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A New (Trifluoromethane)Sulfonylimide Single-Ion Conductor with PEG Spacer for All-Solid-State Lithium-Based Batteries

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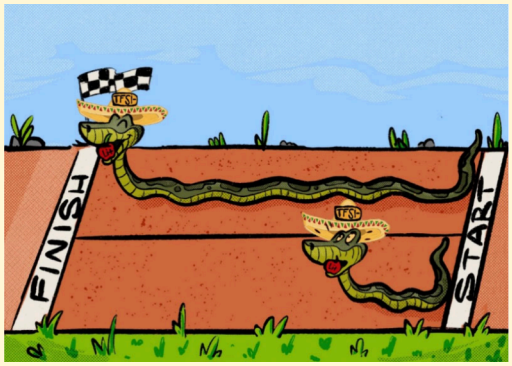
ABSTRACT: **The choice of ionic-liquid-like monomers (ILM) for single-ion conducting polyelectrolytes (SICPs) is crucial for the performance of all-solid-state lithium batteries. In the current study, we propose a novel approach for development of SICPs via design and synthesis of a new ILM with long poly(ethylene oxide) spacer between methacrylic group and (trifluoromethane)sulfonylimide anion. Its homopolymer shows an ionic conductivity that is ∼5 orders of magnitude higher (9.2×10^{-8} S cm^{-1} at 25 °C), in comparison with previously reported analogues, while the conductivity of its random copolymer with poly(ethylene glycol)methyl ethermethacrylate reaches the levels of 10^{-6} and 10^{-5} S cm^{-1} at 25 and 70 °C, respectively. The copolymer provides excellent thermal ($T_{onset} \approx 200$ °C) and electrochemical (4.5 V vs Li$^+$/Li) stabilities, good compatibility with Li metal, and effective suppression of dendrite growth. Li/SICP/LiFePO$_4$ cells are capable of reversibly operating at different C rates, demonstrating excellent Coulombic efficiency and retaining specific capacity upon prolonged charge/discharge cycling at a relatively high current rate (C/5) at 70 °C.**



Single-ion-conducting polyelectrolytes (SICPs) are a relatively new subclass of solid-state polymer electrolytes (SPEs) that have the potential to revolutionize solid-state lithium-based batteries industry, enabling safe operation of Li metal anode in future truly solid-state Li-metal batteries (LiMBs).[1,2] Structurally, SICP is a polyelectrolyte having anionic moieties covalently attached to the polymer backbone and lithium counterions that are free to move.

Although SICPs are known from the early 1980s,[3] the real breakthrough was gained in the middle of 2010s with the application of ionic liquids (ILs) chemistry and (trifluoromethane)sulfonylimide (TFSI) anion,[4−7] in particular. The introduction of anions with high delocalization and low basicity allowed for the increase of overall ionic conductivity in SICPs, generally approaching the level of 10^{-7}−10^{-6} S cm^{-1} at 25 °C.[1,2] Similar to SPEs, SICPs offer high thermal stability, nonvolatility, high electrochemical stability, and prevent any risks of liquid electrolyte leakage outside the battery case.[8] Moreover, since anions in SICPs are chemically bonded to the main backbone, their mobility is limited and only the Li$^+$ cation will contribute to a permanent flow of charge, thus increasing the Li ion transference number (t_{Li+}) close to unity.[9] This is expected to prevent the concentration gradients (polarization), thus contributing to circumvent (at least limit) dendrite growth at the surface of the Li metal anode in LiMBs.

Despite extensive research efforts,[1,2,10] a competitive LiMB utilizing SICP electrolyte that satisfies industrial process needs and meets the market requirements for modern, high energy/power density batteries has yet to be developed. One of the reasons is connected with the insufficient ionic conductivity of SICPs being below that of salt-in-PEO polymer electrolytes (4×10^{-5}−9×10^{-4} S cm^{-1} at 25 °C).[11] Three approaches to overcome this problem have been suggested: (a) synthesis of cross-linked SICPs plasticized with polar organic additives (see, for example, refs 5 and 12−16); (b) preparation of

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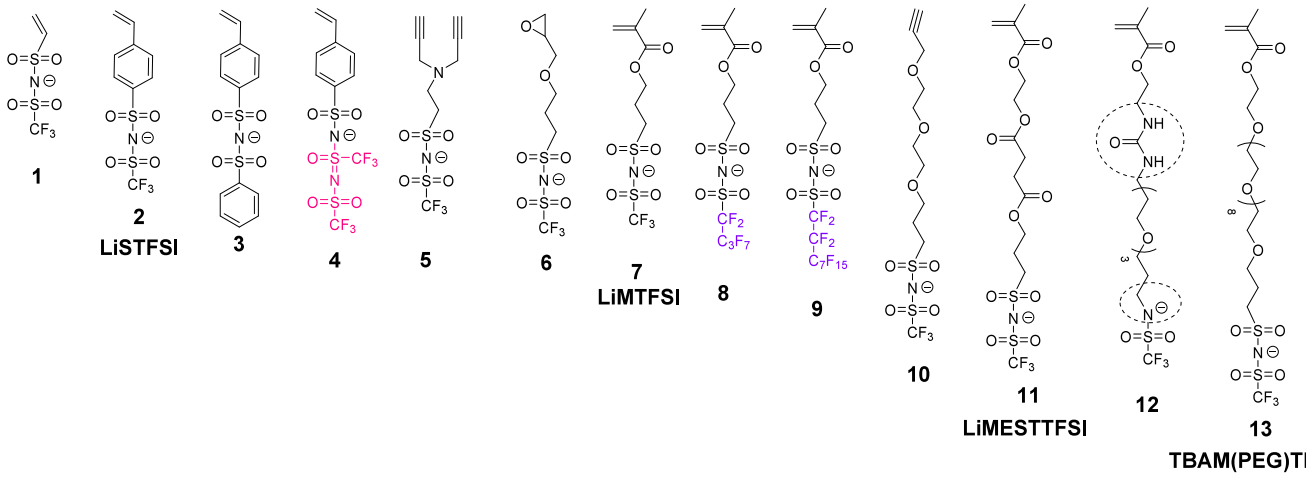
Scheme 1. An Overview of the Ionic Liquid Like Monomers with Delocalized TFSI-Like Anion Reported up to Date in the Literature (See References in the Main Text)



various ionic block copolymers, where the partial incompatibility between ionic and neutral blocks resulted in a microphase-separated morphology, formation of nanoscale domains and concentration of ionic species inside the ion conducting channels (see, for example, refs 7, 17−24); and (c) design and preparation of new ionic monomers with modified TFSI anion (Scheme 1, monomers **3**, **4**, **8**, and **9**)[25,26] or with polar spacer between the reactive group and bonded anion (Scheme 1, monomers **10**−**12**).[25,27−29]

The first approach allowed one to significantly increase the ionic conductivity of solid electrolytes and resulted in excellent battery cycling with high capacity and long-term stability.[5,12−16] At the same time, such SICPs suffered from performance decay due to plasticization and potential leaching/evaporation associated with the addition of liquid polar additives such as ethylene carbonate.

The limitation of the second approach was the application of only two most popular ionic monomers, namely, lithium styrene (trifluoromethane)sulfonylimide (**LiSTFSI**, Scheme 1, **2**) and lithium methacrylate (trifluoromethane)sulfonylimide (**LiMTFSI**, Scheme 1, **7**). While their synthesis is relatively easy, the homopolymers showed high glass-transition temperatures (T_g) equal to 152 and 95 °C, respectively (Table S1, entries 1 and 9). In its turn, such stiff materials could not provide efficient ion mobility below T_g resulting in low ionic conductivity (1.1×10^{-12} S cm^{-1} at 25 °C measured for poly(**LiMTFSI**)). Such high T_g values are a consequence of a very short spacer between the vinyl functional group and the proximity of the TFSI anion to the main polymer chain. To reduce the T_g and increase the ionic conductivity, **LiSTFSI** and **LiMTFSI** were either copolymerized with poly(ethylene glycol) methacrylate (PEGM)[17,22,24] to form ion conducting blocks or polymerized from poly(ethylene oxide) (PEO) used as a neutral block (Table S1, entries 2−4 and 10).[7,18−21,23] This led to a significant decrease in T_g and increase in ionic conductivity of SICPs reaching the level of 10^{-6} S cm^{-1} at 25 °C. Among the disadvantages of such a method, it is possible to mention the complexity of the polymerization process and the use of expensive initiators/agents for microstructure control.

Another direction was associated with the design of new ionic liquid like (ILMs) monomers (Scheme 1 and Table S1). First, the efforts were focused on the modernization of the TFSI anion. The introduction of perfluorinated side chains (Scheme 1, monomers **8** and **9**; Table S1, entries 11 and 12) induced a plasticization effect, thus decreasing the T_g of SICPs down to −61 °C and increasing the ionic conductivity by a half order of magnitude, in comparison with SICPs derived from **LiMTFSI** (Scheme 1, **7**).[25] Similarly, there was an increase in delocalization in the so-called "super-TFSI" anion (Scheme 1, **4**; Table S1, entry 6)[26] allowed for a 1 order of magnitude increase in ionic conductivity, compared to SICP based on its LiSTFSI analogue (Scheme 1, **2**). Unfortunately, it is not possible to estimate the effect of CF_3 group substitution with an aromatic ring in monomer **3** and compare it with polymers based on LiSTFSI (Scheme 1, **3**), as **3** was not homopolymerized or copolymerized. Its utilization for the modification of low-molecular-weight polysiloxanes provided highly viscous SICPs that did not allow for any self-standing film formation (Table S1, entry 5).[27]

Next, attempts to synthesize TFSI anion-based ILMs having different active functional groups compared to methacrylic or styrene ones have been attempted (Scheme 1, monomers **1**, **5**, **6**, and **10**). Although nobody was studying the polymerization of vinyl-TFSI monomer (Scheme 1, **1**),[30] it is obvious that, at sufficiently high degrees of polymerization, it will provide SCIPs with high T_g values, because of the absence of any spacer between the polymer backbone and anion, thus limiting its mobility mostly to the segmental motion of polymer chains. The same relates to ILMs **5**[30] and **6**[31] (see Scheme 1, as well as entries 7 and 8 in Table S1), where the number of carbons in the spacers is similar to that in the well-studied **LiMTFSI** (Scheme 1, **7**). The increase in the length of a spacer up to 11 atoms and the introduction of polar ethylene oxide fragments in ILM **10** led to the formation of anionic SICP that, in combination with 1-methyl-3-ethyl imidazolium cation, exhibited a low T_g (−25 °C) and sufficiently high ionic conductivity (1.7×10^{-6} S cm^{-1} at 25 °C under anhydrous conditions).[28] Continuous increase in the spacer length in monomer **11** (**LiMESTTFSI**) was shown to beneficially affect the ionic conductivity of resultant SICP (Table S1, entry 13).[25] The transfer from **LiMTFSI** to **LiMESTTFSI** in copolymers with PEGM in 1:7 molar ratio resulted in the increase in ionic conductivity from 6.3×10^{-8} to 1.1×10^{-6} S cm^{-1} (25 °C), although the presence of ester functions was reducing the electrochemical stability from 4.4 to 4.2 V vs Li^+/Li at 70 °C

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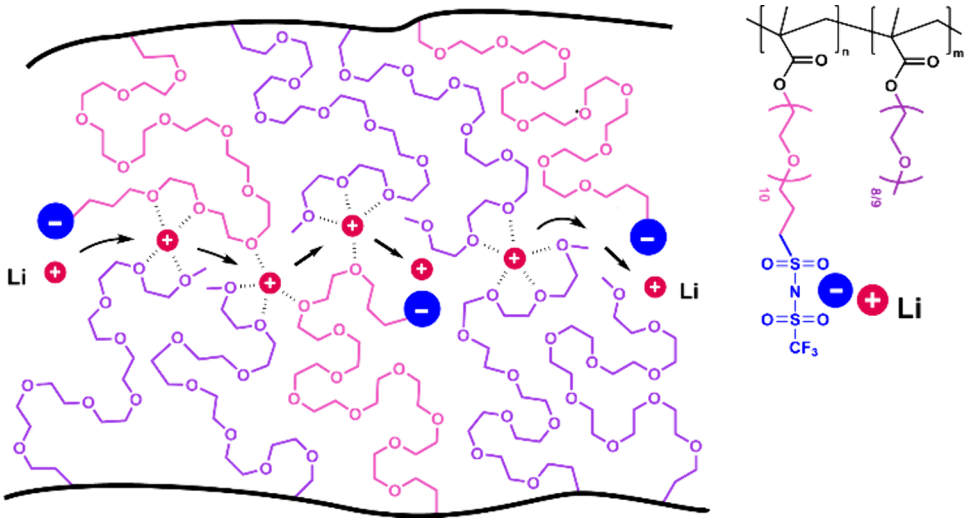
Scheme 2. Structure of Single-Ion Conducting Polymer Electrolytes (SICPs) Developed in the Present Study and the Proposed Route for Li^+ Cation Mobility



for SICPs based on **LiMTFSI** and **11**, respectively.[25] The last breakthrough was achieved by the group of Vidal et al. via synthesis of ILM **12** (Scheme 1 and Table S1, entry 14).[32,33] When combined with 1-methyl-3-ethyl imidazolium cation the polymerization of **12** produced SICP with as high conductivity as 6.5×10^{-4} S cm^{-1} (25 °C). However, the presence of a urea linkage as well as the direct bonding of negatively charged nitrogen to a carbon atom will significantly reduce the electrochemical stability of the respective SICP and will not allow its utilization in LIBs.

Analyzing the structures of ILMs presented in Scheme 1, it can be concluded that the following structural parameters in ILMs are supposed to enhance the ionic conductivity of respective SICPs: (a) the introduction of sufficiently long spacers between the polymer backbone and the chemically attached anion; (b) the presence of the polar ethylene oxide units; and (c) the exception of electrochemically unstable groups in the spacer. Taking this into account, in this work, we developed a new ionic monomer (Scheme 1, **13**), where the methacrylic moiety and TFSI anion are separated by a long and flexible PEG linker. The synthesized monomer, denoted as **TBAM(PEG)TFSI**, was then homo- and copolymerized with PEGM via simple free radical polymerization (Scheme 2). After the exchange to Li^+, all SICPs were thoroughly investigated in terms of their thermal, rheological, and electrochemical behavior. Furthermore, the best-performing SICP was used as a truly solid-state electrolyte in lab-scale Li-metal cells. Finally, it was demonstrated that the newly prepared SCIP based on **LiM(PEG)TFSI** outperformed the previously reported **LiMTFSI**- and **LiMESTTFSI**-derived polyelectrolytes, most notably, in terms of ionic conductivity, specific capacity retention, and rate capability at high charge/discharge regimes in battery cells.

SYNTHESIS OF IONIC LIQUID MONOMER TBAM(PEG)TFSI

For full details/description/acronyms of materials and methods, the reader is referred to the Supporting Information (SI) file. The synthetic pathway for the preparation of **TBAM(PEG)TFSI** monomer (Scheme 3), its ^{1}H, ^{13}C, HSQC, and ^{19}F NMR and IR spectra (Figures S2–S6), high-resolution mass spectra (Figure S7), and elemental analysis are presented in the SI file. The synthesized **TBAM(PEG)TFSI** has a number-average molecular weight (M_n) of 848.94 au with the molecular dispersity index ($Đ$) of 1.030 and represents a viscous light-yellow liquid with a glass-transition temperature (T_g) of −63 °C.

FREE RADICAL HOMOPOLYMERIZATION AND COPOLYMERIZATION OF TBAM(PEG)TFSI

The homopolymer of **TBAM(PEG)TFSI** was prepared via simple free-radical polymerization initiated by AIBN in DMF solution and denoted as **PIL** (Scheme 3). In addition, three copolymers of **TBAM(PEG)TFSI** with PEGM were synthesized in a similar manner by random copolymerization in three different ratios (**coPIL1**−**coPIL3**). GPC in a 0.1 M LiTFSI solution in DMF was used to investigate the molecular weights and the M_w/M_n ratios of the obtained polyelectrolytes. As can be seen from Table 1, for all polymers, the determined M_n values were relatively high, ranging from 62 kDa to 86 kDa. The obtained polymers represented soft yellow waxlike materials, that can easily form coatings, but not the self-standing films. Afterwards, all four polymers underwent ion exchange to substitute tetrabutyl ammonium cation with the Li one. Polyelectrolyte structures and purity were confirmed by ^{1}H, ^{7}Li, and ^{19}F NMR and IR spectroscopy (see Figures S9–S15).

IONIC CONDUCTIVITY MEASUREMENTS

Ionic conductivity (σ_{DC}) as a function of temperature (Figure 1) for **PIL** and **coPILs** was investigated by using electrochemical impedance spectroscopy (EIS). The obtained values for **PIL** and **coPIL1**−**coPIL3** were further compared to the nearest analogues, namely, poly(**LiMTFSI**) and poly(**LiMESTTFSI**) (Scheme 3 and Table 1). Notably, **PIL** demonstrated significantly improved ionic conductivity when compared to its predecessors poly(**LiMTFSI**) and poly(**LiMESTTFSI**), namely, 9.2×10^{-8} S cm^{-1} against 1.1×10^{-12} S cm^{-1} (ref 22) and $<10^{-11}$ S cm^{-1} (ref 25) at 25 °C, respectively (see Table 1). These results indicate that the introduction of the long oxyethylene spacers significantly improves the mobility of the polymer side chains, facilitating

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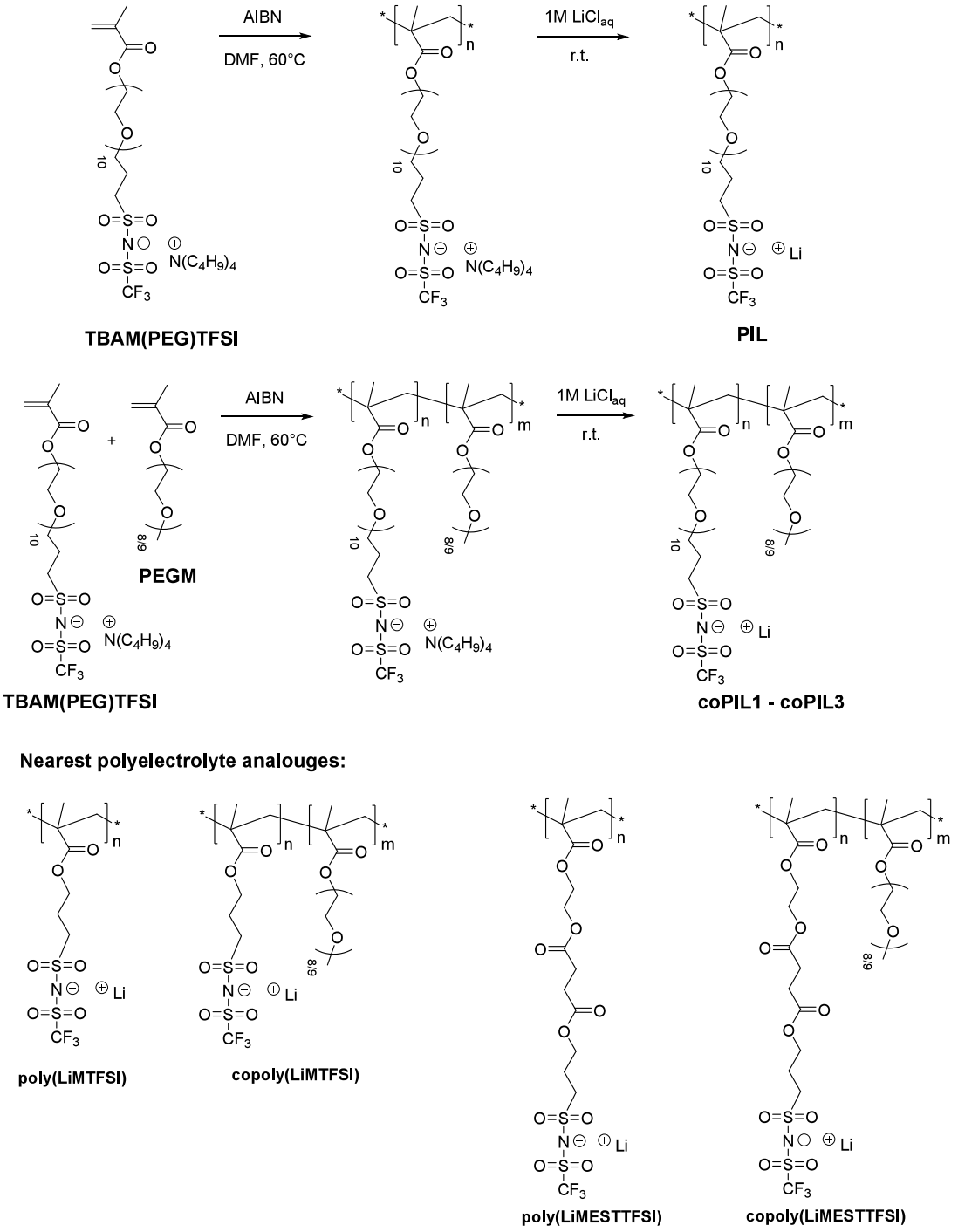
Scheme 3. Synthesis of SICPs Based on M(PEG)TFSI Monomer with Li Cations and Their Nearest Polyelectrolyte Analogues[22,25] Used for Comparison



the Li cation coordination, resulting in the overall increase of ionic conductivity of **PIL** (Figure 1). The copolymerization of **TBAM(PEG)TFSI** with PEGM and subsequent ion exchange to Li cations allowed to further improve the ionic conductivity of the resulting SICPs by nearly 1.5 orders of magnitude at 25 °C (Table 1 and Figure 1).

Thus, it can be concluded that either the length of the PEG spacer equal to 10 EO units is not sufficient to fully solubilize Li cations or that the presence of side dangling PEG chains is pivotal to dilute chemically bonded TFSI anions, to effectively surround Li cations, and to establish their perfect transfer. The greatest boost in ionic conductivity of **coPIL** was achieved when 2 PEGM molar equivalents were taken with respect to 1 mol equiv of **TBAM(PEG)TFSI**, resulting in σ values as high as 3.0×10^{-6} S cm^{-1} at 25 °C (Table 1). The combination of synthesized PEG-based monomer with PEGM provided 1 order of magnitude higher ionic conductivity compared to copolymers with alkyl and ester spacers (i.e., 2.3×10^{-7} S cm^{-1} (ref 22) and 1.2×10^{-7} S cm^{-1} (ref 25) at 25 °C, respectively, for copoly(**LiMTFSI**) and copoly(**LiMESTTFSI**), respectively; see Scheme 3).

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Table 1. Selected Properties of SICPs Prepared by Free Radical (Co)polymerization

polymer	M_n (SEC)[a] (g mol^{-1})	M_w/M_n (SEC)[a]	[ILM]/[PEGM] theoretical molar ratio	[ILM]/[PEGM] experimental ratio[b]	yield (%)[c]	σ_{DC} (S cm^{-1}) 25 °C	σ_{DC} (S cm^{-1}) 70 °C	T_g[d] (°C)	T_{onset}[e] (°C)
PIL	61900	1.9	–	–	78	9.2×10^{-8}	9.8×10^{-6}	−14	205
coPIL1	79500	5.5	1:1	1:1.1	76	1.2×10^{-6}	3.1×10^{-5}	−15	–
coPIL2	83900	5.6	1:2	1:2.8	74	3.0×10^{-6}	3.8×10^{-5}	−46	200
coPIL3	85900	5.8	1:4	1:4.6	76	1.2×10^{-6}	1.8×10^{-5}	−50	200
poly(LiMTFSI)[f]	52700	1.2	–	–	–	1.1×10^{-12}	–	105	250
poly(LiMESTTFSI)[f]	1050000	3.1	–	–	–	$<10^{-11}$	–	18	225

[a]By GPC in 0.1 M solution of LiTFSI in DMF at 50 °C with PMMA standards. [b]By ^{1}H NMR (in DMSO-d_6), calculated using eq S3 in the SI file. [c]Isolated yield. [d]By DSC at a rate of 5 °C/min. [e]Onset weight loss temperature by TGA. [f]For comparison from refs 22 and 25.

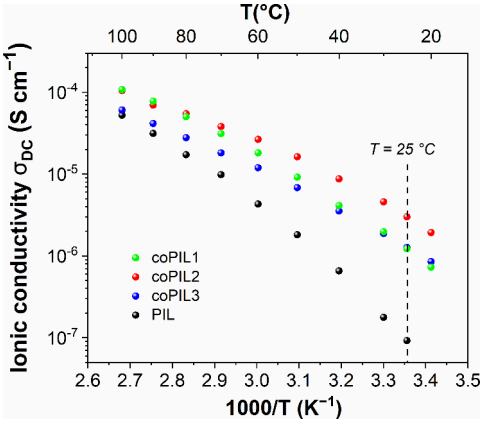

Figure 1. Ionic conductivity versus temperature (from 20 °C to 100 °C) plots for PIL and coPILs.

For both **PIL** and **coPIL1**−**coPIL3** (Figure 1), the temperature dependence of ionic conductivity was not fully linear, thus deviating from Arrhenius' law (Figure 1). In contrast, the inverse temperature dependence of σ_{DC} followed a typical Vogel−Fulcher−Tammann (VFT) behavior for all studied **PILs**. The experimental results were thus fitted with the VFT equation, and the ionic conductivity activation energies (E_a) for SICPs are listed in Table S2. All investigated samples demonstrated E_a values in the range of quasi- or truly SICPs.[34,35] The E_a values before and after 50 °C were extrapolated to carefully investigate the effect of the −EO− units in the homopolymer and the outcome of the addition of −EO− units by copolymerization with PEGM. As reported in Table S2, the E_a of a homopolymer drastically changes above 50 °C, decreasing from 20.91 kJ mol^{-1} to 12.86 kJ mol^{-1}. In contrast, for copolymers **coPIL1**−**coPIL3**, this difference was found to be less pronounced. Such a sharp change in E_a for **PIL** could be related to the intrinsic mobility of the −EO− segments of the polymer repeating unit, where the increase of the temperature above 50 °C can facilitate the Li ion hopping through TFSI anion sites, along with the decrease in the activation energy barrier of the conduction mechanism. The small addition of PEGM in **coPIL1** allowed us to decrease the E_a, while further increases in PEGM content (**coPIL2** and **coPIL3**) leads to an increase of E_a. It was assumed that such visible alteration in E_a values can be assigned to the change of the ionic conduction mechanism, which, in the case of **coPIL2** and **coPIL3**, is governed prevalently by −EO− coordination. Thus, the limited quantity of PEGM in **coPIL1** allows us to increase the side chain mobility, along with reducing the E_a without altering the ion conduction mechanism based on Li$^+$ hopping between TFSI sites. Further addition of nonionic component is useful to decrease the T_g value of the copolymer and increase the ionic conductivity at low temperature; but, at the same time, it is affecting the ion conduction mechanism, leading to higher E_a values.

THERMAL CHARACTERIZATION

The T_g values of polyelectrolytes (Figures S17 and S18) were determined by differential scanning calorimetry (DSC) and are reported in Table 1. Interestingly, **PIL** showed a T_g value of −14 °C, which is significantly lower than the T_g values of the previously synthesized SICP competitors, namely, 105 and 18 °C reported for poly(**LiMTFSI**) and poly(**LiMESTTFSI**), respectively (Table 1). It is evident that the short alkyl linker in LiMTFSI drastically hinders the mobility of the side chains of the resulting macromolecules, whereas the introduction of the long flexible spacer composed of EO units enhances the mobility of the side chains and overall reduces the polymer T_g. As both PIL and poly(LiMESTTFSI) are amorphous polymers and there is no influence of crystallinity, the presence of the sp^2-hybridized carbon in ester segments of poly(LiMESTTFSI) renders them significantly more rigid, which results in a higher T_g in comparison with that of PIL having ether segments in the side chains. **CoPIL1** demonstrated a T_g value that was almost identical (−15 °C) to that of pristine **PIL**. Most likely, in this case, the T_g decreasing effect of PEGM was attenuated by the already low T_g of the homopolymer, making it necessary to introduce a relatively high amount of comonomer to observe a considerable change. Indeed, further dilution with PEGM resulted in a dramatic decrease in T_g, as displayed by **coPIL2** and **coPIL3** (−46 and −49 °C, respectively).

The thermal degradation behavior was studied via TGA in air. The onset weight temperatures for **PIL** and **coPIL2** were found to be 205 and 200 °C, respectively (Table 1). The weight loss profile of **PIL** revealed a one-step degradation mechanism, while two steps can be seen on the TGA curve of **coPIL2** (Figure S19).

RHEOLOGICAL CHARACTERIZATION

Given its highest ionic conductivity across the whole range of examined temperatures, **coPIL2** was selected for further rheological studies in a small amplitude oscillatory flow mode at 25 and 70 °C, and the observed properties were compared with those of copoly(**LiMTFSI**). Figure S20 shows the evolution of the complex viscosity of **coPIL2**. At 1 Hz, the complex viscosity decreased from 750 mPa s to 156 mPa s when tested at 25 and 70 °C, respectively. At both temperatures, the complex viscosity decreased almost linearly

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with the frequency. Figures S20b and S20c show the variation of loss and storage moduli as a function of the frequency at 25 and 70 °C for **coPIL2** and the copoly(**LiMTFSI**) as the reference with the same PEGM:ionic monomer molar ratio of 2:1 The loss modulus was higher than the storage modulus at both temperatures, accounting for the domination of the viscous over the elastic contribution; it is characteristic of an un-cross-linked polymer in a liquid or molten-like state over the entire frequency range. Although both copolymers exhibited viscous behavior, the **coPIL2** demonstrated storage and loss moduli that were 2 orders of magnitude higher than those observed in the range of explored frequencies, thus showing significantly better mechanical properties, in comparison with known copoly(LiMTFSI) analogue.[22]

ELECTROCHEMICAL STABILITY, Li TRANSFERENCE NUMBER, AND COMPATIBILITY WITH LITHIUM METAL

The evaluation of the electrochemical stability window (ESW) is particularly important to establish the voltage range at which the electrolyte can operate without undergoing unwanted degradation processes, which may account for performance decay during battery cycling. The ESW of **coPIL2** was evaluated by cyclic voltammetry (CV) at 70 °C in two distinct laboratory-scale lithium-metal cells, where **coPIL2** was in contact with Li foil and Cu metal electrode or carbon-coated Al electrode for the cathodic and anodic scans, respectively. The voltage window was scanned from the open circuit voltage (OCV) to −0.5 V and from the OCV to 5.0 V vs Li^+/Li redox potential for cathodic and anodic scans separately. The resulting profiles are shown in Figure S21. The anodic breakdown potential approached 4.5 V vs Li^+/Li, while, in cathodic scans, the profiles are reversible and, as expected, only two well-defined peaks were observed between −0.5 and 0.5 V vs Li^+/Li, which accounts for highly reversible lithium plating/stripping processes, thus confirming the efficient transfer of Li^+ ions through the polymer network.

The lithium-ion transference number (t_{Li^+}) of **coPIL2** was evaluated at 70 °C by methods that have been reported by both Evans−Vincent−Bruce[36] and Abraham et al.,[37] housing the electrolyte in a symmetrical cell with Li/**coPIL2**/Li configuration. Results from EIS and polarization current variation analysis are shown in Figures S22 and S23. The t_{Li^+} value was calculated to be equal to 0.96 (or 0.98, considering only the changes in the bulk resistance and applying the Evans−Vincent−Bruce equation). Moreover, the t_{Li^+} of the novel SICP is higher, compared to that of poly(PEGM-*b*-**LiMTFSI**) and poly[(LiMTFSI)-*b*-PEO-*b*-(**LiMTFSI**)] (0.83 (from ref 5[5]) and 0.91 (from ref 23), respectively). Based on the above-reported results, we can speculate that the −EO− fragments of the spacer in the ILM actively participate in the coordination of Li^+ cations, resulting in enhanced mobility and transport.

Furthermore, the stability of **coPIL2** at the Li metal electrode interface (Figure S24) was investigated by means of reversible constant current (galvanostatic) Li plating and stripping test performed at 70 °C at different current densities, ranging from 0.10 to 0.50 mA cm^{-2} (30 min per step). As shown in Figure S24, **coPIL2** demonstrated excellent stability during reversible plating and stripping, even at high current regimes without abnormal voltage drifts and any observable short circuit issues. Moreover, as shown in Figure S25, the resistance of the cell changed only slightly during the initial stabilization period at the beginning of the experiment and became fully stable after 21 days.

ELECTROCHEMICAL BEHAVIOR IN A LABORATORY-SCALE LITHIUM METAL CELL

The **coPIL2** was further assembled in laboratory-scale lithium-metal cells, and its performance was evaluated in a Li/**coPIL2**/LFP configuration with $LiFePO_4$ (LFP) as the positive electrode. The cell was tested at 70 °C at different current rates, denoted as *C*/*n*. As shown in Figure 2a, the first cell was

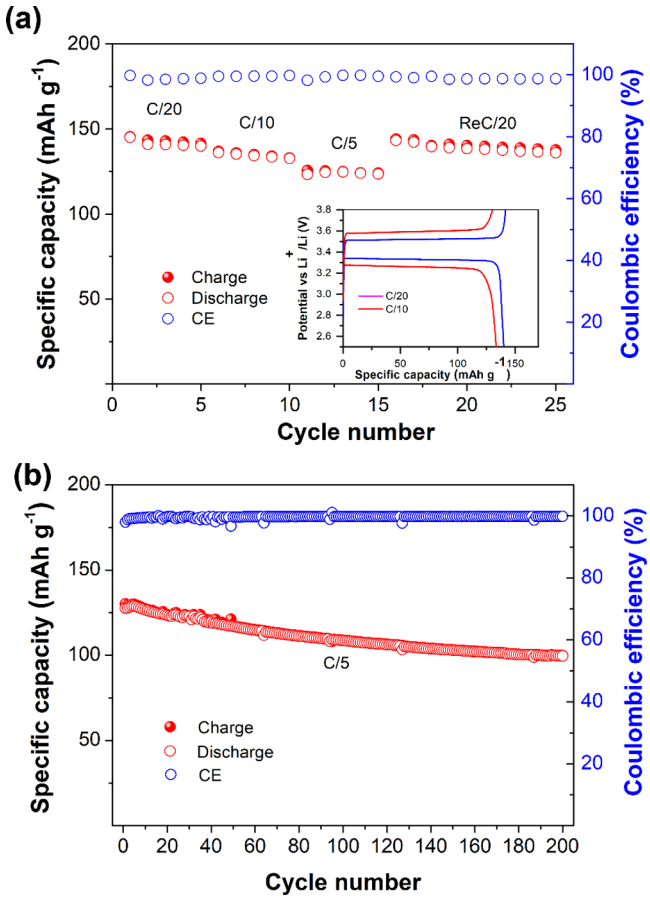

Figure 2. Galvanostatic cycling behavior of Li/coPIL2/LFP solid-state cells at 70 °C. Specific capacity versus cycle number dependence (a) with corresponding charge/discharge voltage versus specific capacity profiles in the inset and (b) specific capacity versus cycle number dependence at C/5 upon prolonged cycling.

cycled starting from relatively low current of 15.7 μA (*C*/20) and up to 63.9 μA (*C*/5), before being subjected to recycling at *C*/20 (rate capability test). The initial specific capacity delivered during first cycles at *C*/20 approached 150 mAh g^{-1}, which is close to the practical capacity delivered by the commercial LFP electrode cycled with standard LP30 liquid electrolyte (i.e., ∼158 mAh g^{-1} at *C*/20).[38] Excellent cycling stability was demonstrated with outstanding Coulombic efficiency (CE) close to 100% during the whole cycling test, as well as remarkable capacity retention of ∼94% after 25 cycles at different *C* rates. The inset of Figure 2a shows charge/discharge potential profiles versus specific capacity at different current rates, which perfectly resemble the typical flat plateaus of the LFP cathode corresponding to the Li^+ ion

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insertion (discharge) in the $FePO_4$ network. The observed profiles remained stable even upon doubling the current rate, with overall limited overpotential that only slightly increased at a higher rate of C/5, supporting the favorable charge transport properties of the system.

A second Li-metal cell was assembled with the same configuration and tested for prolonged charge/discharge cycling. Results are remarkable and the cell delivered capacity values exceeding 125 mAh g^{-1} during initial cycling at a relatively high C rate of C/5 (Figure 2b). The cycling performance of the similar cells based on copoly(**LiMTFSI**)[22] and copoly(**LiMESTTFSI**)[25] is shown in Figures S27 and S28 for comparison. It can be clearly observed that the replacement of an alkyl or ester spacer in the ionic monomer with the one based on −EO− units has drastically improved the battery performance in terms of capacity retention and the output at elevated charge/discharge rates. Indeed, the Li/**coPIL2**/LFP cell provided stable cycling at high Coulombic efficiency, being able to deliver specific capacity exceeding 100 mAh g^{-1} (with almost 65% capacity retention, see Figure 2), while the Li/copol(**LiMTFSI**)/LFP and Li/copol(**LiMESTTFSI**)/LFP cells provided specific capacity values limited to only 40 and 35 mAh g^{-1}, respectively, at the same cycling conditions (see Figures S27 and S28).

CONCLUSION

In the present work, for the first time, the (trifluoromethane)-sulfonylimide anion was chemically bonded to the methacrylic reactive group through a flexible spacer containing 10 oxyethylene units. The synthesized **TBAM(PEG)TFSI** monomer readily underwent homo- and copolymerization with poly(ethylene glycol) methyl ether methacrylate to give solid polyelectrolytes with high molecular weight (up to M_n = 85 900 g mol^{-1}). Simple free-radical homopolymerization of **TBAM(PEG)TFSI** and subsequent ion exchange to Li cations yielded the rubbery material −**PIL** that demonstrated ionic conductivity that was significantly higher, compared to its alkyl- or ester-based spacer previously developed analogues, namely, poly(**LiMTFSI**) and poly(**LiMESTTFSI**) (9.2×10^{-8} S cm^{-1} vs 1.1×10^{-12} and $<10^{-11}$ S cm^{-1} at 25 °C, respectively). Further random copolymerization of **TBAM(PEG)TFSI** with PEGM in 1:1, 1:2, and 1:4 molar ratios was performed and followed by ion exchange with LiCl provided cold flowing rubber-like copolymers (viz., **coPIL1**−**coPIL3**) with enhanced ionic conductivity. Among tested copolymers, the **coPIL2** provided the highest ionic conductivity in the whole range of examined temperatures (3.0×10^{-6} and 3.8×10^{-5} S cm^{-1} at 25 and 70 °C, respectively), excellent compatibility with the Li metal electrode, electrochemical stability, and optimal viscoelastic behavior, allowing the fabrication of the truly solid-state laboratory-scale Li metal cells with LFP-based cathode. Such cells provided stable cycling, high rate capability, excellent Coulombic efficiency, and even sustained more than 200 cycles at a relatively high current rate (C/5) at 70 °C without any observable signs of short circuits and/or dendrite growth. After 200 charge/discharge cycles at the C/5 rate, the cell was able to deliver the specific capacity close to 100 mAh g^{-1}, hence, outperforming previously reported similar Li-metal cells, based on copoly(**LiMTFSI**), poly(**LiMESTTFSI**), or other analogous SICPs.

To conclude, the most striking advantages of the developed SICPs on the basis of the novel ionic monomer **TBAM(PEG)TFSI** are (1) the low glass-transition temperatures (T_g values down to −50 °C); (2) the high ionic conductivity (up to 3.0×10^{-6} S cm^{-1} at 25 °C); (3) the thermal stability sufficient for LiMBs (T_{onset} of 200 °C); (4) the improved storage and loss moduli in comparison with known copoly(**LiMTFSI**) analogue; (5) good anodic electrochemical stability (up to 4.5 V vs Li^+/Li at 70 °C); (6) excellent Li ion transport resulting in a lithium-ion transference number close to unity (t_{Li^+} = 0.96−0.98); (7) superior electrochemical features, which allowed stable cycling in Li/**coPIL2**/LFP cells with capacity outputs close to the LFP practical values and capacity retention at relatively high current charge/discharge rates, pointing out the relevance of this work in the development of next-generation SICPs to be exploited in practical high performing and safe truly solid-state LiMBs.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsmaterialslett.4c01647.

Materials and methods, full experimental details for the synthesis of **TBAM(PEG)TFSI** monomer, homopolymer **PIL** and copolymers **coPIL1**−**coPIL3**, description of the characterization techniques for the determination of **PEGM/LiM(PEG)TFSI** ratio in copolymers, ^1H, ^{13}C, ^{19}F, HSQC NMR, IR and GPC-ESI-HRMS spectra of **TBAM(PEG)TFSI**, DSC traces of **TBAM(PEG)-TFSI**, ^1H, ^7Li, ^{19}F NMR and IR spectra of **PIL** and **coPIL1**−**coPIL3**, DSC and TGA traces of copolymers, electrochemical stability window of **coPIL2** obtained by CV at 70 °C, EIS and polarization current curves of **coPIL2** in Li/**coPIL2**/Li configuration, charge transfer-resistance (R_{ct}) at the electrolyte/electrode interface of cell with Li/**coPIL2**/Li configuration at 70 °C, charge interfacial resistance variation over time in a laboratory-scale Li metal cell with Li/**coPIL2**/Li configuration at 70 °C (PDF)

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Author Contributions

[▽]Dr. G. Lingua and V. Y. Shevtsov contributed equally to this work. The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. CRediT: **Gabriele Lingua** data curation, investigation, writing - original draft, writing - review & editing; **Vladislav Y. Shevtsov** conceptualization, investigation, writing - original draft; **Petr S. Vlasov** data curation, investigation, validation, writing - original draft; **Laura Puchot** data curation, investigation, writing - original draft; **Claudio Gerbaldi** conceptualization, data curation, funding acquisition, methodology, supervision, writing - original draft, writing - review & editing; **Alexander S Shaplov** conceptualization, funding acquisition, investigation, methodology, supervision, writing - original draft, writing - review & editing.

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Notes

The authors declare no competing financial interest.

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