



Synthesis of high molecular flexibility polycarbonates for solid polymer electrolytes



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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 $34\,400\text{ g mol}^{-1}$, 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 $2 \times 10^{-7}\text{ S cm}^{-1}$ at room temperature and 1×10^{-6} to $1 \times 10^{-5}\text{ S cm}^{-1}$ 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.

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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

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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; Purolite, Ferro Corporation) was dried *in vacuo* at 120 °C for 24 h before use.

2.2. Instrumentation

^1H 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. ^1H NMR (400 MHz, DMSO-*d*₆): δ = 0.75 (t, 3H, *J* = 7.7 Hz, -CH₃), 1.26 (q, 2H, *J* = 7.7 Hz, -CH₂-), 1.27 (s, 3H, -CH₃), 1.31 (s, 3H, -CH₃), 3.39 (d,

2H, *J* = 5.5 Hz, -CH₂-OH), 3.47 (d, 2H, *J* = 11.7 Hz, -CH₂-O), 3.55 (d, 2H, *J* = 11.7 Hz, -CH₂-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 NaHCO₃, the reaction mixture was extracted with 2 × 200 ml of ethyl acetate. The organic phases were combined, dried with MgSO₄, 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. ^1H NMR (400 MHz, DMSO-*d*₆): 0.78 (t, 3H, *J* = 7.7 Hz, -CH₃), 0.84–0.87 (m, 3H, -CH₃), 1.20–1.31 (m, 10H, -CH₂-), 1.43–1.50 (m, 2H, -CH₂-), 3.16 (s, 2H, -CH₂-O), 3.25 (d, 4H, *J* = 5.1 Hz, -CH₂-OH), 3.31 (t, 2H, *J* = 6.6 Hz, -CH₂-O), 4.16 (t, 2H, *J* = 5.1 Hz, -OH). ^{13}C NMR (100 MHz, CDCl₃): 7.7 (-CH₃), 14.2 (-CH₃), 22.7 (-CH₂-), 23.5 (-CH₂-), 26.2 (-CH₂-), 29.2 (-CH₂-), 29.7 (-CH₂-), 31.9 (-CH₂-), 42.9 (>C<), 66.3 (-CH₂-OH), 72.2 (-CH₂-O), 75.5 (-CH₂-O). Anal. calcd for C₁₃H₂₈O₃: C, 67.20; H, 12.15. Found: C, 66.80; H, 12.16.

2.3.3. 2-Heptyloxymethyl-2-ethyltrimethylene carbonate (HEC)

To 13.9 g (60.0 mmol) of 2-heptyloxymethyl-2-ethyl-1,3-propanediol in 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 NaHCO₃. The organic phase was separated, dried with MgSO₄ 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. ^1H NMR (400 MHz, CDCl₃): δ = 0.87 (m, 3H, -CH₃), 0.90 (t, 3H, *J* = 7.7 Hz, -CH₃), 1.21–1.37 (m, 8H, -CH₂-), 1.51 (q, 2H, *J* = 7.7 Hz, -CH₂-), 1.51–1.57 (m, 2H, -CH₂-), 3.36 (s, 2H, -CH₂-O), 3.39 (t, 2H, *J* = 6.6 Hz, -CH₂-O-), 4.11 (BB' of AA'BB', 2H, -CH₂-O), 4.31 (AA' of AA'BB', 2H, -CH₂-O). ^{13}C NMR (100 MHz, CDCl₃): 7.5 (-CH₃), 14.2 (-CH₃), 22.7 (-CH₂-), 23.5 (-CH₂-), 26.2 (-CH₂-), 29.2 (-CH₂-), 29.5 (-CH₂-), 31.9 (-CH₂-), 35.6 (>C<), 69.1 (-CH₂-O), 72.0 (-CH₂-O), 73.0 (-CH₂-O), 148.7 (>C=O). Anal. calcd for C₁₄H₂₆O₄: C, 65.09; H, 10.14. Found: C, 65.17; H, 10.07.

2.3.4. 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 NaHCO₃. The organic phase was separated, dried with MgSO₄ 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. ^1H NMR (400 MHz, CDCl₃): δ = 0.91 (t, 3H, *J* = 7.7 Hz,

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