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Single-ion diblock copolymers for solid-state polymer electrolytes

Julien Rolland^a, Elio Poggi^a, Alexandru Vlad^{a,b}, Jean-François Gohy^{a*}

^aInstitute of Condensed Matter and nanosciences (IMCN), Université catholique de Louvain, Place Louis Pasteur 1, 1348 Louvain-la-Neuve, Belgium. ^bInstitute of Information and Communication Technologies, Electronics and Applied Mathematics (ICTEAM), Université catholique de Louvain, Place du Levant 3, 1348 Louvain-la-Neuve, Belgium.

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ABSTRACT

Li-ion battery technology is considered as the most efficient solution for the electrochemical energy storage. While standard liquid electrolyte - based configurations provide best performances, solid state electrolytes are developed as a safer alternative. Herein, we discuss a three step synthesis procedure of self-doped solid block copolymer electrolyte, combining a single-ion poly(lithium methacrylate-*co*-oligoethylene glycol methacrylate) ion conducting block (P(MALi-*co*-OEGMA)) and a structuring polystyrene block (PS). The macromolecular design allows the formation of a self-standing film with excellent mechanical properties provided by the PS anchoring nanodomains while attaining attractive ionic conductivities of up to 0.02 mS/cm at room temperature. Moreover, the single-ion configuration based on polyanionic backbone affords high transference numbers, close to unity, and alleviates the power limitation encountered in salt-doped solid polymer electrolyte (SPE). The electrolyte exhibits a wide electrochemical stability window up to 4.5 V *vs.* Li^+/Li and promote the formation of stable interfaces at the electrodes.

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1 1. Introduction

With an ever-increasing demand for wireless technologies and portable 13
devices, Li-ion batteries (LIBs) have become widespread in our day life.^{1,2} 14
Although many great advances have been made over the past two decades, 15
the challenge is still to design safer, longer lifespan, higher energy density 16
batteries able to power as well the electric vehicles of tomorrow. Tackling 17
this challenge requires the design of new materials at the cathode and at 18
the anode, as well as the development of new electrolyte chemistries.^{1,2,3}

9 Currently, the large majority of commercial LIBs use carbonate-based 20

liquid electrolyte exhibiting high ionic conductivities (>10⁻³ S/cm at room temperature) and thus, the best power performances, despite safety issues like leakage of corrosive and flammable constituents.^{2,4}

Gel polymer electrolyte have considerably reduced leakage hazard by trapping the liquid electrolyte within a polymer gel matrix or a swollen membrane.^{5,6} Many achievements have been made so far to attain a well mature technology currently used in commercial lithium-polymer batteries. The mechanical integrity of gel polymer electrolyte also ensures original battery configurations such as flexible,⁷ stretchable,⁸ transparent⁹ and paintable batteries.¹⁰ The risks of fire and bursting are however unavoidable due to the content of flammable liquid electrolyte.

E-mail address: Jean-François GOHY jean-françois.gohy@uclouvain.be Peer review under responsibility of xxxxx.



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^{*} Corresponding author. Jean-François GOHY

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Solid-state electrolytes remain together with ionic liquids the best49 1 2 alternatives to develop safe all-solid-state lithium cells.^{11,12} Dry polymers 50 and ceramic electrolytes developed over the years have been found to51 3 4 exhibit technologically relevant ionic conductivities.¹³ However, the 52 5 structural rigidity of ceramic membrane and limited deposition techniques 53 6 restrain their implementation only to niche batteries applications such as 54 micro-, thin-film and 3D batteries.14 By combining their lightweight,55 7 easier and conformal implementation, as well as their mechanical56 8 9 strength, solid polymer electrolyte (SPE) appears as an attractive alternative to inorganic electrolytes.¹⁵ To enable both, mechanical strength 57 10 and high ionic conductivity at ambient temperature, various polymers 11 were studied.16 Amongst them, poly(ethylene oxide) (PEO) based 58 12 materials are by far the most implemented systems given their good Li⁺⁵⁹ 13 solvation in the solid-state.^{17,18} The solid-state lithium ion transport in⁶⁰ 14 PEO is enabled through an ion hopping mechanism mainly in the⁶¹ 15 amorphous regions.¹² In the crystalline domains, the ion motion is⁶² 16 severely hampered and is responsible of poor ionic conductivities in PEO-63 17 based electrolytes at ambient temperature (<10⁻⁶ S/cm).¹² Relevant⁶⁴ 18 performances are only attained at elevated temperatures. Thus, much⁶⁵ 19 effort was devoted to lower the melting point at ambient temperature by ⁶⁶ 20 incorporating organic plasticizers, inorganic fillers and nanoparticles.^{17,1967} 21 Ionic conductivities were significantly improved but the mechanical⁶⁸ 22 properties (film forming ability, dimensional stability, etc) were degraded.⁶⁹ 23 Even worse, the ionic conductivity decreased in a matter of days because ⁷⁰ 24 of the rapid crystallization of metastable amorphous regions.¹⁵ Regarding⁷¹ 25 the charge transport, the anion mobility in PEO is usually higher than the ⁷² 26 lithium cation. Transference numbers (t) of about 0.3 are typically⁷³ 27 observed in PEO systems and are responsible for the electrode74 28 polarization with deleterious effect on the power capabilities, dendrite⁷⁵ 29 30 formation and the overall battery performances.²⁰ An acceptable⁷⁶ compromise has to be found between high ionic conductivity, mechanical⁷⁷ 31 strength, transference number (preferably $t_{\text{Li+}} \approx 1$), as well as wide 78 32 79 33 electrochemical stability window. Poly(oligo (ethylene glycol)) methacrylate (POEGMA) was found as a⁸⁰ 34 promising amorphous substitute to PEO raising the room temperature⁸¹ 35

ionic conductivity above 10⁻⁵ S/cm.²¹ In turn, mechanical reinforcement is 82 36 37 required to freeze the dimensional stability of the viscous liquid-like⁸³ polymer. Therefore, various block copolymer architectures have been 84 38 39 developed to combine the two antagonistic properties: high ionic85 conductivity of POEGMA and mechanical stiffness of a structuring86 40 block.²¹⁻²⁵ For instance, by using high glass transition polystyrene, notable87 41 performances were obtained for poly(styrene-block-oligo(ethylene glycol)88 42 43 methacrylate) block copolymer offering good mechanical properties 89 without compromising on ionic conductivity.²⁶ Nevertheless, a great deal 90 44 of work remains to be realized to overcome the power limitations caused 91 45 46 by the small current fraction carried by the lithium cation. The concept of 92 single-ion SPE (and self-doped electrolyte) has been proposed to93 47 circumvent those limitations.^{20,23,27} In a single-ion SPE, the anion is 94 48

tethered onto the polymeric backbone (PEO or POEGMA) allowing only for Li⁺ motion (t⁺ \approx 1).

Here, we discuss on the synthesis, characterization and performances of a series of single-ion block copolymers SPEs that combine i) high ionic conductivity at room temperature due to the POEGMA conductive matrix, ii) mechanical strength thanks to the PS mechanical anchor and iii) single-ion transport through the use of lithium carboxylate groups.

2. Experimental section

Materials:

Lithium perchlorate, lithium bis(trifluoromethane)sulfonimide, lithium trifluoromethanesulfonate, lithium bis(oxalato)borate (battery grade, 99.99 %. Aldrich); benzyl alcohol (99.8 %, Aldrich), α-bromo isobutyrylbromide (98 %, Aldrich) 2,2'-bipyridyl (Bpy, 99%, Aldrich), 4,4'-dinonyl-2,2'-dipyridyl (dNbpy, 97 %, Aldrich), ethyl α bromoisobutyrate (EBiB, 98%, Aldrich), N,N,N',N",N"pentamethyldiethylenetriamine (PMDETA, 99% Aldrich), copper(I) bromide (CuBr, 99.999%, Aldrich), copper(I) chloride (CuCl, >99.995%, Aldrich), were used as received. (Oligoethlene glycol) methyl ether methacrylate (OEGMA, Mn: 500 Aldrich), tert-butyl methacrylate (tBMA, >99%, Aldrich) and, styrene (>99%, Aldrich) were filtered through activated basic alumina column prior to use. All other solvents and reagents were analytical grade and were used without further purification.

Instrumentation:

Proton nuclear magnetic resonance (¹H NMR) spectra were acquired on a 300 MHz and 500 MHz Bruker Advance II. All conversions are determined by ¹H NMR by integration of the characteristics peaks. The conversion of OEGMA-tBMA containing polymers are determined by using trioxane as an internal reference. Molar mass (M_n) and dispersity (D) of the polymers were measured on an Agilent gel permeation chromatography (GPC) system equipped with an Agilent 1100/1200 pump (35 °C; eluent DMF; flow rate 1 mL/min), an Agilent differential refractometer and two PSS GRAM columns. The calibration was performed using polystyrene standards.

Synthesis of benzyl bromoisobutyrate (BnBiB):

Benzyl alcohol (6.21 mL, 0.06 mol, 1.2 eq.) was diluted in dry DCM (50 mL) and cooled down on ice bath. A solution of α -bromoisobutyryl bromide (6.18 mL, 0.05 mol, 1 eq.) and triethylamine (8.3 mL, 0.06 mol, 1.2 eq.) in dry DCM (25 mL) was added dropwise over a period of 30 min. The mixture was stirred at room temperature for 2 h, and then washed five times with acidic water (pH 2). The organic phase was dried over Na₂SO₄ and the solvent removed under reduced pressure. Purification was achieved by fractionated distillation under vacuum to afford a clear oil (44 mg, 88 %). ¹H NMR (300 MHz, CDCl₃) $\delta_{\rm H}$ (ppm): 1.9 (s, 6H, 2xCH₃), 5.2 (s, 2H, CH₂), 7.3 (br m, 5H, H_{Ar}).

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1 Typical synthesis of P(OEGMA-co-tBMA) macroinitiator:

2 A solution of benzyl bromoisobutyrate (BnBiB) (6 µL, 0.0314 mmol, 149

3 eq.), OEGMA_9 (828 $\mu L,$ 1,882 mmol, 60 eq.), tBMA (306 $\mu L,$ 1,88250

4 mmol, 60 eq.), dNbpy (32 mg, 0.0784 mmol, 2.5 eq.) and absolute ethanol51 (1 mL, 40 wt%) was degassed three times by freeze-pump-thaw cycles. 5 The degassed solution was introduced in a Schlenk flask under argon⁵² 6 atmosphere containing CuBr (5 mg, 0.0376 mmol, 1.2 eq.). The mixture⁵³ 7 was degassed three times by freeze-pump-thaw cycles, filled with argon⁵⁴ 8 and stirred in oil bath at 60 °C for 30 min. The polymerization was⁵⁵ 9 stopped by cooling down at room temperature the Schlenk tube and 56 10 exposing the catalyst to air. The reaction mixture was diluted in CH₂Cl₂⁵⁷ 11 and filtered over neutral alumina. The solvent was removed under reduced 58 12 pressure. The residue was diluted in methanol and then purified by 59 13 dialysis (SpectraPor membranes cut off 6000-8000 Da) in methanol over⁶⁰ 14 48 h. The solvent was finally removed under reduced pressure and the 61 15 residue dried under vacuum at 35 °C for 48 h, affording a clear viscous 62 16 liquid. M_n (GPC) = 13 kg.mol⁻¹; dispersity, D, (GPC) = 1.16; ¹H NMR⁶³ 17 (500 MHz, CDCl₃) $\delta_{\rm H}$ (ppm): 7.4 (br m , 5H, H_{Ar}), 4.2 (br s, 23H, CH₂⁶⁴ 18 OEG side chain), 3.9-3.2 (br m, 483H CH₂ oligo ethylene glycol side⁶⁵ 19 66 chain), 2.2-0.8 (br m, 257H, CH₃+CH₂ backbone + CH₃ tert-butyl). 20

21 Procedure for P(OEGMA-co-tBMA)-b-PS block copolymer synthesis: 68

A solution of P(OEGMA-co-tBMA) (325 mg, M_n: 13 kg.mol⁻¹, D: 1.16),69 22 styrene (2.7 mL, 23 mmol, 1000 eq.), PMDETA (6 µL, 0.0302 mmol, 1.270 23 24 eq.), and anisole (1.8 mL, 40 wt%) was degassed three times by freeze-71 25 pump-thaw cycles. The degassed solution was introduced in a Schlenk 72 flask containing CuBr (4 mg, 0.0279 mmol, 1.2 eq.). The solution was 26 degassed three times by freeze-pump-thaw cycles, filled with argon, 73 27 stirred in oil bath at 100 °C for 24h. The polymerization was stopped by 74 28 cooling down the solution and exposing the catalyst to air. The reaction ⁷⁵ 29 mixture was diluted with CH₂Cl₂ and passed through neutral alumina⁷⁶ 30 column. The solvent was removed under reduced pressure. The residue⁷⁷ 31 was precipitated twice in cold hexane. The polymer was recovered and 78 32 dried at 35 °C for 48 h. M_n (GPC) = 37 kg.mol⁻¹; ¹H NMR (500 MHz, ⁷⁹ 33 CDCl₃) δ_{H} (ppm): 7.3-6.3 (br m, H_{Ar}), 4.2 (br s CH₂ oligo ethylene glycol⁸⁰ 34 side chain), 3.9-3.22 (br m CH_2 oligo ethylene glycol side chain), 2.0-0.7⁸¹ 35 82 (br m, CH₃+CH₂ backbone + CH₃ tert-butyl)). 36 83 Synthesis of PS macroinitiator: 37 A solution of EBiB (59 $\mu L,$ 0.243 mmol, 1 eq.), styrene (18.6 mL, 162 84 38 mmol, 400 eq.), PMDETA (51 μL , 0.243 mmol, 0.6 eq.), and anisole (4.2 85 39 mL, 20 wt%) was degassed three times by freeze-pump-thaw cycles. The 40 degassed solution was introduced in a Schlenk flask containing CuBr (29 87 41 42 mg, 0.202 mmol, 0.5 eq.). The solution was degassed three times by freeze-pump-thaw cycles, filled with argon, stirred in an oil bath at 90 $^\circ\mathrm{C}^{89}$ 43 over 15 h. The polymerization was stopped by cooling down the solution 90 44 and exposing the catalyst to air. The reaction mixture was diluted with⁹¹ 45

46 CH₂Cl₂ and passed through neutral alumina column. The solvent was⁹²

47 removed under reduced pressure. The residue was precipitated twice in 93

cold hexane, filtered and dried in vacuo at 35 °C for 15 h, affording a white powder. M_n (GPC) = 12.2 kg.mol⁻¹; D (GPC) = 1.09; ¹H NMR (500 MHz, CDCl₃) δ_H (ppm): 7.3-6.3 (br m, 5 H, H_{Ar}), 2.3-1.2 (br m, 3H, CH-CH₂ backbone).

Typical procedure for PS-b-POEGMA block copolymer synthesis:

A solution of PS-Br (530 mg, M_n: 12.2 kg.mol⁻¹, *D*: 1.09), OEGMA (3.1 mL, 7.1 mmol, 164 eq.), dNbpy (36 mg, 0.089 mmol, 2.05 eq.), and anisole (3.4 mL, 50 wt%) was degassed three times by freeze-pump-thaw cycling. The degassed solution was introduced in a Schlenk flask containing CuCl (4 mg, 0.043 mmol, 1 eq.). The solution was degassed three times by freeze-pump-thaw cycles, filled with argon and stirred in an oil bath at 50 °C for 2h30. The polymerization was stopped by cooling down the solution and exposing the catalyst to air. The reaction mixture was diluted with CH₂Cl₂ and passed through neutral alumina column. The solvent was removed under reduced pressure. The residue was diluted in methanol and then purified by dialysis (SpectraPor membrane, cut off 6000-8000 Da) in methanol over 48 h. The solvent was removed under reduced pressure and the residue dried under vacuum at 35 °C for 24h. Unreacted PS macroinitiator was finally removed by stirring the residue in ether/toluene (95:5 % vol) solution during 24h. The opalescent residue was recovered and dried at 60 °C over 24h. $M_{\rm p}$ (GPC) = 52 kg.mol⁻¹; Đ (GPC) = 1.25; ¹H NMR (500 MHz, CDCl₃) $\delta_{\rm H}$ (ppm) 7.3-6.3 (br m, 720 H, H_{Ar}), 4.2 (br s, 228 H, CH₂ oligo ethylene glycol side chain), 3.9-3.22 (br m, 4430 H, CH₂ oligo ethylene glycol side chain), 2.0-0.7 (br m, 1250 H, CHCH₃-CH₂ backbone).

Typical procedure for PS-*b*-P(OEGMA-*co*-tBMA) block copolymer synthesis:

A solution of PS-Br (757 mg, M_n: 12.2 kg.mol⁻¹, *D*: 1.09), OEGMA (1.9 mL, 4.293 mmol, 85 eq.), tBMA (700 µL, 4.293 mmol, 85 eq.), dNbpy (43 mg, 0.106 mmol, 2.1 eq.), and anisole (2.7 mL, 50 wt%) was degassed three times by freeze-pump-thaw cycling. The degassed solution was introduced in a Schlenk flask containing CuCl (5 mg, 0.051 mmol, 1 eq.). The solution was degassed three times by freeze-pump-thaw cycles, filled with argon, stirred in oil bath at 60 °C for 2h30. The polymerization was stopped by cooling down the solution and exposing the catalyst to air. The reaction mixture was diluted with CH2Cl2 and passed through neutral alumina column. The solvent was removed under reduced pressure. The residue was diluted in methanol and then purified by dialysis (SpectraPor membrane, cut off 6000-8000 Da) in methanol over 48 h. The solvent was finally removed under reduced pressure and the residue dried under vacuum at 35 °C for 24h, to afford a white viscous liquid. M_n (GPC) = 35 kg.mol⁻¹; ¹H NMR (500 MHz, CDCl₃) δ_H (ppm) 7.3-6.3 (br m, H_{Ar}), 4.2 (br s CH₂ oligo ethylene glycol side chain), 3.9-3.22 (br m CH₂ oligo ethylene glycol side chain), 2.0-0.7 (br m, CHCH₃-CH₂ backbone + tertbutyl).

Synthesis of PS-b-P(OEGMA-co-MALi):

PS-b-(POEGMA-co-PtBMA) (1.3 g, 10 g/L), butylated hydroxytoluene

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(BHT) (5 mg) was dissolved in chloroform (170 mL) in Ar atmosphere.49 1 2 Trifuoroacetic acid (1.8 mL, 0.2 M) was added dropwise and the solution 50 stirred in an oil bath at 60 °C for 12h. The reaction is cooled down at 51 3 4 room temperature and the solvent removed under reduced pressure. The 52 residue was dissolved in a minimal amount of THF and purified by 53 5 6 dialysis (SpectraPor membrane, cut off 6000-8000 Da) in methanol over 54 24 h. Single-ion functions were then generated by adding lithium55 7 methoxide (2 mL, 2.2 M in methanol) to the dialysis solution and stirred 56 8 9 during 12h. The polymer was then dialyzed in pure methanol for 24h. To 57 10 remove unreacted PS macroinitiator, the polymer was finally washed by 58 11 stirring the residue in ether/toluene (95:5 %vol) solution during 24h. The 59 12 resulting solid polymer was finally recovered and dried at 60 °C over 2460 h. M_n (GPC) = 33 kg.mol⁻¹; ¹H NMR (500 MHz, CDCl₃) δ_H (ppm) 7.3-6.361 13 (br m, 720 H, H_{Ar}), 4.2 (br s, 74 H, CH₂ oligo ethylene glycol side chain), 62 14 3.9-3.22 (br m, 1422 H, CH₂ oligo ethylene glycol side chain), 2.0-0.7 (br 63 15 m, 738 H, CHCH₃-CH₂ backbone). 16 64

Thin-film preparation: 17

18 Thin-films were prepared by spin-coating a polymer solution onto silicon66 19 substrates. The silicon substrates were first cleaned by piranha solution 67 (H₂SO₄ 98 % : H₂O₂ 35 % - 2/1 vol) and carefully rinsed with ultrapure 68 20 21 water. The substrates were then spun at 4000 rpm for 30 s. A filtered (PTFE 0.2 µm) solution of PS-b-P(OEGMA-co-MALi) at 10 g/L in 69 22 THF/MeOH (50:50 vol%) was spin-coated at 2000 rpm for 40 s. Atomic 23 Force Microscopy (AFM) imaging was performed on a Digital⁷⁰ 24 Instruments Nanoscope V scanning force microscope in tapping mode⁷¹ 25

using NCL cantilevers (Si, 48 N/m, 330 kHz, nanosensors). 26

Self-standing film preparation: 27

Self-standing films were prepared by casting a 10 wt% PS-b-P(MALi-co 28 75 OEGMA) solution in THF/MeOH (50:50 vol%) onto Teflon film. The 29 76 film was first dried under air flux for 12h, and then further dried at 60 °C 30 77 31 under vacuum for 48 h. The obtained films with a thickness ranging from 78 300 µm to 1 mm were stored in a dry Argon glove box. 32 79 For BF₃ doped films, all the following operations were carried into dry 33 80 argon glove box with dry polymer and solvent to prevent lewis acid 34 81 decomposition. To dope the polymer, an equimolar amount, with respect, 35 82 to MALi of BF3 in methanol is added to the PS-b-P(MALi-co-OEGMA) 36 THF/MeOH solution. The self-standing film is obtained by drop casting 84 37 38 of polymer solution onto Tefflon film, further dried under vacuum for 48 85 39 h.

40 Ionic conductivity:

Ionic conductivities were measured by electrochemical impedance₈₈ 41 spectroscopy using a CHI 660 B analyzer. The electrolyte was first drop₈₉ 42 casted (from a 50 g/L solution in MeOH/THF 50:50 vol%) onto a90 43 stainless steel electrode, followed by drying under vacuum at 60 $^{\circ}C_{91}$ 44 during 48h. The set-up was capped with a second stainless steel electrode, 92 45 followed by annealing at 90 °C for 1h. The electrochemical response of $_{93}$ 46 the electrolyte was measured in the 1 mHz-100 kHz frequency range with $_{94}$ 47 48 an AC excitation voltage of 5 mV. 95

Transference number measurement:

The ion transference numbers were determined by using the AC-DC polarization experiment according to the Evans-Bruce protocol.28 Symmetrical Swagelock cell Li/PS-b-P(OEGMA-co-MALi)/Li were assembled by laminating the self-standing SPE film in between two Limetal electrodes. The sandwich was sealed using a Swagelock cell inside an Ar-filled glove box. The cell was first heated at 90 °C in an Espec SH-261 oven followed by stabilization for at least 24 h prior any measurement. Impedance spectra were recorded before and after DC cell polarization by using a CHI 660B electrochemical workstation in a frequency range of 100 kHz - 1 Hz. An AC excitation voltage of 20 mV was used. The cell was subsequently polarized at DC 20 mV and timecurrent dependence recorded until the steady state was reached.

Electrochemical stability window:

The electrochemical stability windows were determined by cyclic voltammetry by using CHI 660B electrochemical workstation. Swagelock cells consisting of a thick polymer film ($\approx 300 \,\mu m$) sandwiched between a stainless steel working electrode and a lithium foil counter- and reference electrode were used. The cells were cycled between 0 V to 6 V vs. Li/Li+ at 0.5 mV/s.

3. Results and discussion

Developing high performance solid state electrolytes requires high ionic conductivities, combined with excellent mechanical strength. These two features are usually in conflict (without considering further the transference numbers). To reach high ionic conductivity, the used polymers have to solubilize the lithium salt and the chain mobility has to be very high to ensure rapid movement of ions through the matrix. Those polymers exhibit usually low glass transition temperature (-60 °C for PEO, -70 °C for POEGMA). Moreover, the polymers have to be fully amorphous for the reasons mentioned above. As a result, their mechanical strength is inevitably poor. To circumvent these drawbacks, block copolymer electrolytes have been found to combine both antagonistic properties: structural integrity and high ionic conductivity. In our molecular design, the ionic conductive block is ensured by oligo(ethylene glycol) chemically anchored to a methacrylic backbone (Figure 1a). Oligo(ethylene glycol) oligomers exhibit excellent conductivities up to 10 ³ S/cm at room temperature, but behave like a liquid.²⁹ Attaching OEG to a methacrylic backbone results in a viscous liquid with no dimensional integrity and thus requires further mechanical strengthening.26 The size of the oligomers has to be considered carefully. For instance, OEG oligomers with less than 15 units, exhibit the best performances given their liquid form, low viscosity and good salt solubility.³⁰ The trend is reversed to some extent when the oligomers are attached to a methacrylic backbone. Below 9 units, the chain motion is restricted and the ionic conductivities are as low as 10⁻⁷ S/cm.³¹ Above 15 units, the oligomers tend to crystallize at room temperature and the attained conductivities are also low, of the order of 10⁻⁶ S/cm. POEGMA bearing oligomers with 9 units seemingly

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- provides the best compromise: totally amorphous and high ionic 5 1
- 2 conductivity, as high as 2 x 10⁻⁵ S/cm at room temperature.²⁶

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electrolyte, the lithium cation is already bound to the polymer backbone. 6 The carboxylate counterion is tethered and randomly distributed along the In conventional SPE, the lithium source usually comes from lithium salt 7 methacrylic backbone, allowing thus only lithium mobility and high dissolved in the conductive matrix. In our single-ion block copolymer 8 transference numbers (Figure 1a).



FIGURE 1: Electrolyte design. (a) Design at the molecular level of the tri-functional block copolymer bearing PS, POEGMA and, PMA'Li⁺ functions; (b) Self-assembly leads to distinct functions: PS domains ensure mechanical anchor, POEGMA matrix is responsible for ionic transport at the solid state whereas PMALi enables Li+ doping and anion immobilization. (c) Atomic force microscopy phase image revealing the nano-scale structure of the electrolyte; (d) Robust self-standing films are obtained after solvent casting.



FIGURE 2: Single-ion SPE synthesis strategy. (a) First approach for P(tBMA-co-OEG₉MA)-b-PS precursor polymerization, (b) Halogen exchange strategy for precursor polymerization, (c) Hydrolysis step followed by neutralization to generate single-ion functions.

Entry ^a	CuBr/CuBr ₂ /dNbpy/OEGMA/tBMA (molar ratio)	Solvent ^b	Conversion ^c OEGMA/tBMA(%)	$M_{n th}^{d}$	$M_{\rm n}^{\rm e}$ (g.mol ⁻¹)	Đ ^e
	((gillior)	(gillior)	
1	1.0 / 0.1 / 2.4 / 60 / 60	Anisole	40 / 49	16 000	16 000	1.24
2	1.0 / 0.1 / 2.4 / 60 / 60	DMF	45 / 61	18 000	16 500	1.23
3	1.1 / 0.1 / 2.4 / 60 / 60	DMF	35 / 43	13 600	13 200	1.21
4	1.2 / 0 / 2.4 / 120 / 0	EtOH	33 / -	19 000	22 000	1.25
5	1.1 / 0.1 / 2.4 / 120 / 0	EtOH	51 / -	29 000	29 000	1.22
6	1.1 / 0.2 / 2.6 / 60 / 60	EtOH	32 / 36	12 200	14 700	1.20
7	1.1 / 0.1 / 2.4 / 60 / 60	EtOH	27 / 33	10 500	12 000	1.19
8^{f}	1.1 / 0.1 / 2.4 / 60 / 60	EtOH	35 / 38	13 200	13 000	1.16
$9^{\mathrm{f},\mathrm{g}}$	1.2 / 0 / 2.4 / 60 / 60	EtOH	30 / 33	11 300	10 000	1.18

TABLE 1: Experimental conditions and results for ATRP polymerization of tBMA and OEG₉MA

^a Reactions initiated by EBiB and carried out at 60 °C during 30 min. ^b Solvent 40 wt%. ^c Conversion determined by ¹H NMR. ^d Theoretical molecular weight calculated on the basis of conversion data. ^e M_n and \tilde{P} measured by GPC using PS calibration. ^f Polymerization initiated by BnBiB. ^g Ligand replaced by Bpy.

Finally, the integration of a polystyrene block induces the formation of glassy nano-domains responsible of the mechanical reinforcement (Figure 1 b-c-d). Only small fraction of PS was necessary to confer the dimensional stability of our electrolyte. As depicted in figure 1c, the investigated diblock was designed to self-organize into a body-centered cubic phase and form an optimized morphology for micrometer thick electrode providing a continuous ion conductive matrix where the tortuosity is limited to offer the best ionic conductivity performance and mechanical stiffness provided by PS nanospheres.

Synthesis of single-ion block copolymers

The PS-*b*-P(MALi-*co*-OEGMA) single-ion block copolymer electrolytes were synthetized *via* a three-step protocol (Figure 2). The first two steps consist in the synthesis of a PS-*b*-P(OEGMA-*co*-tBMA) precursor by atom transfer radical polymerization (ATRP). The carboxylate groups (single-ion functions), are masked by *tert*-butyl groups, which prevent the poisoning of the ATRP catalyst during the polymerization.³² In the final step, the single-ion functions are released by hydrolysis of *tert*-butyl protecting groups. The neutralization of the carboxylic acid functions with a strong lithium base allows to generate the single-ion SPE.

In the first route, the ionic conductive block precursor is first produced by copolymerization of OEGMA and tBMA (Figure 2a). The PS structuring block is then polymerized starting from the P(OEGMA-*co*-tBMA) macroiniator. Table 1 presents the results of a set of ATRP conditions for POEG₉MA and P(tBMA-*co*-OEG₉MA) polymerization. The copolymerizations were realized at 60 °C in presence of the CuBr/dNbpy catalyst with the same comonomer feed (except entries 4, and 5). This catalyst system was selected to generate polymers with a bromo end-chain, known to ensure re-initiation of the second styrene block with

relatively fast kinetics.^{33;34} Several parameters were screened such as the solvent (anisole, DMF, ethanol), the addition of CuBr₂, the ligand (dNbpy, Bpy) and the initiator (EBib, BnBiB).

In each case, polymers with rather low dispersity, below 1.25, were obtained in a relatively short time (30 min). The similar conversions of both monomers, especially in EtOH, suggest that tBMA and OEGMA are randomly incorporated in the resulting copolymer at the same amount as the feed ratio. The relatively close reactivity of both methacrylic monomers can be explained by the presence of bulky oligo(ethylene glycol) side chain that increase steric constraint and favour random incorporation of both monomers. Better dispersities were obtained by performing the copolymerization in EtOH (Entries 6-8), instead of DMF or anisole (Entries 1-3). The addition of 0.1 molar ratio of CuBr₂ (Entries 4-6) and using BnBiB as an initiator further contributed to significantly improve the dispersity values (Entries 8-9), leading to well-defined macroinitiators.

In the next step, the polymerization of the structuring block was realized by re-initiation from the P(tBMA-*co*-OEGMA) bromo end-chain. The polymerization of styrene was performed by using CuBr/PMDETA catalyst at 100 °C for 24 h. The block copolymerization was first investigated in different solvents: anisole, dioxane, DMF (Table 2). For each situation, low conversions were obtained after 24h. Re-initiation efficiencies lower than 55 % were attained. GPC chromatograms of dialyzed polymers clearly show two overlapping peaks corresponding to diblock copolymer and unreacted macroinitiator at lower and higher retention times, respectively (Figure 3).

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CuBr / $M_{\rm n th}^{d}$ $M_{\rm n}^{\rm e}$ Conv^b PMDETA Solvent Entry^a $(g.mol^{-1})$ (molar (%)(g.mol⁻¹) ratio) 1.8 / 2.0 Anisole 37 000 1 < 5 2 1.2 / 1.2 Dioxane 5 21 000 38 000 3 1.2/1.3DMF 11 26 000 77 000 4^{f} 1.2 / 1.3 DMF 14 29 000 85 000

polymerization starting from the P(tBMA-co-OEG₉MA) macroinitiator

TABLE 2: Experimental conditions and results for styrene

^a Reactions conditions : P(tBMA-*co*-OEGMA) (M_n 13 kg.mol⁻¹; \mathcal{D} 1.16), 100 °C, 1000 equiv. styrene. ^b Solvent 50 wt%. ^c Conv = conversion determined by ¹H NMR. ^d Theoretical molecular weight calculated on the basis of conversion data. ^e M_n and \mathcal{D} measured by GPC using PS calibration. ^f Reaction realized with preformed catalyst.



Figure 3: *GPC chromatograms* of $P(tBMA-co-OEG_{9}MA)$ -b-PS polymerized in different solvents and of the $P(tBMA-co-OEG_{9}MA)$ starting macroinitiator.

As expected, incomplete re-initiation leads to a mixture of block copolymer and unreacted macroinitiator after polymerization. However, the re-initiation efficiency seems to be strongly dependent on the nature of the solvent. Changing the solvent from DMF to dioxane improves the re-initiation efficiency whereas with anisole poor re-initiation was observed. These results suggest that some of the bromo chain-ends in the macroinitiator are not able to reinitiate polymerization. A possible explanation for this observation could lie in the conformation of the macroinitiator polymer chain in solution.^{35,36} In this respect, the accessibility of the bromo chain-end could be decreased or even totally screened. Incomplete conversion of macromonomer or macroiniator brushes is indeed usually reported in ATRP and in other controlled (or living) polymerization, causing difficulties in purification.³⁶

The synthetic strategy was thus adapted and the order of monomer addition was reversed. As depicted in Figure 2b, the new approach consists in the ATRP of the styrene block, followed by the copolymerization of the second block. At the first step, a well-defined PS macroinitiator was obtained with D=1.09 (for details on the PS synthesis



PS-Br (Table 3; entry 8).

see experimental section). Now, the PS macroinitiator can be advantageously used as a platform to-polymerize the POEGMA (Table 3) or P(MALi-*co*-OEGMA) (Table 4) block. However the copolymerization of a methacrylate block from a PS macroinitiator requires halogen exchange methodology in ATRP.^{37,38} This strategy was successfully applied here to the synthesis of PS-*b*-POEGMA and PS-*b*-P(tBMA-*co*-OEGMA) copolymers, despite the incomplete re-initiation efficiency. Pure PS-*b*-POEGMA was however recovered from the polymerization mixture after ether/toluene washing step (Figure 4). In the case of PS-*b*-P(tBMA-*co*-OEGMA), pure block copolymer was only obtained after the hydrolysis step due to the solubility of P(tBMA-*co*-OEGMA) in ether (Figure 5).

In practice, the experimental conditions were optimized for PS-b-POEGMA and then applied for the PS-b-P(tBMA-co-OEGMA) synthesis. The synthesis of PS-b-POEG₉MA was carried out by using CuCl/dNbpy catalyst. The effect of several parameters was screened such as the solvent, the temperature and the concentration of monomer. Amongst anisole, dioxane and DMF, only polymerizations performed in anisole led to well-defined block copolymers with relatively narrow mass distribution (Table 3; Entry 1-3). Looking at the temperature effect, the polymerizations performed at 60 °C allow to get the best compromise between efficient re-initiation and low dispersity (Table 3; Entry 1, 4-6). Finally by lowering the concentration of the polymerization medium to 70 wt%, better control is achieved leading to well-defined block copolymers with D=1.19 (Table 3; Entry 7-8). The optimized conditions presented in the Entry 8 (Table 3) were transposed to the synthesis of the PS-b-P(tBMA-co-OEGMA) copolymers with variable tBMA/OEGMA molar ratio (Table 4).

As encountered for the OEGMA/tBMA homopolymerization, the conversion of both monomers is similar and is proportional to the molar reactant feed. These results further support that tBMA and OEGMA are randomly incorporated during the polymerization.

The PS-*b*-P(MALi-*co*-OEGMA) single-ion electrolytes were finally obtained by the hydrolysis of *tert*-butyl groups. The hydrolysis is

performed in presence of a 10 fold excess of trifluoroacetic acid for 12 h (reflux of chloroform).

Entry ^a	Solvent	Wt% ^b	Temperature (°C)	Reaction time (h)	Conversion ^c OEGMA (%)	$M_{n th}^{d}$ (g.mol ⁻¹)	$M_{n NMR}^{e}$ (g.mol ⁻¹)	D^{f}
1	Anisole	50	60	2.5	26	29 400	56 000	1.21
2	Dioxane	50	60	2.5	36	37 200	60 000	1.29
3	DMF	50	60	2.5	60	55 900	87 000	1.50
4	Anisole	50	50	2.5	27	30 200	69 200	1.25
5	Anisole	50	70	1.8	25	28 600	45 000	1.30
6	Anisole	50	80	1.5	18	23 200	40 000	1.27
7	Anisole	60	60	2.5	20	24 800	50 000	1.20
8	Anisole	70	60	2.5	30	32 500	57 000	1.19

TABLE 3: Experimental conditions and results for PS-b-POEG₉MA polymerization

^a Reactions conditions: PS / CuCl / dNbpy / OEGMA = 1/1/2.05/160. ^b Solvent wt% ^c Conversion determined by ¹H NMR. ^d Theoretical molecular weight. ^e M_n determined by ¹H NMR. ^f \mathcal{P} measured by GPC.

Entry ^a	OEGMA/tBMA (molar ratio)	Conversion OEGMA/tBMA(%) ^b	<i>M</i> _p ^c (g.mol⁻¹)	f _{MALi} d (%)	<i>M</i> n [°] (g.mol⁻¹)	D^{c}
1	85 / 85	23 / 25	34 000	76 ^e	29 000	1.23
2	85 / 85	25 / 27	35 000	53	33 400	1.23
3	102 / 68	24 / 25	33 500	41	32 500	1.23
4	127 / 43	25 / 26	44 000	28	43 000	1.25

TABLE 4: Experimental conditions and results for PS-b-P(MALi-co-OEGMA) synthesis

^a Reaction conditions: PS / CuCl / dNbpy 1:1:2.05, anisole 70 wt%, 60 °C, 2h30. ^c Conversion determined by ¹H NMR. ^c $M_{\rm p}$, $M_{\rm n}$ and ϑ are respectively molar mass of PS-*b*-P(tBMA-*co*-OEGMA), molar mass of PS-*b*-P(PMALi-*co*-OEGMA) obtained after hydrolysis and dispersity measured by GPC using PS calibration. ^d MALi fraction assessed by ¹H NMR. ^e Higher fraction of MALi obtained after hydrolysis during 24 h.

The hydrolysis yield is assumed to be complete after the total disappearance of the straight and characteristic peak of tert-butyl protons on the ¹H NMR spectra. The fraction of MALi is then determined by integration of protons signal of the remaining OEG side-chain and the protons corresponding to the polymer backbone. Reaction time has been optimized to hydrolyze mainly the tBu protecting groups and to limit as much as possible the hydrolysis of the OEG side chains. Increasing the reaction time resulted in deeper OEGMA side chain hydrolysis (Table 4; Entry 1). Subsequent neutralization with lithium base and ether/toluene washing allow to separate unreacted macroinitiator from well-defined block copolymer chains as shown on GPC chromatograms (Figure 5)

Conduction characteristics

The ionic conductivities of the single ion block copolymer SPE and conventional salt-doped SPE are detailed in Figure 6. First, the effect of MALi content was investigated.



Figure 5: GPC chromatograms of PS-b-P(MALi-co-OEGMA) at different MALi/OEGMA ratio (Table 4).

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Figure 6: *Ionic conductivities* (a) MALi content dependence for single-ion electrolyte and BF₃ effect, (b) high performance salts-doped PS-b-POEGMA electrolytes (EO/Li 20:1) at 20 °C.

The ionic conductivities versus OEGMA/MALi ratio are shown in Figure 6a and correlated with the EO/Li⁺ ratio. For every case, the single-ion BF₃ free SPE displays very low ion transport, with conductivities of the order 10⁻⁸ - 10⁻¹¹ S/cm at room temperature. The ionic conductivity has been found to gradually increase with a decrease in the MALi content which is consistent with previous report for POEGMA based electrolytes.²⁶ Indeed, increasing MALi load results in higher lithium concentration in the electrolyte. Based on crown ether mechanism, the number of EO[Li⁺] complexes increases with the concentration and consequently reduce the segmental motion of OEG side chain crucial for ion diffusion. Even worse, the ion-pair formation and salt clustering is usually formed at EO/Li ratio below 8 thus, trapping and hindering the lithium cation motion.³⁹ Even if the salt concentration affects the ionic conductivity, only slight variations have been reported.²⁶ The salt concentration alone does not explain the trend. For weakly entangled polymers like POEGMA, the inter-chain ion hopping mechanism is expected to severely impact the ionic conductivity.¹² In the ion conductive block; the distance between OEGMA units is spaced by MALi groups. The ion hopping distance is thus increased and the ion motion lowered. This effect is more pronounced for conductivities as the MALi content increases.

Even if the macromolecular architecture has been optimized, the ionic conductivities remain low, of about 10⁻⁸ S/cm. In fact, similar performances are characteristic for a wide range of single-ion moieties.^{20,23,27} The poor performances are attributed to strong ion-pairing with the carboxylic group.

The Li⁺ ions are thus trapped onto the polymeric backbone bearing the counter ions and only weakly contribute to ionic current. Providing satisfactory conductivities require a higher degree of dissociation. The addition of lewis acid was therefore exploited here, the process being known to induce charge delocalization of carboxylate groups and then enhance the degree of dissociation.⁴⁰ Remarkably, the addition of boron trifluoride raises the ionic conductivity of all studied configuration by 3

orders of magnitude, with a maximum of 2.10^{-5} S/cm reached. These values compete with those obtained for high performances lithium salt such as LiBOB, LiTFSI, LiTFS dissolved in PS-*b*-POEG₉MA as reflected in Figure 6b. It is worth mentioning that BF₃ is particularly sensitive to moisture traces. All electrolyte film process should be carried out under stringent dry inert atmosphere.

The rise in the transference number as a result of the single-ion design was confirmed by AC-DC polarization spectroscopy.²⁸ Transport numbers as high as 0.84 were obtained for the single-ion electrolytes, which is much higher than 0.2-0.3 usually observed for standard salt-doped systems.¹⁵ Thus, by combining the high ionic conductivity and transference numbers close to unity, the single-ion PS-*b*-P(MALi-*co*-OEGMA) electrolytes outperform the simple salt-doped systems.

Electrochemical stability

The electrochemical stability of PS-b-P(MALi-co-POEGMA) with and without added BF3 were investigated by cyclic voltammetry. The results are shown in Figure 7. The PS-b-P(MALi-co-POEGMA) exhibits a wide electrochemical stability window up 5 V, even when complexed with BF₃. Both formulations exhibit an anodic peak above 4.5 V that can be attributed either to polymer electrolyte degradation and to the stainlesssteel electrode corrosion. In the BF3 containing electrolyte, an anodic peak appears only at the first cycle around 3.5 V. Upon incorporation of BF₃, the reactivity of the electrolyte is seemingly increased at anodic potentials and promote the oxidation of the electrolyte.⁴¹ At the second scan, the peak is less pronounced and suggests the formation of a stable electrolyte interface at the electrode that prevents further electrolyte oxidation on the subsequent cycle. At the cathodic potential below 2 V vs. Li+/Li, the formation of solid electrolyte interface (SEI) is inevitable as demonstrated by strong electrochemical response around 1.3 and 0.8V. At these potentials, complex reduction reactions occur and promote the degradation of the electrolyte at the interface with the electrode.42 However, as observed for the anodic processes, the cathodic response

diminishes on the following cycles and is almost suppressed at the 5th cycle. Due to the solid form of the electrolyte, a stable SEI is generated at the interfaces between the electrode and the electrolyte. Unlike the situation of liquid or gel electrolytes, this interface is structurally robust and cannot be stripped and reformed by supplying fresh electrolyte at each

cycles. A stable and protective SEI is thus formed and prevents further electrolyte deterioration.





Figure 7: Cyclic voltammetry of (a) PS-b-P(MALi-co-OEGMA) single-ion electrolyte and (b) in presence of BF3 at a scan rate of 0.5 mV/s. The curves are shifted for more clarity.

4. Conclusion

Herein, we describe a very convenient method for the preparation of single-ion electrolytes. The three steps synthesis allows to get well-defined PS-*b*-P(MALi-*co*-POEGMA) single-ion electrolytes with dispersity below 1.25.

The macromolecular design offers self-standing flexible membranes and combines outstanding ionic conductivities. By inducing charge delocalization, the main limitations of single-ion electrolyte have been vanished and the accordingly obtained ionic conductivities around 2.10⁻⁵ S/cm compete with conventional doped electrolyte values at room temperature. At same ionic conductivities, single-ion SPEs rise the Li⁺ transference number and thus potentially alleviate power limitation encountered in solid electrolytes.

The single-ion electrolyte displays also a wide electrochemical stability up to 4.5 V vs. Li^+/Li and excellent passivation behavior by promoting the formation of a stable solid electrolyte interface.

By merging together mechanical stiffness, excellent ionic conductivities, high transference number and wide electrochemical stability window, this single-ion SPE appears as a promising candidate for safe and performing solid-state electrolyte.

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Highlights:

- We disclose a convenient 3 steps synthesis for high performance solid electrolyte.
- The single-ion electrolyte design has been optimized to afford the mechanical and ion transport performances
- Single-ion electrolytes containing BF_3 have attractive ionic conductivities as high as 0.02 mS/cm at room temperature.
- The single-ion electrolyte promotes the formation of a stable SEI