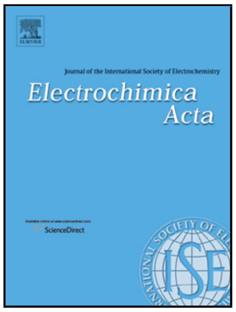

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Synthesis of high molecular flexibility polycarbonates for solid polymer electrolytes

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Graphical abstract

Highlights

- A new polycarbonate was synthesized and showed a record-low T_g of −49.4 °C.
- Crosslinking provided mechanically stable polymer electrolyte films.
- Ionic conductivity up to 2×10^{-7} S cm^{-1} at room temperature was demonstrated.

Abstract

A new self-plasticizing aliphatic polycarbonate comprising flexible alkyl and alkyl ether side groups was designed and synthesized from six-membered cyclic carbonate monomers with the aim of producing a material with high molecular flexibility (low T_g) and concomitant high ionic conductivity when used as a polymer electrolyte. The T_g of the novel polycarbonate was determined to be −49.4 °C at a molecular weight of 34 400 g mol^{-1}, which is the lowest reported T_g to date for a substituted poly(trimethylene carbonate). UV-crosslinked polymer electrolytes were produced based on this novel material together with LiTFSI salt and showed ionic conductivities in the range of 2×10^{-8} to 2×10^{-7} S cm^{-1} at room temperature and 1×10^{-6} to 1×10^{-5} S cm^{-1} at 100 °C. The limited ionic conductivities of these electrolytes indicate that high molecular flexibility alone does not guarantee fast ion transport in solid polymer electrolytes and that other factors, such as the polarity of the polymer host material, will also influence the transport properties of the electrolyte.

Keywords: polycarbonate; ring-opening polymerization; glass transition temperature; polymer electrolyte; ionic conductivity

1. Introduction

The development of new, functional materials to help us deal with current or future challenges and enable new technological advancements is a continuously ongoing effort. In this respect, aliphatic polycarbonates constitute an interesting class of polymers that has recently seen a surge in scientific attention [1]. This can be associated with the idea that these materials can be synthesized through sequestering carbon dioxide, thereby fixating this greenhouse gas and preventing its release into the atmosphere [2, 3]. Also contributing to the current interest in aliphatic polycarbonates are the numerous recent examples of their use in biomedical applications [4-7].

Apart from synthesis through copolymerization of epoxides with carbon dioxide, ring opening polymerization is a broadly utilized technique for synthesizing aliphatic polycarbonates [1, 8]. Particularly six-membered cyclic carbonates are well-suited for controlled ring-opening polymerization under mild conditions using a variety of different initiator/catalyst systems [1, 9]. Together with ample possibilities for post-polymerization functionalization and facile methods for monomer synthesis, this has led to a great diversity of materials derived from an equally impressive array of different monomers [7, 10].

While a lot of attention has been directed toward the use of aliphatic polycarbonates for biomedical applications, it has recently been shown that polycarbonate materials are also promising candidates for solid polymer electrolytes for Li-ion batteries by virtue of their ability to dissolve and conduct lithium ions [11-15]. However, the application of solid polymer electrolytes, including aliphatic polycarbonates, in Li-ion batteries is currently limited by the insufficient ionic conductivity of the materials [16]. In a typical SPE, the mobility of dissolved ions is inherently linked to the segmental motion of the host polymer chains [17, 18]. Thus, in order to achieve high ionic conductivity, the molecular flexibility of the host polymer should be as high as possible, i.e., the glass transition temperature, T_g, of the material should be as low as possible.

The simplest aliphatic polycarbonate derived from a six-membered cyclic carbonate monomer is poly(trimethylene carbonate) (PTMC). While PTMC has a relatively low T_g of −16 °C at high molecular weights [13], it is nowhere near the commonly used SPE host material poly(ethylene oxide) (PEO; T_g close to −60 °C [19]) in terms of molecular flexibility. While several examples can be found of PTMC derivatives with an increased crystallinity, rigidity and T_g [20-24], few deliberate efforts seem to have been made to create more molecularly flexible materials. Some examples of low-T_g PTMC derivatives include the allyl-functional poly(5-allyloxy-1,3-dioxan-2-one) with a T_g of −40 °C at moderate molecular weights [25] and poly(2-allyloxymethyl-2-

ethyltrimethylene carbonate) with a T_g of −30 °C, at an unspecified molecular weight [26]. These polymers all comprise pendent allyl ether functionalities that function as plasticizers to lower the T_g of the materials [27]. There are, however, other possible functional moieties that may plasticize the material and lower the glass transition temperature even more than the allyl ether group. Through inspiration from traditional low-molecular-weight plasticizers and careful monomer design, essentially *self-plasticizing* polymers can be synthesized by incorporating flexible side chains that increase the free volume of the material [28]. In an effort to improve the ionic conductivity of polycarbonate-based SPEs, we have used this approach to create a novel aliphatic polycarbonate with alkyl and alkyl ether side groups that give the material an exceptionally low T_g, and demonstrate its applicability for use in solid electrolytes for Li-ion batteries.

2. Experimental

2.1 Materials

All chemicals were obtained from commercial sources and used as received unless otherwise noted. Dry dichloromethane (DCM; Fisher Scientific) was obtained by storing over activated 4 Å molecular sieves. Trimethylolpropane monoallyl ether was a gift from Perstorp AB, Sweden. 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU; Acros Organics) was distilled under reduced pressure. Lithium bis(trifluoromethanesulfonimide) (LiTFSI; Purolyte, Ferro Corporation) was dried *in vacuo* at 120 °C for 24 h before use.

2.2 Instrumentation

^{1}H NMR spectra were recorded at 25 °C on a JEOL Eclipse+ 400 MHz NMR spectrometer using the residual solvent signal as an internal standard.

Molecular weight determination was performed through gel permeation chromatography (GPC) on a Verotech PL-GPC 50 equipped with a refractive index detector and two PolarGel-M organic GPC columns. Samples were injected using a PL-AS RT autosampler and chloroform was used as the eluent at a flow rate of 1 ml min^{-1}. Flow rate fluctuations were corrected by an internal standard and the system was calibrated against narrow polystyrene standards.

Thermal properties were measured using differential scanning calorimetry on a TA Instruments DSC Q2000. Samples were hermetically sealed in aluminium pans in a glovebox under an argon atmosphere. These were then rapidly cooled to –70 °C followed by heating at 10 °C min^{-1} to 100 °C for measurement.

Rheological properties were measured on a TA Instruments AR 2000 using an 8 mm aluminium oscillating parallel plate geometry. The oscillating stress was kept constant at 100 Pa while the frequency was ramped at a constant normal force of 0.5±0.1 N (crosslinked sample) or a fixed gap of 600 μm (non-crosslinked sample).

2.3 Synthesis

2.3.1 (5-Ethyl-2,2-dimethyl-1,3-dioxan-5-yl)methanol

To 100 g (0.745 mol) of trimethylolpropane in 400 ml of acetone was added 1 g of Amberlyst 15 ion-exchange resin (H^+-form, washed with acetone before use) and the reaction was left to proceed under magnetic stirring at room temperature overnight. The solution was filtered to remove the ion-exchange resin and the solvent was removed through rotational evaporation. The product was isolated through distillation under reduced pressure, yielding 97.3 g (75%) of pure product as a colorless, viscous liquid, b.p. 112–113 °C/8 mbar. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 0.75 (t, 3H, J = 7.7 Hz, –CH_3), 1.26 (q, 2H, J = 7.7 Hz, –CH_2–), 1.27 (s, 3H, –CH_3), 1.31 (s, 3H, –CH_3), 3.39 (d, 2H, J = 5.5 Hz, –CH_2–OH), 3.47 (d, 2H, J = 11.7 Hz, –CH_2–O), 3.55 (d, 2H, J = 11.7 Hz, –CH_2–O), 4.49 (t, 1H J = 5.5 Hz, –OH).

2.3.2 2-Heptyloxymethyl-2-ethyl-1,3-propanediol

To a solution of 26 g (0.15 mol) of (5-ethyl-2,2-dimethyl-1,3-dioxan-5-yl)methanol, 24 ml (0.15 mol) of 1-bromoheptane and 8.1 g (25 mmol) of tetrabutylammonium bromide (TBAB) was added 20 g (0.36 mol) of freshly ground KOH. The mixture was heated under stirring at 40 °C overnight. The reaction was quenched by adding 100 ml of deionized water and the reaction mixture was extracted with 300 ml of hexane. The organic phase was washed with another 2×100 ml of deionized water and 100 ml of brine. Evaporation of the solvent afforded the crude intermediate 5-ethyl-5-((heptyloxy)methyl)-2,2-dimethyl-1,3-dioxane. To this was added 200 ml of THF and 50 ml of 1 M aqueous HCl and the mixture was refluxed overnight. After neutralization with 100 ml of saturated aqueous $NaHCO_3$, the reaction mixture was extracted with 2×200 ml of ethyl acetate. The organic phases were combined, dried with $MgSO_4$, filtered and evaporated. The product was isolated through distillation under reduced pressure to yield 20.6 g (59%) of the title compound as a colorless, viscous liquid, b.p. 161–162 °C/5 mbar. ^{1}H NMR (400 MHz, DMSO-d_6): 0.78 (t, 3H, J = 7.7 Hz, –CH_3), 0.84–0.87 (m, 3H, –CH_3), 1.20–1.31 (m, 10H, –CH_2–), 1.43–1.50 (m, 2H, –CH_2–), 3.16 (s, 2H, –CH_2–O), 3.25 (d, 4H, J = 5.1 Hz, –CH_2–OH), 3.31 (t, 2H, J = 6.6 Hz, –CH_2–O), 4.16 (t, 2H, J = 5.1 Hz, –OH).

^{13}C NMR (100 MHz, $CDCl_3$): 7.7 ($–CH_3$), 14.2 ($–CH_3$), 22.7 ($–CH_2–$), 23.5 ($–CH_2–$), 26.2 ($–CH_2–$), 29.2 ($–CH_2–$), 29.7 ($–CH_2–$), 31.9 ($–CH_2–$), 42.9 (>C<), 66.3 ($–CH_2–OH$), 72.2 ($–CH_2–O$), 75.5 ($–CH_2–O$). Anal. calcd for $C_{13}H_{28}O_3$: C, 67.20; H, 12.15. Found: C, 66.80; H, 12.16.

2.3.4 2-Heptyloxymethyl-2-ethyltrimethylene carbonate (HEC)

To 13.9 g (60.0 mmol) of 2-heptyloxymethyl-2-ethyl-1,3-propanediolin 160 ml of dry DCM, under nitrogen, was added, gradually over the course of 50 min, 12.2 g (75.0 mmol) of solid 1,1’-carbonyldiimidazole (CDI). Residues of CDI stuck to the inside of the glassware were rinsed into the reaction mixture using a small amount of DCM. The resulting solution was immediately washed with 2×160 ml 1 M HCl and 160 ml of saturated aqueous $NaHCO_3$. The organic phase was separated, dried with $MgSO_4$ and the solvent was evaporated. The product was isolated through distillation under reduced pressure to obtain 9.54 g (62%) of 2-heptyloxymethyl-2-ethyltrimethylene carbonate as a colorless liquid, b.p. 163–164 °C/0.4 mbar. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.87$ (m, 3H, $–CH_3$), 0.90 (t, 3H, $J = 7.7$ Hz, $–CH_3$), 1.21–1.37 (m, 8H, $–CH_2–$), 1.51 (q, 2H, $J = 7.7$ Hz, $–CH_2–$), 1.51–1.57 (m, 2H, $–CH_2–$), 3.36 (s, 2H, $–CH_2–O$), 3.39 (t, 2H, $J = 6.6$ Hz, $–CH_2–O–$), 4.11 (BB’ of AA’BB’, 2H, $–CH_2–O$), 4.31 (AA’ of AA’BB’, 2H, $–CH_2–O$). ^{13}C NMR (100 MHz, $CDCl_3$): 7.5 ($–CH_3$), 14.2 ($–CH_3$), 22.7 ($–CH_2–$), 23.5 ($–CH_2–$), 26.2 ($–CH_2–$), 29.2 ($–CH_2–$), 29.5 ($–CH_2–$), 31.9 ($–CH_2–$), 35.6 (>C<), 69.1 ($–CH_2–O$), 72.0 ($–CH_2–O$), 73.0 ($–CH_2–O$), 148.7 (>C=O). Anal. calcd for $C_{14}H_{26}O_4$: C, 65.09; H, 10.14. Found: C, 65.17; H, 10.07.

2.3.5 2-Allyloxymethyl-2-ethyltrimethylene carbonate (AEC)

To 20.9 g (120 mmol) of trimethylolpropane monoallyl ether in 320 ml of dry DCM, under nitrogen, was added, gradually over the course of 70 min, 24.3 g (150 mmol) of solid 1,1’-carbonyldiimidazole (CDI). Residues of CDI stuck to the inside of the glassware were rinsed into the reaction mixture using a small amount of dry DCM. The resulting solution was immediately washed with 2×320 ml 1 M HCl and 320 ml of saturated aqueous $NaHCO_3$. The organic phase was separated, dried with $MgSO_4$ and the solvent was evaporated. The product was isolated through distillation under reduced pressure to obtain 14.4 g (60%) of 2-allyloxymethyl-2-ethyltrimethylene carbonate as a colorless liquid, b.p. 138–139 °C/0.6 mbar. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.91$ (t, 3H, $J = 7.7$ Hz, $–CH_3$), 1.53 (q, 2H, $J = 7.7$ Hz, $–CH_2–$), 3.40 (s, 2H, $–CH_2–O$), 3.97 (ddd app dt, 2H, $J = 1.5, 5.5$ Hz, $–CH_2–O–$), 4.13 (BB’ of AA’BB’, 2H, $–CH_2–O$), 4.33

(AA’ of AA’BB’, 2H, –CH_2–O), 5.20 (ddt app dq, 1H, *J* = 1.5, 10.3 Hz, =CH–H), 5.26 (ddt app dq, 1H, *J* = 1.5, 17.2 Hz, =CH–H), 5.85 (ddt, 1H, *J* = 5.5, 10.3, 17.2 Hz, –CH=).

2.3.6 Homopolymerization of HEC

In an argon-filled glovebox, an oven-dried 4 ml vial was charged with 0.65 g (2.5 mmol) of HEC. 50 µl of a solution of 0.5 M benzyl alcohol initiator and 0.1 M of DBU catalyst (0.025 mmol initiator, 0.005 mmol catalyst, for DP = 100) in dry toluene was added. The vial was sealed and heated under magnetic stirring at 60 °C for 145 h. Aliquots were taken at regular intervals and dissolved in $CDCl_3$ containing 1% of benzoic acid to quench the DBU catalyst and the conversion of monomer to polymer was determined through ^1H NMR. The product was dissolved in 0.5 ml of DCM with addition of a droplet of acetic acid to quench the DBU catalyst. The polymer was precipitated in methanol and dried *in vacuo* at ~37 °C over P_2O_5. Yield: 0.44 g (68%). M_n (GPC, chloroform): 34 400 g mol^{-1}, PDI = 1.53. ^1H NMR (400 MHz, $CDCl_3$): δ = 0.87 (t, *J* = 7.7 Hz, –CH_3, poly), 0.88 (m, –CH_3, poly), 1.23–1.33 (m, –CH_2–, poly), 1.47 (q, *J* = 7.7 Hz, –CH_2–, poly), 1.49–1.56 (m, –CH_2–, poly), 3.29 (s, –CH_2–O, poly), 3.35 (t, *J* = 6.6 Hz, –CH_2–O–, poly), 4.09 (s, –CH_2–O, poly), 5.15 (s, –CH_2–O, α-end), 7.34–7.40 (m, –Ph, α-end). ^{13}C NMR (100 MHz, $CDCl_3$): 7.6 (–CH_3), 14.2 (–CH_3), 22.8 (–CH_2–), 22.8 (–CH_2–), 26.2 (–CH_2–), 29.3 (–CH_2–), 29.7 (–CH_2–), 32.0 (–CH_2–), 42.0 (>C<), 68.0 (–CH_2–O), 70.1 (–CH_2–O), 71.8 (–CH_2–O), 155.3 (>C=O).

2.3.7 Copolymerization of HEC and AEC

In an argon-filled glovebox, an oven-dried 8 ml vial was charged with 0.06 g (0.3 mmol) of AEC and 0.7 g (2.7 mmol) of HEC, targeting a 90:10 mol% composition of the HEC–AEC copolymer. 60 µl of a solution of 0.5 M benzyl alcohol initiator and 0.1 M of DBU catalyst (0.03 mmol initiator, 0.006 mmol catalyst, for DP = 100) in dry toluene was added. The vial was sealed, transferred out of the glovebox and heated under magnetic stirring at 60 °C for 116 h. The polymer was dissolved in 0.7 ml of DCM with addition of a few droplets of acetic acid to quench the DBU catalyst. The polymer was precipitated in methanol and dried *in vacuo* at ~37 °C over P_2O_5. Yield: 0.52 g (68%).

2.3.8 Polymerization kinetics

In addition to the homopolymerization of HEC, the homopolymerization kinetics of AEC were also investigated. In a glovebox under an argon atmosphere, an oven-dried 4 ml vial was charged with 0.50 g (2.5 mmol) of AEC. To the vial was added 50 µl of a solution of 0.5 M benzyl alcohol initiator and 0.1 M of DBU catalyst (0.025 mmol initiator, 0.005 mmol catalyst, for DP = 100) in dry toluene. The vial was sealed and heated at 60 °C under magnetic stirring. Aliquots were taken at regular intervals and dissolved in $CDCl_3$ containing 1% of benzoic acid to quench the DBU catalyst. The conversion of monomer to polymer was determined through ^1H NMR.

2.4 Electrolyte preparation

Controlled ratios of crosslinkable poly(HEC-*co*-AEC), LiTFSI and the radical initator 2,2-dimethoxy-2-phenylacetophenone (4 wt% relative to the crosslinkable polymer) were dissolved in anhydrous THF in an argon-filled glovebox. After complete dissolution, the solutions were transferred to small vials, placed in a transfer chamber and put under a flow of dry nitrogen for 24 hours for evaporation of the bulk of the solvent. The resulting salt-in-polymer solutions were cast in 0.4 mm deep PTFE moulds and crosslinked through irradiation under a 365 nm, 36 W UV lamp setup in the glovebox for 20 min. Any remaining solvent residues were evaporated in a vacuum-oven system in the glovebox. During the first 20 hours, the system was pumped slowly from 200 mbar to full vacuum (<1 mbar) at ambient temperature. Thereafter, the temperature was increased to 60 °C and kept at that temperature for 40 hours at full vacuum. The samples were then removed from the mould and circular samples were punched out from the electrolyte films.

2.5 Ionic conductivity

The ionic conductivity of the electrolytes was determined through electrochemical impedance spectroscopy. Electrolyte films were placed between two stainless steel blocking electrodes in a Swagelok-type cell. The cell was then heated in an oven until the sample reached 100 °C, measured by means of a thermocouple inserted close to one of the electrodes, and kept at that temperature for 30 minutes. The sample was then allowed to cool down and measurements were done from 100 °C to 30 °C with an interval of 10 °C, with an additional measurement at 25 °C, using a Schlumberger Impedance/Gain-phase Analyzer SI 1260 between 1 Hz–1 MHz with an amplitude of 10 mV. The bulk ionic resistance (low-frequency *x*-axis intercept of the semicircle in the Nyquist plot) was extracted by fitting the data to an appropriate circuit using ZView (Scribner Associates).

3. Results and discussion

The molecular flexibility and glass transition temperature of a polymer is related to the free volume of the polymer chains. Thus, in order to obtain aliphatic polycarbonates with a lower T_g relative to the parent PTMC structure, the free volume of the polymer needs to be increased. This can be achieved by incorporating flexible, plasticizing pendent groups in the polymer structure. Examples of such a group is the allyl ether group that, when attached as a side group to a PTMC backbone, has been shown to give polycarbonates with a T_g as low as −40 °C [25, 26]. Even more molecular flexibility should be possible to achieve with side groups based on long hydrocarbon chains, similar to the well-known phthalate esters used to plasticize PVC [28]. Using this design approach, the cyclic carbonate monomer 2-heptyloxymethyl-2-ethyltrimethylene carbonate (HEC) was synthesized in four steps as shown in Scheme 1. The plasticizing heptyl ether moiety was introduced to an acetonide-protected trimethylolpropane in the second step through Williamson ether synthesis using a procedure described by Halldorsson et al. for the synthesis of alkyl ethers of acetonide-protected glycerol [29]. Deprotection through acid hydrolysis afforded the 1,3-diol that was ring-closed to the cyclic carbonate using 1,1’-carbonyldiimidazole (CDI).

In addition to acting as a plasticizer, the heptyl ether moiety also comprises a potentially Li^+-coordinating ether oxygen. This is potentially beneficial in order to increase the solubility of lithium salts in an otherwise largely non-polar host matrix. The 2,2-disubstituted trimethylene carbonate monomer also comprises, in addition to the heptyl ether moiety, an ethyl substituent. This is preferred over the alternative methyl group, which could be obtained by replacing trimethylolpropane with trimethylolethane as the starting material, since the ethyl group is a better plasticizer than the shorter methyl group when present as a side group in aliphatic polycarbonates [30].

In order to create mechanically stable materials from low-T_g amorphous polymers, some means of crosslinking is necessary. Most examples of cyclic carbonate monomers have only been polymerized to rather modest molecular weights [10], while it has been shown that, at least for PTMC, a molecular weight in excess of 100 000 g/mol is needed for molecular entanglements to act as physical crosslinks to stabilize the material [31]. Thus, another means of crosslinking is necessary to obtain mechanically stable materials from low-molecular-weight, low-T_g polymers. For this reason, the monomer 2-allyloxymethyl-2-ethyltrimethylene carbonate (AEC), which comprises chemically crosslinkable allyl groups, was synthesized through ring-closing of trimethylolpropane monoallyl ether with CDI.

The HEC monomer was polymerized in bulk through organocatalytic ring-opening polymerization, employing benzyl alcohol as an initiator for a controlled degree of polymerization of 100, and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as the polymerization catalyst, giving an amorphous polymer with $M_n = 34\,400$ g mol^{-1} (from GPC). As shown in Figure 1, the polymerization kinetics were remarkably slow given the potency of DBU as a polymerization catalyst [9] and excessive catalyst loadings were required in order for the polymerization to be reasonably fast at moderate temperatures. Even at a catalyst loading of 20% relative to the initiator, >100 h were needed to reach full conversion at 60 °C. This can be compared to the polymerization of the parent monomer trimethylene carbonate (TMC), which can be polymerized in bulk within minutes at 65 °C using the same initiator/catalyst system [32]. This can possibly be the effect of either steric hindrance because of the bulky substituents or the change in polarity of the reaction medium caused by this non-polar monomer compared to TMC. As seen in Figure 1, homopolymerization of AEC was also rather sluggish, but more rapid than for HEC. It can be noted that we have also experienced similarly slow polymerizations using other monomers bearing bulky, non-polar side groups, with DBU as well as with other catalyst systems in bulk (unpublished data). Endo et al. have also demonstrated that, under anionic conditions, polymerization is less thermodynamically favorable for six-membered cyclic carbonate monomers with bulky substituents [33]. On the other hand, it appears that at least AEC can be organocatalytically polymerized at high rates in solution at room temperature [34].

Using these established polymerization conditions, a crosslinkable copolymer of HEC with 10 mol% of AEC was then synthesized (Scheme 2). The polymer structures were confirmed by NMR spectroscopy and the structures along with assigned ^{1}H NMR spectra of poly(HEC) as well as poly(HEC-*co*-AEC) can be seen in Figure 2. The aforementioned non-polarity of the HEC repeating unit was confirmed by the insolubility of the HEC–AEC copolymer in acetonitrile. This is not surprising given the immiscibility of acetonitrile with heptane, but prevented the use of acetonitrile as a solvent for the casting of electrolytes, necessitating the use of tetrahydrofuran as an alternative, more non-polar solvent.

The monomer HEC was designed specifically to attain low-T_g polycarbonates and, as can be seen in Figure 3, DSC analysis revealed a remarkably low T_g of −49.4 °C for the HEC homopolymer. To the best of our knowledge, this is the lowest glass transition temperature reported for a PTMC-derived aliphatic polycarbonate. The inclusion of 10 mol% of AEC did not increase the T_g substantially. DSC also confirmed that both the HEC homopolymer and the HEC–AEC copolymer were fully amorphous.

The HEC–AEC copolymer was stabilized by introducing covalent crosslinks through UV irradiation of a mixture of the polymer with the radical initiator 2,2-dimethoxy-2-phenylacetophenone. Successful crosslinking was confirmed by measuring the mechanical properties using oscillatory rheology. As can be seen in Figure 4, before crosslinking the copolymer has a largely liquid-like behavior, as indicated by the high values of the loss modulus (G'') relative to the storage modulus (G'). In contrast, the crosslinked sample shows an essentially constant G'', which is typical for a material with covalent crosslinks. Furthermore, as $G' > G''$, the crosslinked polymer shows mechanical stability and behaves as a solid material throughout this frequency interval. The slight frequency dependence of G' observed, particularly at high frequencies, is indicative of an “imperfect” network, i.e., a covalently linked polymer network with elements of dangling chains. The rheological behavior of the crosslinked poly(HEC-*co*-AEC) is reminiscent of that of a Kelvin–Voigt material, although, as G'' is not directly proportional to the oscillating frequency, a more complex viscoelastic model would be required to accurately describe this material.

Along with mechanically stabilizing the material, crosslinking also lowered the molecular flexibility of the polymer chains, as indicated by a notable increase in T_g from −48.2 °C to −38.9 °C. When LiTFSI was added to the material, the T_g increased further, as can be seen in Figure 5. This is typical of polymer electrolytes, and is caused by transient crosslinks introduced by the coordination of Li^+ to the polymer chains [35]. As well as being prominent in polyethers, we have previously also observed this behavior in polycarbonate electrolytes [13]. Nevertheless, all synthesized electrolytes displayed T_gs notably lower than undoped high-molecular-weight PTMC (−15 °C), thus indicating that a substantial degree of the molecular flexibility induced by the side-chains is kept after crosslinking and addition of salt.

The ionic conductivity of the electrolytes, as determined by electrochemical impedance spectroscopy, is shown in Figure 6. The temperature dependence of the ionic conductivity of the electrolytes shows VTF (Vogel–Tammann–Fulcher) behavior, indicating that the ionic transport is coupled to the segmental relaxation of the chains of the polymer host matrix [36]. Maximum conductivity is found for the sample with a [carbonate]:[Li^+] ratio of 5; the conductivity clearly decreases for higher salt concentrations, most likely due to ion association as well as the effect of physical crosslinking by the lithium ions. In PTMC$_x$LiTFSI, the conductivity maximum was found at slightly lower molar salt concentrations ([carbonate]:[Li^+] = 8–13) [13]. For PTMC electrolytes, however, these compositions correspond to 17.8 and 26 wt%, respectively, which is in the same range as for the top-performing electrolyte in this study where a [carbonate]:[Li^+] ratio of 5 corresponds to 18.5 wt% of LiTFSI.

Nevertheless, despite the notably low glass transition temperatures of the electrolytes, they all display rather modest values of the ionic conductivity, reaching up to 2×10^{-7} S cm^{-1} at room temperature for the electrolyte with a [carbonate]:[Li^+] ratio of 5. This indicates that the high molecular flexibility of the host polymer is insufficient to achieve fast ion transport in the materials and that other factors may be influencing the conductivity as well. One such factor may be the non-polar characteristics of this polymer system compared to other typical polymer electrolyte hosts. This could lead to increased ion pairing [37, 38], thus effectively reducing the concentration of charge carriers and lowering the ionic conductivity. The bulky side groups may also influence the chain and ion dynamics in other ways than is evident by the value of the T_g, e.g. by sterically hindering coordination sites from coming in close proximity to each other, thereby impeding the movement of ions between coordination sites.

4. Conclusions

The electrolytes presented in this study represent an attempt to create highly molecularly flexible polycarbonate hosts that can facilitate efficient transport of Li-ions. In this effort, an aliphatic polycarbonate with a T_g close to −50 °C was synthesized and UV-crosslinked to form solid polymer electrolytes together with LiTFSI salt. While reasonable levels of ionic conductivity were obtained for these electrolytes, the ion transport was slower than what could be expected based on their low glass transition temperatures. This is indicative that other factors, such as the polarity of the host material, are also of importance when designing new solid polymer electrolytes that will allow fast Li-ion conduction. It is possible that the non-crosslinked polymers would show slightly higher conductivities, but their lack of mechanical stability would effectively prevent their use in practical applications. The knowledge gained from this study will thus be highly valuable for the design and synthesis of new generations of solid polymer electrolytes with a combination of low glass transition temperatures and high ionic conductivity.

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Figure captions

Scheme 1. Synthesis of the HEC monomer starting from trimethylolpropane. Reaction conditions: (i) acetone, Amberlyst 15, r.t.; (ii) 1-bromoheptane, KOH, TBAB, 40 °C; (iii) THF, HCl, H_2O, reflux; (iv) CDI, DCM, r.t.

Scheme 2. Synthesis of poly(HEC-*co*-AEC) through organocatalytic ring-opening polymerization.

Figure 1. Polymerization kinetics of HEC and AEC in bulk at 60 °C. Solid lines represent exponential fits, the dashed line represents extrapolation of the exponential fit for AEC polymerization.

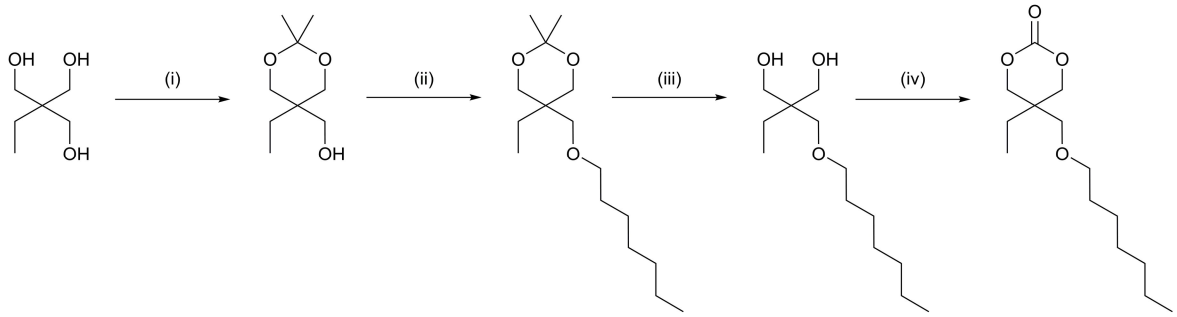
Figure 2. ^{1}H NMR spectra of poly(HEC) (top) and poly(HEC-*co*-AEC) (bottom) with relevant peaks labeled. Insets show an enlarged version of the allyl area of the spectra.

Figure 3. DSC traces for poly(HEC) and poly(HEC-*co*-AEC) showing the glass transitions with T_gs indicated by the dashed lines.

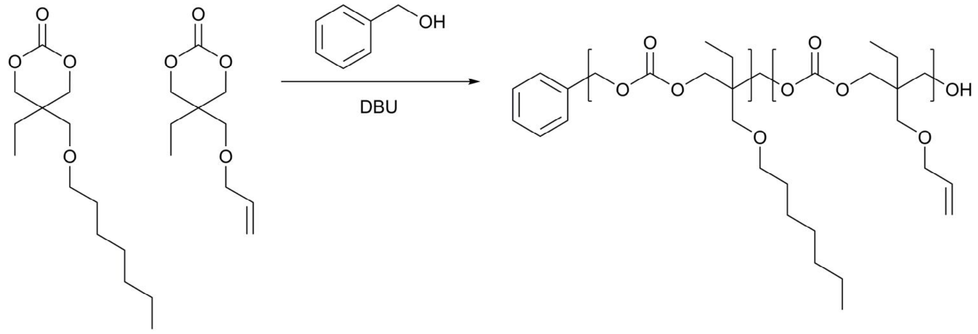
Figure 4. Comparison of mechanical properties of poly(HEC-*co*-AEC) before (left) and after (right) crosslinking, as determined by oscillatory rheology.

Figure 5. Glass transition temperature vs. salt concentration for crosslinked poly(HEC-*co*-AEC) electrolytes. The annotated numbers refer to the [carbonate]:[Li$^+$] ratio. ∞ indicates the crosslinked copolymer without added salt.

Figure 6. Total ionic conductivity for crosslinked poly(HEC-*co*-AEC) electrolytes containing LiTFSI salt. *x* denotes the [carbonate]:[Li$^+$] ratio. Dashed lines represent VTF fits.



Scheme 1



Scheme 2

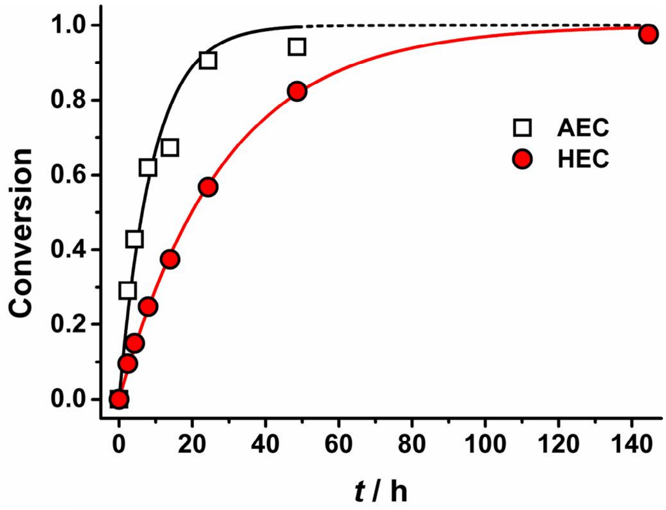
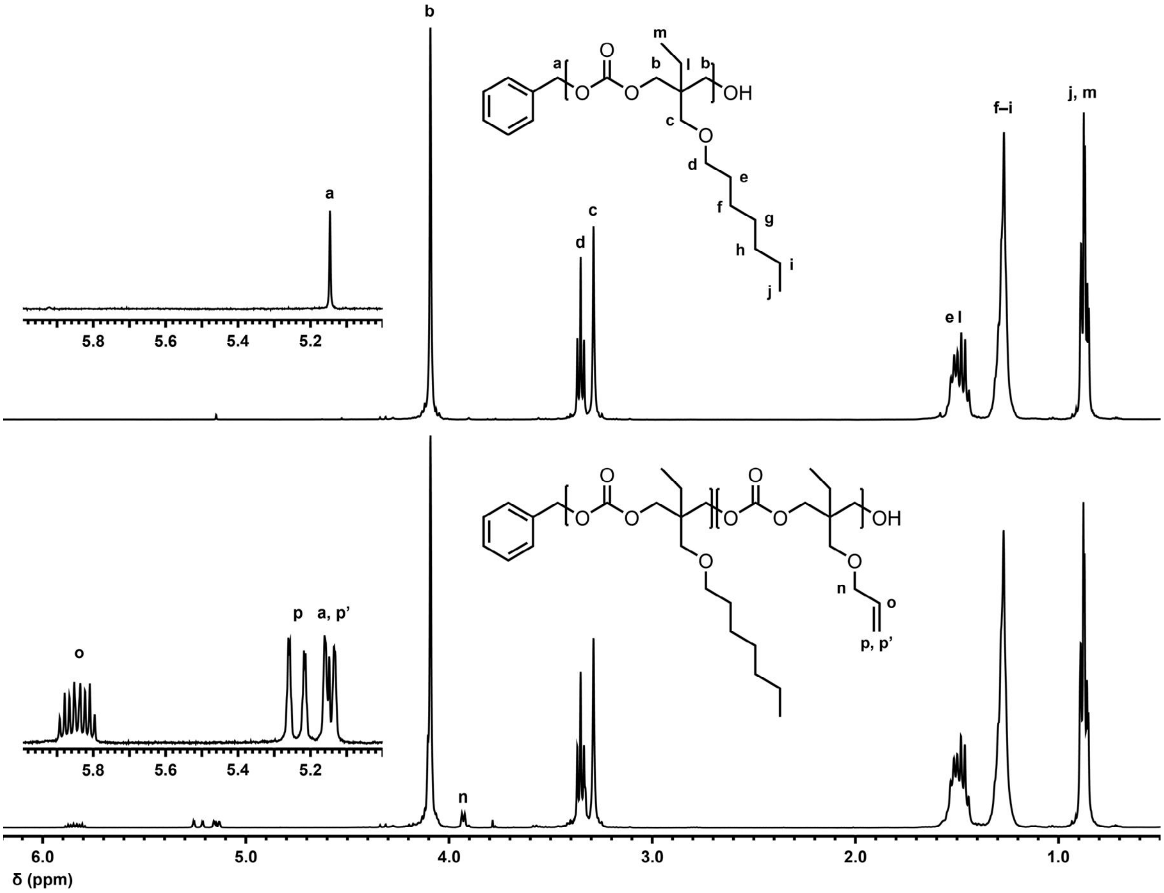

1.0
0.8
0.6
0.4
0.2
0.0
Conversion
0
20
40
60
80
100
120
140
t / h
AEC
HEC

Fig. 1


b
a
c
d
e l
f–i
j, m
m
l
OH
O
o
n
p
a, p'
p, p'
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5.6
5.4
5.2
6.0
5.0
4.0
3.0
2.0
1.0
δ (ppm)

Fig. 2

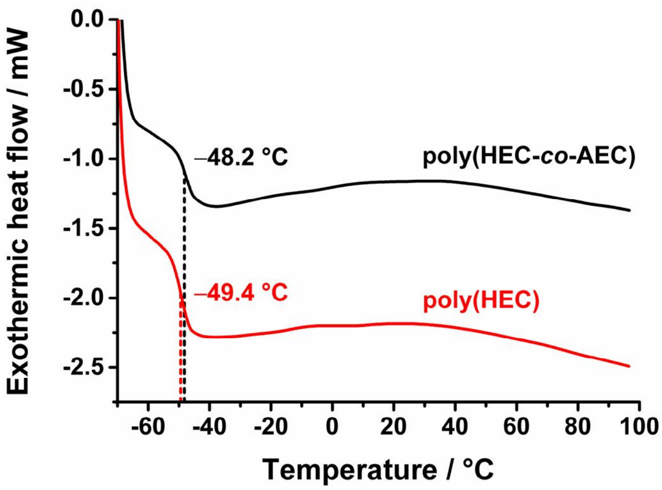

Exothermic heat flow / mW
0.0
-0.5
-1.0
-1.5
-2.0
-2.5
–48.2 °C
poly(HEC-*co*-AEC)
–49.4 °C
poly(HEC)
-60
-40
-20
0
20
40
60
80
100
Temperature / °C

Fig. 3

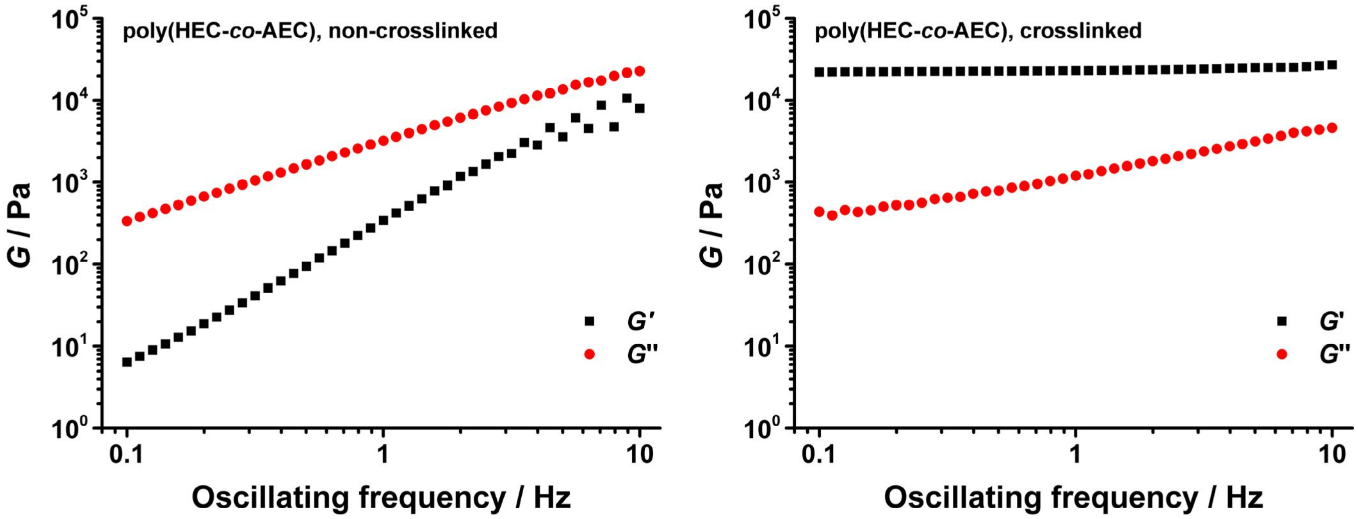

poly(HEC-*co*-AEC), non-crosslinked
G / Pa
10^5
10^4
10^3
10^2
10^1
10^0
■ G′
● G''
0.1
1
10
Oscillating frequency / Hz
poly(HEC-*co*-AEC), crosslinked
G / Pa
■ G'
● G''
Oscillating frequency / Hz

Fig. 4

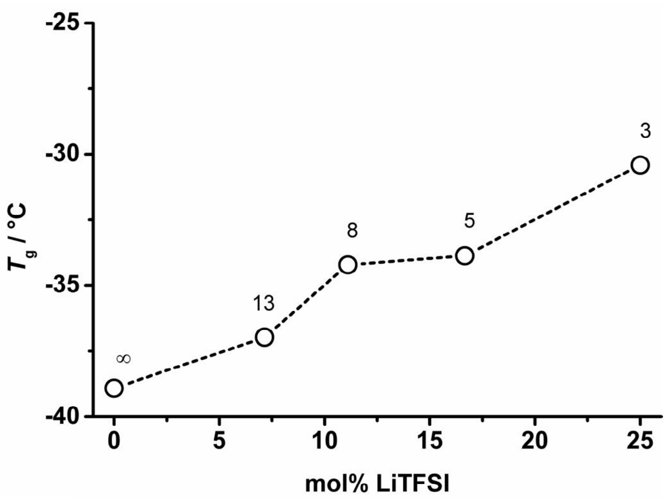

-25
-30
-35
-40
T_g / °C
0
5
10
15
20
25
mol% LiTFSI
∞
13
8
5
3

Fig. 5

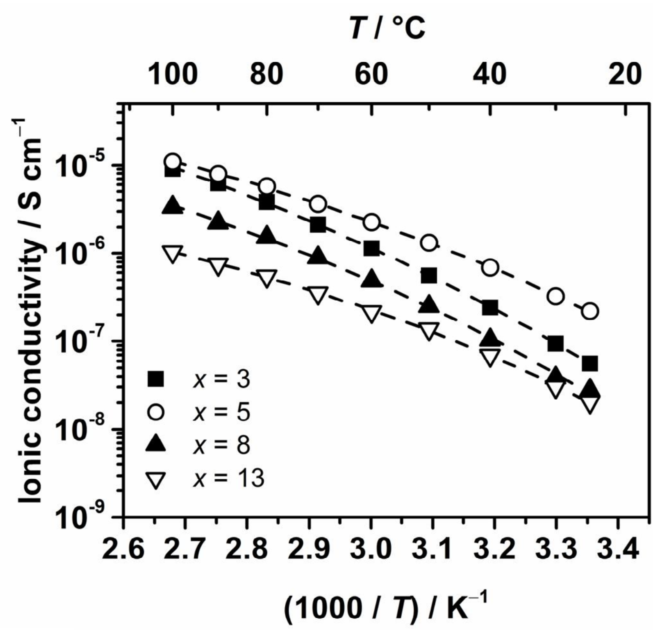
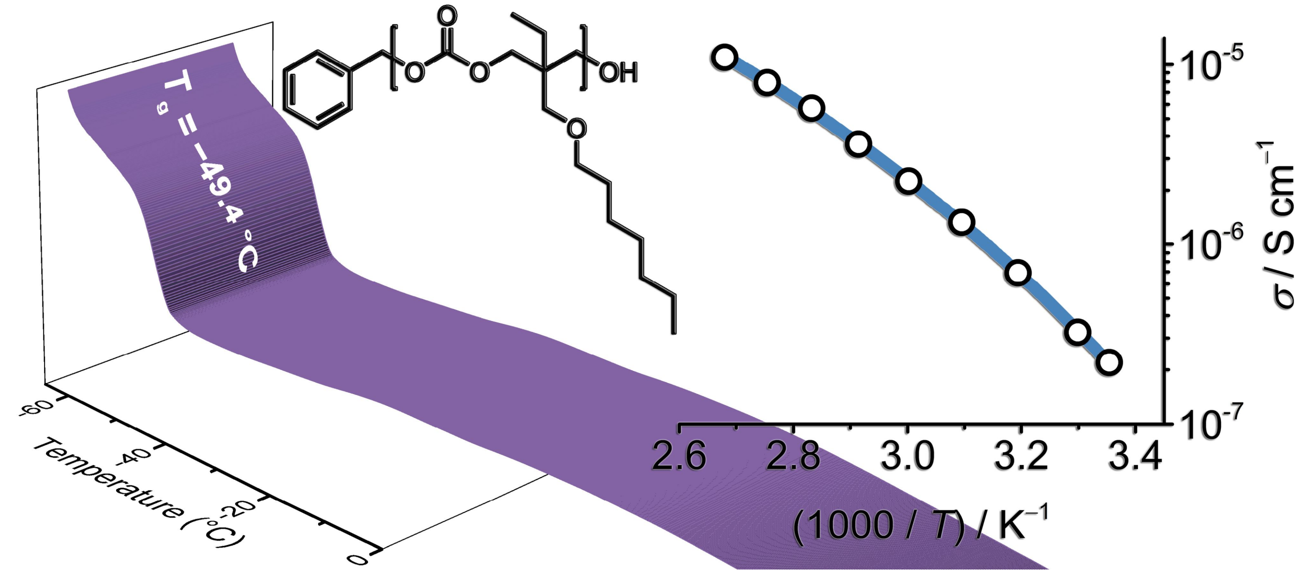

T / °C
100
80
60
40
20
10^{-5}
10^{-6}
10^{-7}
10^{-8}
10^{-9}
Ionic conductivity / S cm^{-1}
2.6
2.7
2.8
2.9
3.0
3.1
3.2
3.3
3.4
(1000 / T) / K^{-1}
■ x = 3
○ x = 5
▲ x = 8
▽ x = 13

Fig. 6



Graphical abstract