Sequential Co-Click Reactions with Poly(glycidyl propargyl ether) toward Single-Ion Conducting Electrolytes

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Supporting Information

ABSTRACT: We utilize the direct, monomer-activated anionic ring-opening polymerization of glycidyl propargyl ether (GPE) to obtain a clickable polyether backbone ([P(GPE)] with high molecular weights and narrow distributions. First, P(GPE) was individually clicked with three different azide-functionalized pendant groups: LiTFSI-N₃, EG₃-N₃, and Bn-N₃. LiTFSI serves as a lithium ion source with immobilized anion, tri(ethylene glycol) as an additional source of ion-conductive medium, and the benzyl substituent is used to improve the mechanical properties. To combine all these properties in one single polymer electrolyte, we sequentially co-clicked the named azides onto P(GPE). The final material composition, the [O]/[Li] ratio, as well as the glass transition temperature can be adjusted via the azide feed ratios. A self-standing electrolyte material with close-to-unity lithium transport number and very high electrochemical stability was obtained. We present an innovative clickable PEG platform to synthesize a ready-to-use anion-immobilized solid polymer electrolyte with tunable thermal properties in a single, sequential reaction step.

INTRODUCTION

Poly(ethylene glycol) (PEG) is referred to as a highly versatile, nontoxic polymer with excellent aqueous solubility because of its strong dipole character along the polymer chain. It is used in a broad variety of applications, such as a surfactant in cosmetics (e.g., shampoos), food additives (e.g., antifoaming agent), as well as for biomedical and pharmaceutical purposes.

In the application of solid polymer electrolytes (SPEs) for lithium-ion battery applications, noncrystalline PEG is a well-suited, ion-conducting matrix material. Therefore, it is favorable to reduce the amount of crystalline domains in SPE materials. For this, the introduction of oligo(ethylene glycol) (OEG) side chains into complex polymer architectures has proven successful in several published attempts. For example, Hawker et al. demonstrated almost 2 orders of magnitude increased lithium ion conductivity at room temperature compared to linear PEG using poly(allyl glycidyl ether) with OEG side chains. Compared to linear PEG, poly(glycidyl ethers) show almost no or only little crystallization at room temperature but still possess lithium-ion-coordinating and -transporting ether repeating units. In this respect, poly(glycidyl propargyl ether) [P(GPE)] offers a polyether backbone with a pendant side-group which is applicable in the very well-known copper(I)-catalyzed alkyn–azide cycloaddition (CuAAC) click chemistry. Very recently, direct polymerization of the unprotected alkyn GPE- monomer has been demonstrated by Frey et al. In their report, P(GPE) homopolymers as well as main chain copolymers with ethylene oxide were synthesized to molecular weights between 3 and 9.5 kg mol−1 and dispersities in the range of 1.18−1.60. It should be noted that very recently also the direct polymerization of glycidyl azide via a Lewis-acid monomer-activated mechanism was presented by Feng et al., which also represents a CuAAC-clickable polymer. Prior to this, poly(epichlorohydrine) had to be converted to poly(glycidyl azide) (PGA). Unlike P(GPE), PGA possesses only one ether oxygen per repeating unit. Furthermore, in many cases the azide of a desired chemical functionality is more easily accessible than the corresponding alkyn, which is necessary for clicking with PGA.

Among the most efficient lithium ion source salts for lithium electrolytes is the well-established lithium bis(trifluoromethanesulfonyl) imide (LiTFSI). It contains the highly charge-delocalized, soft TFSI-anion which allows for a very high degree of Li⁺ dissociation. It has been shown repeatedly for simple SPE/lithium salt mixtures (e.g., PEG/LiTFSI) that only about 20% of the overall conduction is provided by Li⁺-cations, whereas the majority is caused by migration of the anions (TFSI⁻). This causes a number of
disadvantages, including strong Nernst polarization within the cell, limited battery power performance, and enhanced lithium dendrite growth during charging of the battery cell, which may finally lead to its short-circuit.9 The so-called “single-ion conduction” approach (SIC) tackles these issues. It describes the spatial fixation of the anion by covalently binding it to a polymer chain and thereby preventing any anionic contribution to the conductivity. The amount of charge that is transported only by Li+ ions is measured by the so-called lithium transport number \( t_{Li^+} \):

\[
 t_{Li^+} = \frac{\sigma_{Li^+}}{\sigma_{cations} + \sigma_{anions}}
\]

The resulting single-ion conductors may be realized by covalently binding the anion to a scaffold, for example, an inorganic framework or a polymer chain. In the ideal case, anionic contribution to the ionic conductivity can thereby be suppressed, enhancing the electrochemical performance as well as the lifespan of a lithium-ion battery.20

A variety of very different single-ion-conducting SPE systems with a fixed TFSI anion have been presented so far. Zhou et al. prepared AB block copolymers comprising a poly(1,2-diethylene glycol acrylate) and a methoxy-oligoethylene glycol acrylate (n = 8) B-block.21 In this system, more than 90% of the overall conductivity takes place via Li+ ion transport, which is quite remarkable. Furthermore, the introduction of the comparably hard, TFSI-functionalyzed polystyrene block enhances the mechanical stability of the block copolymers. Armand et al. prepared a P(STFSILi)-PEO-P(STFSILi) polyionic ABA-triblock copolymer with an ionic conductivity of \(1.3 \times 10^{-3}\) S cm\(^{-1}\) at 60 °C and a lithium transport number of >0.85.22 Matyjaszewski et al. have recently attached both an OEG unit as well as a single LiTFSI unit onto a methacrylate macromonomer using CuAAC as click reaction.23 Photoinduced atom-transfer radical polymerization of this macromonomer yielded single-ion conductor homopolymers with conductivities of around \(10^{-3}\) S cm\(^{-1}\) at room temperature and almost unity transport numbers.

Here, we applied the monomer-activated anionic ring-opening polymerization (AROP) to the commercially available, alkyne-functionalized GPE (Scheme 1). We took a closer look into the reaction kinetics of the monomer-activated AROP using an in situ near-infrared probe. In the synthesis we aimed for high molecular weights and narrow molecular weight distributions.

We have chosen this clickable P(GPE) architecture as the synthesis platform for a series of clicked homopolymers as well as sequentially co-clicked polymers. For this purpose, we chose three different azide-functionalized click-reactants introducing the desired material properties: first, we synthesized LiTFSI-N3 (Scheme 1, green box), containing a highly charge-delocalized TFSI-anion with a weakly coordinated Li+ counterion. Upon grafting it onto the P(GPE) backbone, we spatially fixed the anion to the polymer to eliminate any possible contribution of the anion to the ionic conductivity. Quantitative polymer-analogous coupling using the CuAAC click chemistry with a LiTFSI-azide and poly(ethylene glycol) acrylicate (EG3-N3, Scheme 1, blue box) to increase the amount of Li+ coordinating ether oxygens as well as benzyl azide (Bn-N3, Scheme 1, red box) to enhance the mechanical rigidity of the material. While maintaining a constant P(GPE) backbone length of 100 repeating units, we prepared fully grafted polymers with each of the named azides as well as sequentially co-clicked versions with varying contents of LiTFSI and EG3-N3. Thereby, the (ether)-oxygen-to-lithium ratio \((\sigma_O/\sigma_{Li})\) and the mechanical properties of the electrolyte material could conveniently be adjusted. Finally, we performed electrochemical experiments using the co-clicked \(P(GPE-(EG3-ran-Bn-ran-LiTFSI))\). Whereas the ionic conductivity values are rather modest and need further improvement, the materials show excellent electrochemical stability up to 5 V as well as lithium transport numbers well above 0.9.

**EXPERIMENTAL SECTION**

**Materials.** GPE (≥90%, Sigma-Aldrich) was dried over CaH2, distilled in passive vacuum, and stored at −30 °C under argon atmosphere. Trisobutyl aluminum [(iBu)3Al; 25 wt % in toluene, Sigma-Aldrich] is highly pyrophoric and was used without further purification. Tetra-n-octyl ammonium bromide (TOAB; ≥98%, Sigma-Aldrich) was dried in high vacuum at 80 °C for several hours. Trifluoromethanesulfonamide (95%, Sigma-Aldrich) was purified by sublimation. 3-Chloropropanesulfonyl chloride (98%, Sigma-Aldrich) was distilled in passive vacuum and stored at −30 °C under argon atmosphere. The following chemicals and materials were
used as received and without further purification: triethyl amine (TEA; \( 299\% \), Sigma-Aldrich), copper sulfate pentahydrate (CuSO\(_4\). 5H\(_2\)O; \( 288\% \), VWR Chemicals), (+)-sodium i-ascorbate (Na-Asc; \( 98\% \), Sigma-Aldrich), benzyl azide (Bn-N\(_3\); \( 94\% \), Alfa Aesar), sodium azide (Na\(_2\)N\(_3\); \( 99.5\% \), Sigma-Aldrich), tri(ethylene glycol) monomethyl ether hydroxide (OH-EG\(_3\); \( 95\% \), Sigma-Aldrich), lithium hydride (99.95\%, Sigma-Aldrich), pyridinium-p-toluenesulfonylimide (p-TsCl; \( >99\% \), Sigma-Aldrich), lithium ribbon (99.9\%, trace metal basis, \( 0.38 \) mm, Sigma-Aldrich), copper foil (99.99\%+, 0.25 mm, ChemPur), CR2032 coin cell cases (20 mm x 3.2 mm) with gaskets, wave spring, and stainless steel spacers (MTI corporation/PI KEM). Ethanol of p.a. grade was used as received. Tetrahydrofuran (THF), diethyl ether, and chloroform were purchased in p.a. grade and distilled beforehand. Dry toluene for polymerization was stirred over CaH\(_2\) and freshly distilled before use. Dry DMF with 0.5 wt % lithium bromide. The chromatograph was carried out in stabilized THF with 0.25 wt % tetrabutylammonium bromide (TBAB). The SEC was calibrated with Polymer Standards Service as external standard and 1,2-dichloroethane as the internal standard.

**Characterization.** \(^1\)H and \(^{13}\)C NMR spectra were recorded on a Bruker AC 300 spectrometer (300 MHz). Size exclusion chromatography (SEC) measurements of the P(GPE) homopolymers were carried out in stabilized THF with 0.25 wt % tetrabutylammonium bromide (TBAB). The chromatograph was equipped with two Varian MIXED-C columns (300 x 7.5 mm), run at room temperature and at a flow rate of 0.5 mL min\(^{-1}\) using a RI (refractive index) detector. The SEC was calibrated with PEG purchased by Polymer Standards Service as external standard and 1,2-dichloroethane as the internal standard.

SEC measurements of the graft copolymers were carried out in DMP with 0.5 wt % lithium bromide. The chromatograph was equipped with two PSS GRAM columns (100/3000 x 5 mm), run at room temperature and at a flow rate of 0.5 mL min\(^{-1}\) using an RI detector. The SEC was calibrated with polystyrene as the external standard, which was purchased from PSS Polymer Standards Service.

Differential scanning calorimetry (DSC) measurements were conducted on a Mettler Toledo DSC 2, calibrated with indium and zinc at a heating rate of 10 K min\(^{-1}\) under continuous nitrogen flow. Thermogravimetric analysis (TGA) was performed on a Mettler Toledo TGA/SDTA 851 at heating rates of 10 K min\(^{-1}\) under nitrogen.

Fourier transformed near infrared (FT-NIR) spectroscopy measurements were conducted during all polymerizations using a Hellima Analytics NIR immersion probe and a spectrometer system by Zeiss. In every case a background measurement of the pure solvent was performed before the reaction at the reaction temperature and then subtracted from the raw measurement. In predefined time-intervals, NIR spectra between wavelengths of 1350–2100 nm were recorded. Additionally, the time-dependent signal intensity at two predefined wavelengths was recorded directly. These were set to 1648 nm (6062 cm\(^{-1}\), ethene stretch vibration, corresponds to monomer concentration) and 1802 nm (5549 cm\(^{-1}\), ether vibration, corresponds to polymer backbone concentration).

**Electrochemical Characterization.** All electrochemical measurements were performed on a BioLogic VMP3 potentiostat operated by the software EC-Lab V11.01. The temperature was controlled by a Vötsch VT 4002 oven. All preparations, cell assembly, and disassembly were performed in an argon-filled glove box. The SPE melt filled a 0.4 cm hole of a 130 \( \mu \)m thick Kapton spacer, located on a 380 \( \mu \)m thick lithium non-blocking electrode that defined the active surface area (\( A \approx 13 \text{ mm}^2 \)) of the cell. Another 380 \( \mu \)m thick lithium non-blocking electrode was then placed on top of the electrolyte-spacer assembly followed by a 500 \( \mu \)m thick stainless-steel blocking electrode to ensure equal distribution of the spring pressure. The coin cell was then pressed at rt using the crimping machine. The temperature program consisted of an initial annealing interval at 70 °C for \( t_s = 12 \) h to ensure good contact between the electrolyte and electrodes. Then, a PEIS spectrum was recorded in analogy to the ionic conductivity measurements.

Subsequently, a CA measurement was conducted by applying a dc potential of \( E_{dc} = 50 \text{ mV} \) until a steady current was obtained. After the dc polarization a second impedance spectrum was recorded. The data were fitted using the software EC-Lab V11.01. With the initial and steady-state values for the interfacial resistance (\( R_{b} \) and \( R_{c} \)) obtained by the fits and for the current (\( I_0 \) and \( I_f \)) as well as the applied dc potential (\( \Delta V \)), the lithium transport number was calculated using the following equation:

\[
\sigma = \frac{I_f}{R_{b} A} \frac{\Delta V - I_f R_{b}}{I_0 \Delta V - I_f R_{b}}
\]

The electrochemical stability window of the neat polymers and SPEs were studied via cyclic voltammetry (CV). Copper–lithium Cu/SPE/Li asymmetric CR2032 coin cells were assembled and hermetically sealed in an argon-filled glovebox. The SPE melt filled a 0.4 cm hole of a 130 \( \mu \)m thick Kapton spacer, located on a 250 \( \mu \)m thick copper non-blocking electrode that defined the active surface area (\( A \approx 13 \text{ mm}^2 \)) of the cell. A 380 \( \mu \)m thick lithium non-blocking electrode was then placed on top of the electrolyte-spacer assembly followed by a 500 \( \mu \)m thick stainless-steel blocking electrode. The assembly was pressed at rt using the crimping machine. CV experiments were performed by scanning a potential between \( E_1 = -0.2 \text{ V} \) and \( E_2 = 5.0 \text{ V} \) versus Ref (\( \text{Ref} = E = 0 \text{ V} \) vs \( \text{ECO} \)) and reverse scan toward \( E = 0 \text{ V} \) vs \( \text{ECO} \) at a constant temperature of 70 °C and a scan rate of de/dt = 1 mV s\(^{-1}\). Prior to the CV measurements, an annealing interval was conducted at 70 °C for \( t_s = 12 \) h in order to obtain a good contact between the electrolyte and the electrodes.

**Preparation of the Initiator Stock Solution.** A stock solution of tetracycl ammonium bromide (TOAB) in dry toluene was prepared and stored over CaH\(_2\) under argon atmosphere. The concentration was determined precisely by \(^1\)H NMR spectroscopy (details in the Supporting Information, S1).

**Synthesis of Tr(ethylene glycol) Azide.** EGG3-N\(_3\) was synthesized in two steps according to literature procedures.\(^{28,29}\) All reaction conditions and characterization data are presented in the Supporting Information (S2).

**Synthesis of Lithium 3-Azidoproanesulfonfonyltrifluoro-methanesulfonilimide (LiTFSI-N\(_3\)).** LiTFSI-N\(_3\) was synthesized in two
The Supporting Information (S4.1).

Characterization Data

... tube equipped with a magnetic stir bar and sealed with a glass stopper. The polymerization was started by addition of the (s, 3H) (Figure 3C).

Typical Procedure for the Homopolymerization of GPE. The polymerization was carried out in analogy to a literature procedure for the monomer-activated polymerization of ethoxymethyl glycidyl ether and is comparable to the work of Frey et al.3 All actions were performed under argon atmosphere. Freshly distilled GPE was added into a custom-made, flame-dried Schlenk tube (fitting the NIR immersion probe), weighed precisely, and dissolved in dry toluene. A precise aliquot of TOAB initiator stock solution in toluene (1/1 equiv) was added and the mixture was equilibrated at −20 °C in a cryostat. The polymerization was started by addition of the (Bu)3Al activator (solution in toluene, 25 wt %, 5 equivalents). After full monomer conversion according to NIR spectroscopy (typically after ca. 40−60 min), the cryostat was set to 25 °C at which the reaction was stirred for another 2 h to consume any remaining monomer. The reaction was then terminated by addition of approx. 1 pipette of ethanol. After aqueous workup, the polymer was repeatedly precipitated into cold diethyl ether. Dissolving the polymer in cold chloroform and subsequent filtration allowed for the removal of the tetractrylammonium species. P(GPE) homopolymers could be synthesized in very high yield (>90%) and were obtained as colorless, low-viscous thermoplasts.

The CuAAC reactions utilizing a CuSO4·5H2O catalyst mixture were performed under argon in a custom-made, flame-dried Schlenk tube equipped with a magnetic stir bar and sealed with a glass stopper. The polymerization was started by addition of the (Bu)3Al activator (solution in toluene, 25 wt %, 5 equivalents). After full monomer conversion according to NIR spectroscopy (typically after ca. 40−60 min), the cryostat was set to 25 °C at which the reaction was stirred for another 2 h to consume any remaining monomer. The reaction was then terminated by addition of approx. 1 pipette of ethanol. After aqueous workup, the polymer was repeatedly precipitated into cold diethyl ether. Dissolving the polymer in cold chloroform and subsequent filtration allowed for the removal of the tetractrylammonium species. P(GPE) homopolymers could be synthesized in very high yield (>90%) and were obtained as colorless, low-viscous thermoplasts.

The Supporting Information (S4.1).

All reaction conditions and characterization data are presented in the Supporting Information (S5).

Typical Procedure for the CuAAC Coupling Reaction of P(GPE)100. The CuAAC reactions utilizing a CuSO4·5H2O catalyst mixture were performed under argon in a flame-dried Schlenk tube equipped with a magnetic stir bar and sealed with a glass stopper. The synthesis was performed in analogy to literature.50,52 P(GPE)100 as well as the azide(s) were dissolved in the respective solvent and degassed. Sodium ascorbate and copper(II)-sulfate pentahydrate were added to start the reaction. The mixture was stirred overnight at room temperature.

P(GPE-EG3)100. The reaction was performed in THF under addition of TEA to support copper solubility (phase transfer agent). After complete conversion, the reaction mixture was filtrated through a small amount of THF, precipitated in cold diethyl ether, and then centrifuged. Precipitation was typically repeated 2−3 times. Finally, the polymer was dried at 50 °C in vacuum.

P(GPE-Bn)100. The reaction was performed in analogy to P(GPE-EG3)100.

P(GPE-Bn)100 1H NMR (300 MHz, CDCl3): δ 7.12 (s, 2H), 7.22 (m, 5H), 7.48 (s, 2H), 4.40 (s, 2H), 3.35 (s, 5H) (Figure 3D).

All reaction conditions and characterization data are presented in the Supporting Information (S4.2).

Table 1. Synthesized Homopolymers P(GPE)100, P(GPE)150, P(GPE)200, and P(GPE)300 Including Their Corresponding Characterization Data

<table>
<thead>
<tr>
<th>N_target</th>
<th>p_NMR (%)</th>
<th>Mw_theo (g mol⁻¹)</th>
<th>Mw_b (g mol⁻¹)</th>
<th>D_b</th>
<th>Mz_b (g mol⁻¹)</th>
<th>Tg (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P(GPE)100</td>
<td>100</td>
<td>&gt;99</td>
<td>11 300</td>
<td>10 100</td>
<td>1.10</td>
<td>11 200</td>
</tr>
<tr>
<td>P(GPE)150</td>
<td>150</td>
<td>&gt;99</td>
<td>17 000</td>
<td>16 200</td>
<td>1.05</td>
<td>17 700</td>
</tr>
<tr>
<td>P(GPE)200</td>
<td>200</td>
<td>&gt;99</td>
<td>22 500</td>
<td>23 700</td>
<td>1.07</td>
<td>25 300</td>
</tr>
<tr>
<td>P(GPE)300</td>
<td>300</td>
<td>&gt;99</td>
<td>33 700</td>
<td>28 800</td>
<td>1.15</td>
<td>32 000</td>
</tr>
</tbody>
</table>

*S*For all reactions: solvent: toluene. Temperature within the first 30 min: −20 °C. [Activator]/[initiator]: 5:1. Monomer concentration: less than 0.06 g mL⁻¹. Determined via SEC (eluent: THF, RI signal, PEG calibration). Glass transition temperature, determined via DSC (second heating curve). In all samples no melting temperature was detected.

#### RESULTS AND DISCUSSION

The synthesis of P(GPE) homopolymers was performed in a comparable way to the work of Frey et al.14 Thereby, an activator−initiator combination was utilized, which was first described by Deffieux and Carlotti.29 A strong Lewis acid like triisobutylaluminum coordinates to the epoxide oxygen and thereby induces a strong dipolar moment (activated monomer). This allows for comparably soft nucleophiles—as in this case a bromide—to attack and open the three-membered ring.

We adjusted the polymerization procedure by using higher monomer-to-initiator-ratios, applied a sterically more demanding reaction mixture through basic alumina oxide as well as silica and subsequent precipitation into cold ethanol. Because of very strong interactions between the remaining copper species and the TFSI-anion, removal of all copper catalyst traces typically required to repeat the filtering steps ca. three times. Finally, the material was treated with an excess of aqueous Li2CO3 solution to ensure all TFSI counterions are Li+ and it was dried at 80 °C in vacuum.

H NMR (300 MHz, DMSO-d6): δ 8.13−7.98 (s, 1H), 4.47 (2× s, 4H), 3.38 (s, 5H), 3.10−2.89 (t, J = 7.5 Hz, 2H), 2.19 (t, J = 7.5 Hz, 2H) (Figure 3B).

All reaction conditions and characterization data are presented in the Supporting Information (S4.3).

P(GPE-(EG3-ran-Bn-ran-LiTFSI))100. The co-click reactions were performed in DMF. LiTFSI-N3 followed by Bn-N3 and finally a slight excess of EG3-N2 were added to the reaction mixture in this order in time intervals of ca. 60 min. After complete conversion, the filtered reaction mixture was dried and re-dissolved in Millipore water. Tetrasodium EDTA was added to the solution as a chelating copper-complexing agent. The solution was stirred for at least 1 h (color shifts toward pale blue), forming the [Cu4(EDTA)]3− complex. Diluted HCl was added dropwise to adjust a pH value of ca. 1−2, upon which the polymer precipitated quickly and quantitatively. The aqueous phase was then removed by centrifugation and decantation. The polymer was re-dissolved in Millipore water under addition of an aqueous solution of Li2CO3. This procedure was typically repeated 3−5 times, until the supernatant solution was colorless. In the last workup cycle, the polymer was slowly titrated neutral with Li2CO3 solution to avoid excess salt in the final product. Finally, the polymer was dried at 80 °C in vacuum.

H NMR (300 MHz, DMSO-d6): δ 8.05/8.00 (2× s, 100H), 7.26 (m, 165H), 5.52 (s, 66H), 4.46 (m, 330H), 3.75 (m, 1t, 66H), 3.40 (m, 764H), 3.18 (s, 99H), 2.97 (t, J = 7.5 Hz, 66H), 2.20 (t, J = 7.5 Hz, 66H) (Figure 3E).

All reaction conditions and characterization data are presented in the Supporting Information (S5).
A mechanism for this side reaction based on thermally induced alkyne decomposition and radical formation was suggested by Schlaad et al.32 We achieved molecular weights between 10 and 30 kg mol\(^{-1}\) \((N = 100–300)\) and very low dispersities in the range of 1.05–1.15 for the P(GPE) homopolymers (Table 1).

Prior to the polymerizations, an initiator stock solution of TOAB in toluene was prepared and its concentration was precisely determined by \(^1\)H NMR spectroscopy (Supporting Information S1) to ensure accurately adjusted [monomer]/[initiator] ratios. The ('Bu)\(_3\)Al activator was added in fivefold excess in relation to the initiator concentration. The demand for such high activator loadings to achieve high molecular weights has been discussed in the literature repeatedly for the AROP of various substituted epoxides.14,33,34 Aqueous workup was applied to remove the aluminum catalyst. The amount of the amphiphilic tetraoctylammonium was significantly reduced by dissolving the polymer in chloroform and filtering through basic aluminum oxide.

The polymerizations were monitored in situ by a FT-NIR immersion probe, operating at wavelengths between 1300 and 2000 nm. The first overtone of a characteristic C–H stretching vibration of the epoxide ring is located at 1648 nm, which corresponds to a wavenumber of ca. 6062 cm\(^{-1}\) (Figure 1A).35 Its intensity is linearly correlated to the concentration of intact epoxide rings according to the Beer–Lambert law. The signal decreases upon monomer consumption and allows for monitoring the reaction. Figure 1B shows the decrease in intensity of this signal. Within a time-frame of ca. 30 min, no further decrease in the signal intensity could be observed. The plot reveals an extremely fast polymerization rate and almost perfect first-order kinetics. It can be fitted by an exponential decay, yielding a half-life time constant of about 6 min. The FT-NIR technique is a very suitable method for in situ monitoring of the very fast monomer-activated AROP of GPE, as no samples have to be taken during the polymerization and the technique is not limited to a small reaction volume.35 Polymerizations were always only terminated when no further decrease in the epoxide signal could be observed in FT-NIR.

The SEC curves of the P(GPE) homopolymers are shown in Figure 2. The molecular weight increases continuously from P(GPE)\(_{100}\) to P(GPE)\(_{300}\) as expected. All polymers show narrow polydispersities between 1.05 and 1.15. Tailing effects are observed at the higher elution volume flanks (at lower molecular weight). This is a well-known observation for a variety of polyethers and indicates even more narrow actual dispersities compared to the measured ones. In the curves of P(GPE)\(_{200}\) and P(GPE)\(_{300}\) very small shoulders at approximately twice the peak molecular weight indicate some interchain coupling during the polymerization.

The \(^1\)H NMR spectrum of P(GPE) (Figure 3A) shows that 100% of the alkyne protons (signal c at ca. 2.5 ppm) are intact after the anionic polymerization. In the next step, the P(GPE)\(_{100}\) backbone was used as polyalkyne in a CuAAC. It was individually clicked with different azides (LiTFSI-N\(_3\), EG3-N\(_3\), N-Methyl-EG3-N\(_3\), Bn-N\(_3\)) to introduce low-molecular-weight pendant groups. As catalyst, an in situ-generated copper(I)-species was applied, utilizing CuSO\(_4\) together with sodium ascorbate as reducing agent in analogy to a literature procedure.30,31 All performed click reactions are summarized in Table 2, including important SEC and DSC characterization data.

For obtaining P(GPE-LiTFSI)\(_{100}\), we first synthesized LiTFSI-N\(_3\), as described in the work of Matyjaszewski et al.23 to introduce a lithium salt with an immobilized anion (Scheme 1, green box). In this molecule a propyl-spacer separates the TFSI-anion from the azide unit. Other than methyl or ethyl, propyl has been shown to suppress HCl-elimination and to provide enough flexibility for the azide in the click chemistry.23 The click reaction was conducted at room temperature in DMF because of the limited solubility of the TFSI-salt in more nonpolar solvents. The reaction progress was controlled by \(^1\)H NMR. After the click reaction using a very slight excess of LiTFSI-N\(_3\), the spectrum (Figure 3B) shows the total absence of the alkyne signal and its adjacent methylene protons (signals b and c in Figure 3A). An aromatic singlet (signal c at ca. 8
ppm in Figure 3B) and two sets of downfield-shifted methylene signals (b from the polyalkyne, d from the TFSI-N3) further confirm the complete conversion of P(GPE)100 into P(GPE-LiTFSI)100 with close to 100% grafting density.

SEC measurements show the shift in molecular weight from ca. 11 000 g mol⁻¹ of P(GPE)100 (Figure 4, curve 1, \(\bar{D}\) = 1.10) to ca. 33 000 g mol⁻¹ of P(GPE-LiTFSI)100 (Figure 4, curve 5, \(\bar{D}\) = 1.14) while maintaining a narrow molecular weight distribution. The highly ionic P(GPE-LiTFSI)100 as well as all other LiTFSI-containing co-clicked polymers could not be dissolved in THF. Therefore, we conducted the SEC measurements in DMF with 0.5 wt % lithium bromide. P(GPE-LiTFSI)100 was obtained as a white, brittle, and crystalline powder. The material properties seem to be defined predominantly by the ionic nature of the LiTFSI domains. This was supported by the drastic increase in glass transition temperature from ca. −30 °C in P(GPE)100 to +101 °C in P(GPE-LiTFSI)100 determined by DSC (Figure 5). It has to be noted that P(GPE-LiTFSI)100 exhibits an intrinsic ratio of ether oxygens to lithium cations ([O]/[Li]) amounting to 2:1. However, the optimum [O]/[Li] ratio for typical PEG/LiTFSI-blend electrolytes lies in a range between ca. 12:1 and 20:1.36,37

Like LiTFSI-N3, EG3-N3 was exemplarily grafted onto P(GPE)100 to yield P(GPE-EG3)100 (Scheme 1, blue box). Complete conversion of the click reaction was confirmed by ¹H NMR (Figure 3C) and SEC (Figure 4, curve 3). Attaching the triethylene glycol side chains to P(GPE)100 leads to a 5 °C reduction in \(T_g\) (Figure 5, blue curve). This phenomenon is referred to as "internal plasticization" and is caused by an increased free volume with reduced packing density.38,39 This causes steric hindrance to the segmental mobility of the polymer backbone.

### Table 2. Synthesized Graft Copolymers (Mono-Clicks and Co-clicks) Including Their Corresponding Characterization Data

<table>
<thead>
<tr>
<th>solvent</th>
<th>(p_{NMR}) (%)</th>
<th>(M_n,\text{theo}) (g mol⁻¹)</th>
<th>(M_n^a) (g mol⁻¹)</th>
<th>(\bar{D})</th>
<th>(M_p) (g mol⁻¹)</th>
<th>(T_g) (^b) (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P(GPE-EG3)100</td>
<td>THF &gt;99</td>
<td>27 100</td>
<td>27 445</td>
<td>1.21</td>
<td>30 400</td>
<td>−36</td>
</tr>
<tr>
<td>P(GPE-Bn)100</td>
<td>THF &gt;99</td>
<td>22 100</td>
<td>22 900</td>
<td>1.19</td>
<td>26 200</td>
<td>19</td>
</tr>
<tr>
<td>P(GPE-LiTFSI)100</td>
<td>DMF &gt;99</td>
<td>37 300</td>
<td>36 700</td>
<td>1.15</td>
<td>42 500</td>
<td>101</td>
</tr>
<tr>
<td>P(GPE-(EG30.33-ran-Bn0.33-ran-LiTFSI0.33))100</td>
<td>DMF &gt;99</td>
<td>32 100</td>
<td>33 300</td>
<td>1.14</td>
<td>39 200</td>
<td>36</td>
</tr>
<tr>
<td>P(GPE-(EG30.50-ran-Bn0.30-ran-LiTFSI0.20))100</td>
<td>DMF &gt;99</td>
<td>30 800</td>
<td>41 100</td>
<td>1.28</td>
<td>37 500</td>
<td>24</td>
</tr>
</tbody>
</table>

\(^a\)Determined via SEC (eluent: THF, RI signal, PEG calibration). \(^b\)Glass transition temperature, determined via DSC (second heating curve). In all samples no melting temperature was detected.
polymer—at least until a critical side chain length ($n_s$) induces side chain crystallinity and opposes the trend.

To introduce mechanical stability, benzyl azide (Bn-N$_3$) was also applied as a click reagent to investigate the influence of the stiff aromatic unit onto the very soft, flexible P(GPGE) backbone in P(GPGE-Bn)$_{100}$ (Scheme 1, red box). Repeatedly, $^1$H NMR (Figure 3D) and SEC (Figure 4, curve 2) measurements indicate complete grafting. Compared to P(GPGE)$_{100}$, the $T_g$ is increased by about 50 K up to ca. +20 °C in P(GPGE-Bn)$_{100}$ (Figure 5).

Finally, we aimed to combine the advantages of the three named azides in one single polymer material by co-clicking them to the P(GPGE) backbone: a single-ion conducting Li-salt fixed TFSI-anion (LiTFSI-N$_3$), Li$^+$-conducting polyether moieties in the polymer main chain as well as in the clicked side chains (EG3-N$_3$) and increased mechanical stability (Bn-N$_3$). In this P[GPGE-(EG3-Bn)LiTFSI] system, the ratio of the lithium salt to the lithium ion transporting ether oxygens (and thereby the [O]/[Li] ratio) as well as the mechanically reinforcing benzyl moieties can be adjusted easily by varying the content of the respective azide in the click reaction.

For the synthesis, first the sequence of azide addition needed to be optimized according to their relative reactivities. For this, we conducted the click reaction with all the three azides in a 1:1:1 feed-in ratio of azides led to grafting with a built-in ratio of 35% EG3-N$_3$, 31% Bn-N$_3$, and 34% LiTFSI-N$_3$. This yields an actual composition of P[GPGE-(EG3$_{0.35}$-ran-Bn$_{0.31}$-ran-LiTFSI$_{0.34}$)]$_{100}$, which corresponds to an expected [O]/[Li] ratio of 9:1. Additionally, we prepared a second co-clicked graft copolymer with a targeted composition of P[GPGE-(EG3$_{0.50}$-ran-Bn$_{0.30}$-ran-LiTFSI$_{0.20}$)]$_{100}$ which made it clear that LiTFSI-N$_3$ has the lowest reactivity among these three azides. In a subsequent test, we applied a mixture of 0.7 equiv each of EG3-N$_3$ and Bn-N$_3$ with respect to 1 equiv polymer backbone alkyne. The resulting polymer showed a composition of approx. P[GPGE(EG$_{0.68}$-ran-Bn$_{0.32}$)], which made it clear that the reactivities indeed vary as EG3-N$_3$ > Bn-N$_3$ > LiTFSI-N$_3$.

Thus, in the following sequential co-click reactions, LiTFSI-N$_3$, followed by Bn-N$_3$ and finally a slight excess of EG3-N$_3$ were added in this order in time intervals of ca. 60 min.

On the basis of these results, the three azides (LiTFSI-N$_3$, EG3-N$_3$, and Bn-N$_3$) were sequentially co-clicked in a 1:1:1 ratio onto P(GPGE)$_{100}$. The resulting P[GPGE-(EG3$_{0.33}$-ran-Bn$_{0.33}$-ran-LiTFSI$_{0.33}$)]$_{100}$ is expected to have a [O]/[Li] ratio of 9.1:1. Additionally, we prepared a second co-clicked graft copolymer with a targeted composition of P[GPGE(EG3$_{0.50}$-ran-Bn$_{0.30}$-ran-LiTFSI$_{0.20}$)]$_{100}$, which made it clear that LiTFSI-N$_3$ has the lowest reactivity among these three azides. In a subsequent test, we applied a mixture of 0.7 equiv each of EG3-N$_3$ and Bn-N$_3$ with respect to 1 equiv polymer backbone alkyne. The resulting polymer showed a composition of approx. P[GPGE(EG$_{0.68}$-ran-Bn$_{0.32}$)], which made it clear that the reactivities indeed vary as EG3-N$_3$ > Bn-N$_3$ > LiTFSI-N$_3$.

According to $^1$H NMR spectroscopy (Figure 3E), we achieved quantitative grafting in the sequential co-clicks. The 1:1:1 feed-in ratio of azides led to grafting with a built-in ratio of 35% EG3-N$_3$, 31% Bn-N$_3$, and 34% LiTFSI-N$_3$. This yields an actual composition of P[GPGE-(EG3$_{0.35}$-ran-Bn$_{0.31}$-ran-LiTFSI$_{0.34}$)]$_{100}$, which is very close to the expected values. In the SEC trace (Figure 4, curve 4) the achieved number average molecular weight ($M_n = 33 300$ g mol$^{-1}$) is in good accordance with the expected theoretical value (32 100 g mol$^{-1}$). The dispersity is not increased significantly after the sequential co-click reaction (Table 2). The presence of only one glass transition step in the DSC (Figure 5) suggests that the co-clicked graft copolymer is an amorphous single-phase system. The glass transition...
temperature ($T_g = 36 \, ^\circ C$) corresponds roughly to the average value of $P(GPE-EG3)_{100}$ ($T_g = -36 \, ^\circ C$), $P(GPE-Bn)_{100}$ ($T_g = 19 \, ^\circ C$), and $P(GPE-LiTFSI)_{100}$ ($T_g = 101 \, ^\circ C$).

In the case of $P(GPE-EG3)_{0.50-ran-Bn0.33-ran-LiTFSI0.33)_{100}$ the amount of LiTFSI is reduced and replaced by a higher content of EG3. According to $^1$H NMR, the actual composition deviates only little from the targeted values, resulting in a final polymer of $P(GPE-EG3)_{0.50-ran-Bn0.33-ran-LiTFSI0.33)_{100}$ which corresponds to a $[O]/[Li]$ ratio of 22:1. The $T_g$ is observed at 24 °C (Figure 5), which is 12 K lower than for $P(GPE-EG3)_{0.50-ran-Bn0.33-ran-LiTFSI0.33)_{100}$. This can be very well understood considering the increased amount of built-in EG3 component with a low $T_g$. The TGA measurements of both co-clicked materials show thermal stability up to more than 300 °C (Supporting Information S5), measured both under air as well as under nitrogen atmosphere.

For the two co-clicked polymers, the temperature-dependent ionic conductivity was measured using coin cells with symmetrical stainless-steel (blocking) electrodes by PEIS (see Experimental Section). The overall ionic conductivity of the electrolytes was determined in the temperature range between 25 and 80 °C in the frequency range of 1 MHz to 1 Hz with an excitation amplitude of 20 mV. In Figure 6a, Nyquist plots of $P(GPE-EG3)_{0.33-ran-Bn0.33-ran-LiTFSI0.33)_{100}$ ($[O]/[Li] = 9.0$) as well as $P(GPE-EG3)_{0.33-ran-Bn0.33-ran-LiTFSI0)_{100}$ ($[O]/[Li] = 22$) at 80 °C are presented as typical examples. All Nyquist plots could be fitted using the depicted equivalent circuit in which the bulk conductivity is expressed by an RC element. The nonideal capacitive behavior of the electrolyte system can be fitted more accurately if the capacitors are replaced by constant phase elements. The ionic conductivities of the presented electrolytes at room temperature are comparably low ($1.2 \times 10^{-5}$ S cm$^{-1}$ for $[O]/[Li] = 22$, $3.9 \times 10^{-5}$ for $[O]/[Li] = 9.0$, see Table 3). Interestingly, they differ from each other by almost 2 decades, indicating a high potential for optimization. This trend continues also at higher temperatures, which can be followed in the corresponding Arrhenius plots (Figure 6b). Both polymers show a typical Vogel–Tamman–Fulcher temperature dependence; thus, the ionic conducting mechanism is most likely determined by polymer segmental motions. The increased conductivity of the $[O]/[Li] = 22$ polymer can thus most likely be attributed to its lower $T_g$ ($12 \, ^\circ K$) compared to the $[O]/[Li] = 9$ sample (Table 2). Compared to PEG-systems ($T_g \approx -30$ to $-40 \, ^\circ C$), the compositions presented here have appreciably high $T_g$ values (25 and 36 °C). This may be considered the main reason for their low ionic conductivities. However, the low conductivity drop at a certain temperature, which is typically visible in linear PEG electrolytes at their corresponding crystallization temperature.

The lithium transport number was determined for the higher-conducting $P(GPE-EG3)_{0.50-ran-Bn0.33-ran-LiTFSI0.20)_{100}$ ($[O]/[Li] = 22$) in a symmetrical coin cell setup with lithium metal (non-blocking) electrodes applying the method described by Bruce and Vincent. It amounts to 0.91 and can be considered very high, which matches the expectation of a single-ion conductor. The interfacial resistances before ($R_{ss}$) and after the chronoamperometric polarization ($R_{ca}$) as well as the initial current ($I_0$) and the steady-state current ($I_{ss}$) values are summarized in Table 3 (further details: Supporting Information Figure S7.1). For the polymer with $[O]/[Li] = 9$, we observed no steady-state current and could therefore not determine a lithium transport number. The low ionic conductivity of this material leads to very low current values in the chronoamperometric polarization step, which could explain this behavior. Anyhow, the concept of anion immobilization toward SIC is successfully realized in the presented concept.

The current density of the lithium plating/stripping peaks lies in the µA range, which is comparably low, and is more pronounced during the first measuring cycle. This can be explained by the rather low ionic conductivity of the electrolytes. No anodic breakdown potential could be observed within the measuring range up to 5.0 V. In the case of $[O]/[Li] = 22$, a peak between 4 and 5 V was observed, which was not present any more in the second cycle. Therefore, this nonreproducible peak can rather be assigned to a small amount of reacting impurities, reduction of the SPE at the copper electrode or the formation of a solid electrolyte interface, rather than decomposition of the actual electrolyte material. Two reversible peaks appear in both electrolytes at ca. 1.7 and 3.0 V (anodic scan), respectively, and have cathodic counterparts at slightly lower voltages. The reversibility of these processes can be confirmed as these peaks appear even more pronounced in the second scan. The overall electrochemical stability of the polymers can be considered very high as the current density values remain below 10 µA throughout the complete measured potential up to +5 V for two full cycles.

**CONCLUSIONS**

In summary, the monomer-activated AROP of GPE could be elegantly utilized to synthesize high molecular weight P(GPE) homopolymers in the range of 10 000–30 000 g mol$^{-1}$ while maintaining narrow molecular weight distributions ($D = 1.05–1.15$). A near-infrared spectroscopy immersion probe provided a convenient method for in situ monitoring of these very fast...
polymerization reactions. The wide scope and versatility of P(GPE) was utilized under mild CuAAC conditions to attach LiTFSI, benzyl, and triethylene glycol pendant side groups to build different graft copolymer architectures. For the first time, we attached these three moieties in a sequential co-click reaction to P(GPE), obtaining a self-standing material applicable as single-ion conducting SPE with tunable conductivity. Therefore, the P(GPE)-backbone as well as the EG3 side groups are intended to provide lithium-ion conductivity. LiTFSI is an inherent source of Li+-ions with spatially fixed counterions that cannot contribute to ionic conductivity. Benzyl units reinforce the material to form free-standing, mechanically stable films. Although the P(GPE)-(EG3-ran-Bn-ran-LiTFSI)-electrolytes show modest conductivity at room temperature, we could measure a close-to-unity lithium transport number and excellent electrochemical stability up to 5.0 V. The significant difference in ionic conductivity of almost 2 orders of magnitude between the [O]/[Li] = 9 and the [O]/[Li] = 22 SPEs indicates a high potential for subsequent optimization of this electrolyte system.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.macromol.9b00206.

Synthesis details, and experimental and analytical details (PDF)

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