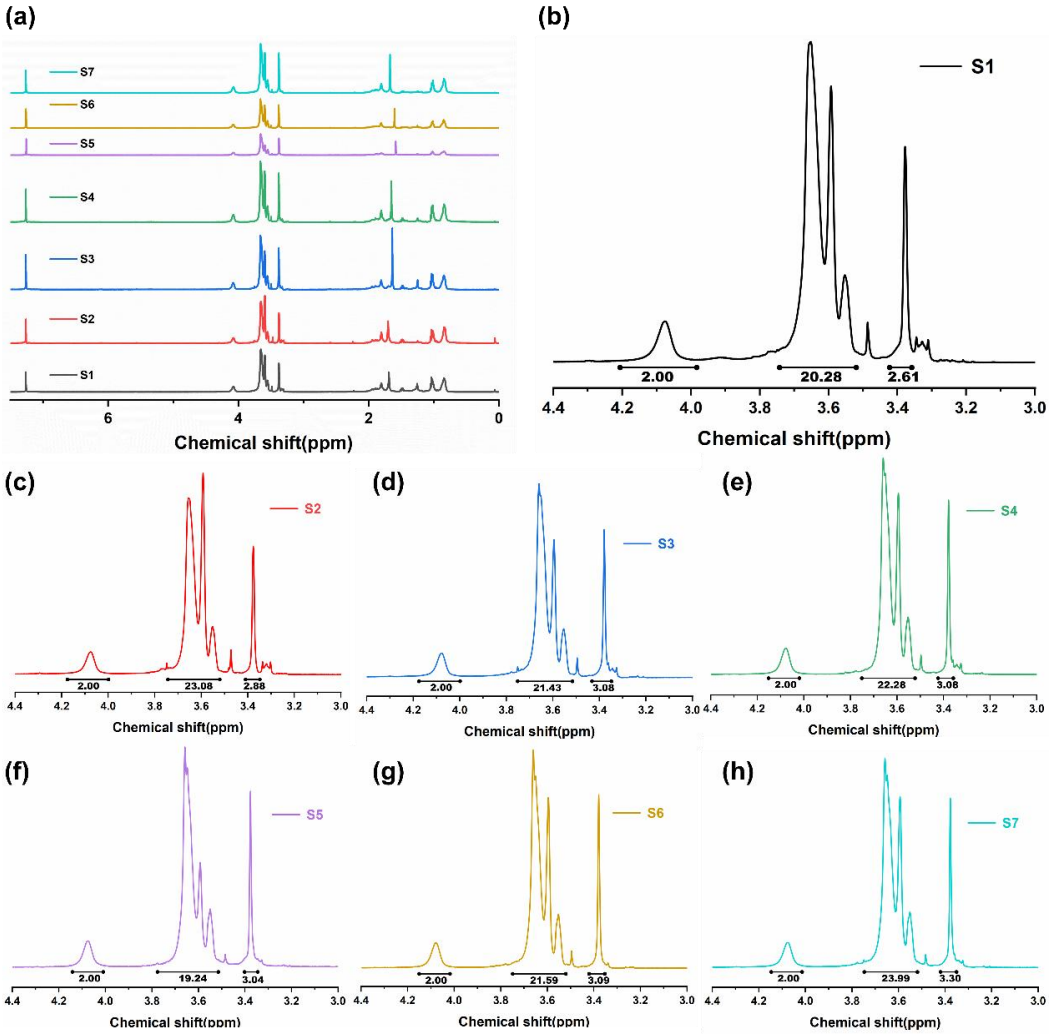

Figure S1. The full ^{1}H NMR spectra and integral area diagram of the seven PMMA$_n$-b-PPEGMA$_m$-b-PMMA$_n$ samples.

The block lengths were calculated using the following equations,

$$N_{(PMMA)} = \frac{I_{3.50-3.74} - I_{(PEGMA)}}{3}$$

$$m_{(PPEGMA)} = \frac{M_{n(PPEGMA)} - M_{n(EPh-II)}}{M_{n(PEGMA)}}$$

$$n_{(PMMA)} = \frac{m_{(PPEGMA)} \times N_{(PMMA)}}{2}$$

Where $\mathbf{M_{n(Eph\text{-}II)}}$ denotes the molecular weight of initiator EPh-II, and the factor of 2 reflects the symmetric B–A–B structure with two identical PMMA end blocks. The NMR-derived molecular weight of the tri-block copolymer is then obtained from:

$$M_{n,NMR} = M_{n(PPEGMA)} + 2n_{(PMMA)}M_{n(MMA)}$$

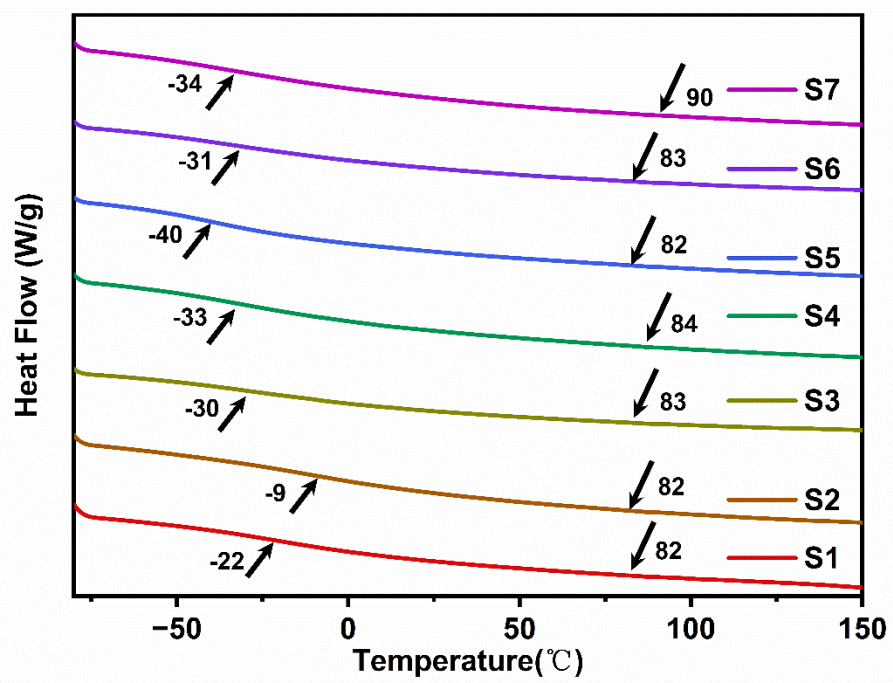

Figure S2. DSC thermograms of $PMMA_n$–b–$PPEGMA_m$–b–$PMMA_n$ based SPE membranes after LiTFSI salt incorporation.