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Poly(benzyl methacrylate)-poly[(oligo ethylene glycol) methyl ether methacrylate] triblock-copolymers as solid electrolyte for lithium batteries

Andreas Bergfelt[a,*], Laurent Rubatat[b], Daniel Brandell[a], Tim Bowden[a]

[a] Department of Chemistry - Ångström Laboratory, Uppsala University, Box 538, SE-751 21 Uppsala, Sweden
[b] CNRS/UNIV Pau & Pays Adour, Institut des Sciences Analytiques et de Physico-Chimie pour l´ Environnement et les Materiaux, UMR5254, 64000 Pau, France

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ABSTRACT

A triblock copolymer of benzyl methacrylate and oligo(ethylene glycol) methyl ether methacrylate was polymerized to form the general structure PBnMA-POEGMA-PBnMA, using atom transfer radical polymerization (ATRP). The block copolymer (BCP) was blended with lithium bis(trifluoro methylsulfonate) (LiTFSI) to form solid polymer electrolytes (SPEs). AC impedance spectroscopy was used to study the ionic conductivity of the SPE series in the temperature interval 30 °C to 90 °C. Small-angle X-ray scattering (SAXS) was used to study the morphology of the electrolytes in the temperature interval 30 °C to 150 °C. By using benzyl methacrylate as a mechanical block it was possible to tune the microphase separation by the addition of LiTFSI, as proven by SAXS. By doing so the ionic conductivity increased to values higher than ones measured on a methyl methacrylate triblock copolymer-based electrolyte in the mixed state, which was investigated in an earlier paper by our group. A Li|SPE|$LiFePO_4$ half-cell was constructed and cycled at 60 °C. The cell produced a discharge capacity of about 100 mAh g^{-1} of $LiFePO_4$ at C/10, and the half-cell cycled for more than 140 cycles.

1. Introduction

The electrolytes used today constitute a major threat to Li-battery safety [1–4]. Replacing flammable and harmful liquid electrolytes with solid polymer electrolytes (SPEs) would drastically improve this situation. SPE materials are today well-known for energy storage applications, but still suffer from too low ionic conductivity for most commercial products. However, with an increase in operating temperature to 60 °C–80 °C, which is not an obstacle for electric vehicles, their ionic conductivity increases drastically [5–7]. Energy storage materials made from polymers are therefore certainly an interesting option for these applications and the SPE area can be foreseen to experience a renaissance during the coming decade(s) [8–10].

Increasing the ionic conductivity and their lithium ion transport number of said SPEs would further boost their use, since the main challenge is to combine mechanical stability with ionic conductivity. The main conduction mechanism in SPEs is the ionic transport through the segmental motion of the polymer main chain, which in this context constitutes a paradox: a more flexible polymer can transport ions better, but then fails in terms of rigidity [11]. The popular use of low-T_g polyethers, such as poly(ethylene oxide) (PEO), rely on the dissolution of lithium salt though the interaction of ether groups found in the main chain, and increasing the temperature increases the segmental motion and thus the ionic conductivity. One way to further increase the flexibility of the functional ether group, and simultaneously reduce the non-conductive crystalline domains, is to lace the ether groups outside the main chain as in a comb polymer [12]. Comb polymers hold the promise of higher ionic conduction since the mobility of the side chain is higher than for the polymer backbone. Here, the main chain could for example be a polyacrylate with oligoether side chains giving higher ionic conductivity due to increased flexibility [13,14]. A problem faced by increasing the flexibility of the polymer is that the material becomes softer and thus loose its mechanical properties, which also holds true for comb polymers. One way to overcome this problem is to use a block copolymer (BCP) design approach, where the blocks separate into discrete phases such as a soft ionic conducting phase and a hard mechanically stable phase [15–17].

BCP electrolytes constitute complex systems, comprising several variables in terms of polymer composition, salt concentration, and morphological organization. Yet, understanding phase behavior in BCPs with added salts, and how these phases behave over a wide temperature range, need to be understood in order to link ionic conductivity and mechanics requirements, since this is fundamental for the development of mechanically robust SPEs with good lithium ion conduction [18,19]. Phase separation becomes an important issue for systems where salt addition has the possibility to induce phase separation. While many

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[*] Corresponding author.
E-mail address: andreas.bergfelt@kemi.uu.se (A. Bergfelt).

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different BCP SPE systems have been evaluated throughout the years, the most studied system so far is the polystyrene-polyethylenoxide (PS-PEO) copolymers where ionic conductivity, mechanical properties and micro phase separation have been studied in depth [20–23].

One drawback with working with PEO is that it's SPEs are generally semi-crystalline below 60 °C, which has a negative impact on the ionic conductivity [24]. One way to avoid this is to move the PEO functionality to a side-chain in the polymer, thus creating a comb copolymer. We have previously synthesized and studied two such comb copolymer systems in order to study the effect of random copolymerization compared to block copolymerization, where both the ionic conductivity and the miscibility of the blocks were studied [12,25]. An interesting finding was that the BAB block copolymer, where B is methyl methacrylate and A oligo(ethylene glycol) methyl ether methacrylate, did not microphase separate. From an application point of view this is not desirable, since the hypothesis is that by separating hydrophobic and hydrophilic constituents on the same polymer chain, a local nano-scale ordering of these segments with different polarity can be realized, promoting both ionic conductivity and mechanical stability. This can, in turn, result in better power performance of the batteries.

To better understand the microphase separation in SPEs and their electrochemical and battery performance, we have here synthesized a new type of BAB triblock copolymer based on benzyl methacrylate and oligo(ethylene glycol) methyl ether methacrylate, PBnMA-POEGMA-PBnMA, see Fig. 1. The electrolytes were prepared with bis(trifluoro methylsulfonate) (LiTFSI) to form SPEs. The best performing electrolyte was evaluated with SAXS and TEM to study the morphology, and a battery device was constructed to evaluate the electrochemical performance.

2. Experimental section

2.1. Materials

Materials used were oligo(ethylene glycol) methyl ether methacrylate (OEGMA, $M_w = 500\ \mathrm{g\ mol^{-1}}$, Sigma), benzyl methacrylate (BnMA, Sigma), dichloromethane (DCM, Fischer Scientific), diethyl ether (Fischer Scientific), cyclohexane (Acros Organics), ethanol (Solveco), CuBr (Sigma), $CuBr_2$ (Sigma), 2,2′-bipyridyl (Sigma), ethylene glycol (Sigma), α-bromoisobutyryl bromide (Sigma), basic Al_2O_3 (Sigma), dry tetrahydrofuran with molecular sieves (THF, Acros Organics), and $CDCl_3$ (Larodan Fine Chemicals). Solvents were used without further purification. Lithium bis(trifluoromethane)sulfonimide (LiTFSI, Purolyte, Ferro Corporation) was dried at 120 °C for 24 h before use.

2.2. Initiator synthesis

The synthesis of the di-functional initiator was adapted from literature [28,29]. 18.6 mL (82.5 mmol) α-bromoisobutyryl bromide was added to 2 mL (35.6 mmol) ethylene glycol and 11.5 mL (82.5 mmol) of tri-ethyl amine in 100 mL dry THF using a dropping funnel under argon atmosphere. The reaction was cooled in an ice bath. The reaction was left overnight before the salt was filtered off with a Buchner funnel. THF was evaporated and the solid dissolved in DCM (100 mL) and washed three times with saturated $NaHCO_3$ (100 mL). The organic phase was dried with $MgSO_4$, filtered and evaporated to give a white solid. The product was recrystallized from ethanol and dried in a vacuum oven to give the desired product 2-(2-bromoisobutyryloxy)ethyl methacrylate as white needles, hereafter denoted di-EBiB. ^1H NMR (400 MHz, $CDCl_3$) δ 4.42–4.44 (4H), 1.95–1.91 (12H).

2.3. Synthesis POEGMA macroinitiator

The OEGMA monomer was passed through a column of basic Al_2O_3 in order to remove the radical inhibitor. The monomer (OEGMA, 31.63 mL, 63.3 mol), solvent (ethanol, 30 mL), initiator (di-EBiB, 123 mg, 0.44 mmol), $CuBr_2$ (9.2 mg, 0.0041 mmol), and ligand (bpy, 213 mg, 1.36 mmol) were added to a 100 mL Schlenk flask. The flask was sealed with a silicone septum, degassed, backfilled three times with N_2, and then left under N_2. CuBr (98 mg, 0.68 mmol) was then added, and the Schlenk flask was placed in an oil bath at 60 °C for 2 h. The system was quenched with acetone, filtered through basic Al_2O_3, and precipitated twice in 300 mL of a 1:1 mixture of diethyl ether and cyclohexane. The solvents were removed using rotary evaporation and the final product was dried in a vacuum oven. The typical yield is circa 30 wt% (POEGMA: M_n, GPC = 31,085 $\mathrm{g\ mol^{-1}}$, PDI = 1.13).

2.4. Polymer synthesis triblock copolymer

BnMA was passed through a column with 10 mL basic Al_2O_3 to remove the radical inhibitor. The monomer (BnMA, 4.94 mL, 46.2 mmol), solvent (ethanol, 6 mL), macroinitiator (POEGMA, 1.54 g), $CuBr_2$ (3 mg, 22.3 μmol), and PMDETA (29 mg, 0.19 mmol) were added to a 50 mL Schlenk flask and three freeze-pump-thaw cycles were performed with N_2. CuBr (36.8 mg, 0.37 mmol) was added before the flask was sealed with a silicone stopper and placed in an oil bath at 60 °C for 20 min. The reaction was then quenched with acetone, filtered through 20 mL of basic Al_2O_3, and precipitated in 300 mL of a 1:1 mixture of diethyl ether and cyclohexane. The solvents were removed using rotary evaporation and the final product was dried in a vacuum oven. (PBnMA-POEGMA-PBnMA: M_n, GPC = 52,810 $\mathrm{g\ mol^{-1}}$, PDI = 1.22).

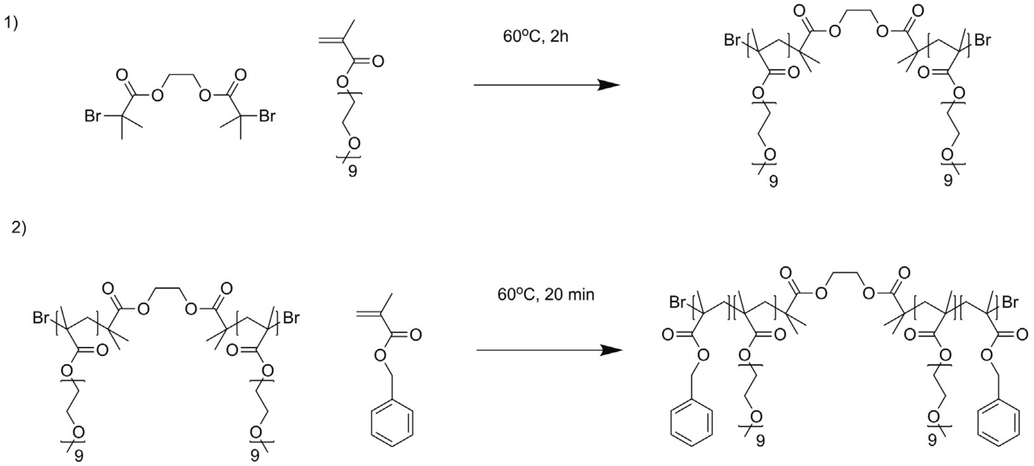

Fig. 1. Synthesis scheme for the triblock copolymer, using ATRP.