Allyl glycidyl ether-based polymer electrolytes for room temperature lithium batteries

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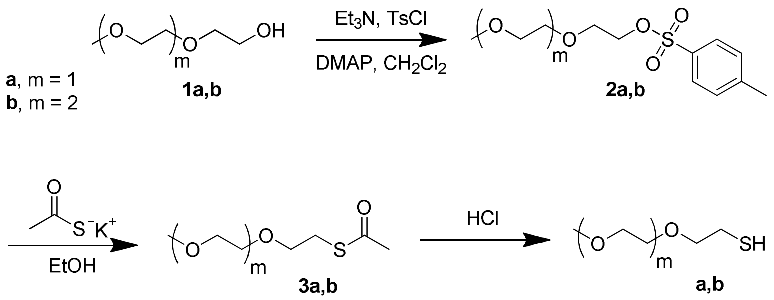
Supporting information

The following describes the synthesis of 2-(2-methoxyethoxy)ethanethiol (mPEG$_2$SH) and 2-(2-(2-methoxyethoxy)ethoxy)ethanethiol (mPEG$_3$SH). Below that follows the synthesis and characterization of oligomeric funtionalized copolymers. This material is available free of charge via the Internet at http://pubs.acs.org.



Scheme S1. Synthesis of compounds **4a** and **4b** was undertaken similarly to previously reported.[38,39]

Synthesis of 2-(2-methoxyethoxy)ethanethiol (4a)

Me-EO-EO-OH (**1a**) → Me-EO-EO-OTs (**2a**)

A flask was charged with Methoxy-ethoxy-ethoxy-alcohol (**1a**) (40.0 g, 0.333 mol, 1.0 eq), dichloromethane (1.0 L), triethylamine (40.0 g, 0.495, 1.5 eq) and *p*-dimethylaminopyridine (0.40 g, 3.3 mmol, 0.01 eq) and cooled to 0 °C and stirred for 15 minutes. Subsequently p-tosylchloride (76 g, 0.400 mol, 1.0 eq) was added in portions to the reaction mixture to control the exothermic nature of the reaction. After addition the reaction mixture was allowed to warmed up to room temperature and stirred for an additional 18 hours. The reaction was stopped by the addition of saturated $NaHCO_3$ (aq) (500 mL) was added and the organic layer was separated from the aqueous layer. The organic layer was subsequently washed with brine (300 mL) and dried with sodium sulfate, filtered and the organic solvent was evaporated *in vacuo*. Purification of the crude was achieved through column chromatography (silica, 2:1 Hexanes/Ethyl Acetate) yielding 80 g (□ = 88 %) of a colorless oil of **2a**. ^1H NMR (600 MHz, $CDCl_3$): δ = 2.44 (s, 3 H, CH_3), 3.35 (s, 3 H, OCH_3), 3.48 (m, 2 H, CH_2), 3.58 (m, 2 H, CH_2), 3.69 (t, 2 H, CH_2), 4.17 (t, 2 H, CH_2), 7.33 (d, 2 H, Ar-H), 7.80 (d, 2 H, Ar-H)

Me-EO-EO-OTs (**2a**) → Me-EO-EO-SAc (**3a**)

A solution of **2a** (60,0 g, 0.217 mol, 1.0 eq) in ethanol (1.0 L) was cooled to 0 °C, after which potassium thioacetate (50 g, 0.434 mol, 2.0 eq) was added slowly in portions. The reaction mixture was allowed to be warmed up to room temperature, and stirred for 18 hours. The reaction mixture was filtered to remove excess salts, followed by evaporation of the ethanol *in vacuo*. Tetrahydrofuran (400 mL) was added and the suspension was filtered after which the solvent of the filtrate was evaporated. To the crude dichloromethane (500 mL) was added and the organic layer was washed with a brine/water mixture (2:1). The organic layer was dried with sodium sulfate, filtered and the solvent evaporated. The crude was purified by filtration over silica using a 2:1 Hexanes/Ethyl Acetate mixture. After evaporation of the solvent, 32 g (□ = 83 %) of pure **3a** was obtained as a yellow/red oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 2.33 (s, 3 H, CH_3), 3.10 (t, 2 H, SCH_2) 3.38 (s, 3 H, OCH_3), 3.53 (m, 2 H, CH_2), 3.60 (m, 4 H, CH_2).

Me-EO-EO-SAc (**3a**) → Me-EO-EO-SH (**4a**)

A solution of **3a** (32.0 g, 0.180 mol) in a mixture of concentrated HCl (37% aqueous, 100 mL), water (200 mL) and methanol (200 mL) was heated at 60 °C for 18 hours, after which the reaction was allowed to cool down to room temperature. The reaction mixture was extracted with dichloromethane (2 × 500 mL), organic layers were combined, dried with sodium sulfate, filtered and the solvent evaporated giving 21.6 g (88 %) of **4a** as a yellowish oil. The samples were stored with some acetic acid to prevent dithiol formation. The oil was distilled at immediately prior to use yielding a clear liquid with 98.47% purity by gas chromatography. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.57 (t, 1 H, SH), 2.71 (q, 2 H, CH_2), 3.39 (s, 3 H, OCH_3), 3.55 (m, 2 H, CH_2), 3.62 (m, 4 H, CH_2).

Synthesis of 2-(2-(2-methoxyethoxy)ethoxy)ethanethiol (4b)

Me-EO-EO-EO-OH (**1b**) → Me-EO-EO-EO-OTs (**2b**)

A flask was charged with Methoxy-ethoxy-ethoxy-alcohol (**1b)** (100.0 g, 0.600 mol, 1.0 eq), dichloromethane (2.0 L), triethylamine (122.0 g, 1.20, 2.0 eq) and *p*-dimethylaminopyridine (0.74 g, 6.0 mmol, 0.01 eq) and cooled to 0 °C and stirred for 15 minutes. Subsequently p-tosylchloride (138 g, 0.720 mol, 1.2 eq) was added in portions to the reaction mixture to control the exothermic nature of the reaction. After addition the reaction mixture was allowed to warmed up to room temperature and stirred for an additional 18 hours. The reaction was stopped by the addition of water (500 mL), and the organic layer was separated from the aqueous layer. The organic layer was subsequently washed with saturated $NaHCO_3$ (aq) (500 mL), brine (300 mL) and dried with sodium sulfate, filtered and the organic solvent was evaporated *in vacuo*. Purification of the crude was achieved through column chromatography (silica, 2:1 Hexanes/Ethyl Acetate) yielding 170 g (□ = 88 %) of a colorless oil of **2b**. ^1H NMR (600 MHz, $CDCl_3$): δ = 2.44 (s, 3 H, CH_3), 3.37 (s, 3 H, OCH_3), 3.53 (m, 2 H, CH_2), 3.60 (m, 6 H, CH_2), 3.68 (t, 2 H, CH_2), 4.16 (t, 2 H, CH_2), 7.34 (d, 2 H, Ar-H), 7.80 (d, 2 H, Ar-H).

Me-EO-EO-EO-OTs (**2b**) → Me-EO-EO-EO-SAc (**3b**)

A solution of **2b** (53.0 g, 0.167 mol, 1.0 eq) in ethanol (1.0 L) was cooled to 0 °C, after which potassium thioacetate (50 g, 0.434 mol, 2.6 eq) was added slowly in portions. The reaction mixture was allowed to be warmed up to room temperature, and stirred for 18 hours. The reaction mixture was filtered to remove excess salts, followed by evaporation of the ethanol *in vacuo*. Tetrahydrofuran (600 mL) was added and the suspension was filtered after which the solvent evaporated from the filtrate. To the crude dichloromethane (500 mL) was added and the organic layer was washed with a brine/water mixture (1:1, 500 mL total volume). The aqueous layer was washed with dichloromethane (200 mL). The combined organic layers were dried with sodium sulfate, filtered and the solvent evaporated. The crude was purified using column chromatography (silica, 2:1 Hexanes/Ethyl Acetate) giving 33 g (□ = 89%) of pure **3b** as a yellow/red oil. ^{1}H NMR (600 MHz, $CDCl_3$): $\delta = 2.33$ (s, 3 H, CH_3), 3.09 (t, 2 H, SCH_2) 3.38 (s, 3 H, OCH_3), 3.55 (t, 2 H, CH_2), 3.60 (t, 2 H, CH_2), 3.64 (m, 6 H, CH_2).

Me-EO-EO-EO-Sac (**3b**) → Me-EO-EO-EO-SH (**4b**)

A solution of **3b** (33.0 g, 0.140 mol) in a mixture of concentrated HCl (37% aqueous, 100 mL), water (100 mL) and methanol (200 mL) was heated at 60 °C for 18 hours, after which the reaction was allowed to cool down to room temperature. The reaction mixture was extracted with dichloromethane (2 × 500 mL), organic layers were combined, dried with sodium sulfate, filtered and the solvent evaporated giving 25.0 g (99 %) of **4b** as a yellowish oil. The samples were stored with some acetic acid to prevent dithiol formation. The oil was distilled at immediately prior to use yielding a clear liquid with 99.98% purity by gas chromatography. ^{1}H NMR (600 MHz, $CDCl_3$): $\delta = 1.57$ (t, 1 H, SH), 2.69 (q, 2 H, CH_2), 3.37 (s, 3 H, OCH_3), 3.54 (m, 2 H, CH_2), 3.61 (t, 2 H, CH_2), 3.64 (m, 6 H, CH_2).

^{1}H NMR of thiol-functionalization of PAGE

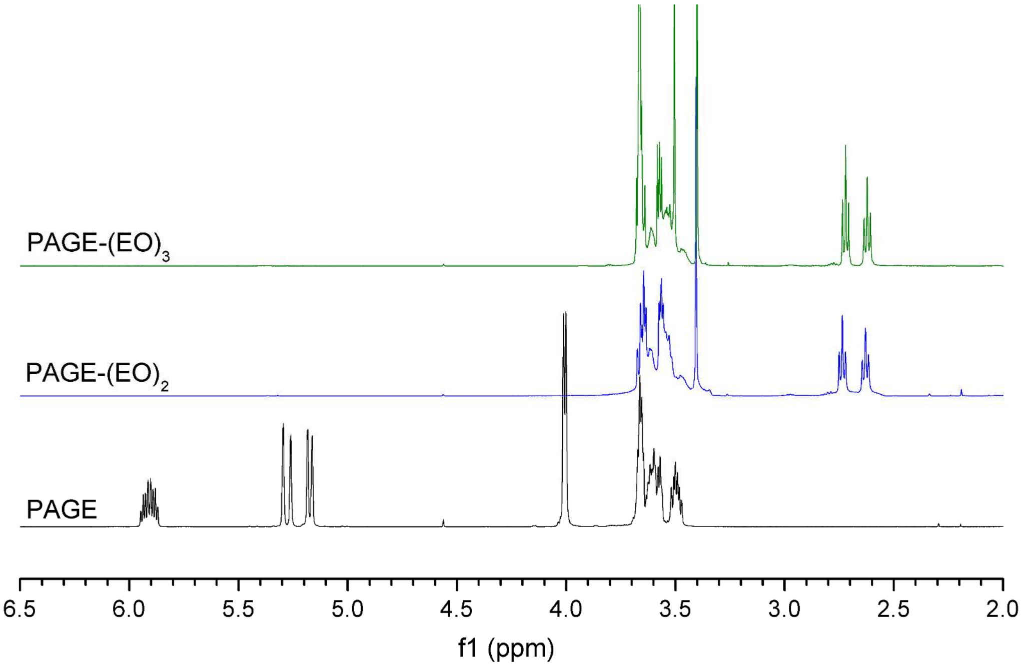
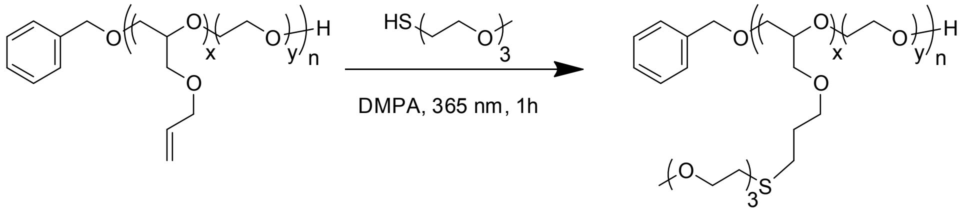


Figure S1. 1H NMR of parent PAGE polymer and thiol functionalized products. Complete consumption of allyls to thioether confirmed by disappearance of peaks between 5.0-6.0 and appearance of corresponding thioether peaks in 2.5-3.0 range.

Synthetic outline and characterization of thiol-functionalization of P(EO-*co*-AGE)



Scheme S2. Synthesis of EO-oligomer functionalized copolymer by thiolene coupling.

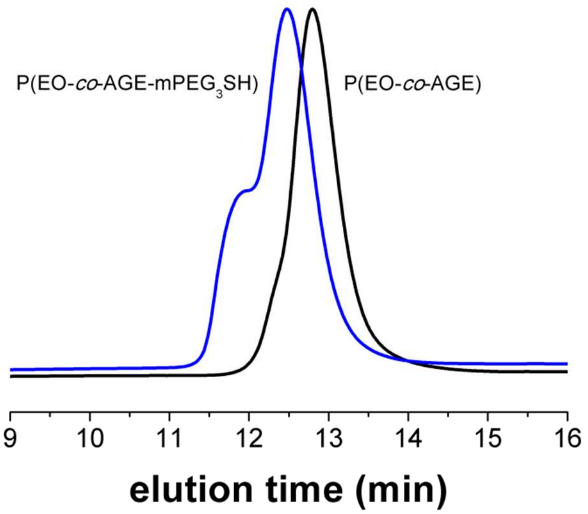


Figure S2. GPC trace of copolymer before (black) and after (blue) functionalization. Significant crosslinking observed.

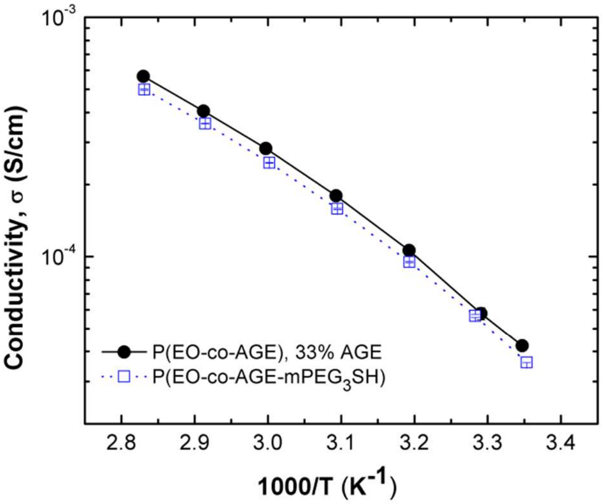


Figure S3. Ionic conductivity of thiol-functionalized copolymer compared to its parent material.