

Facile access to CO₂-sourced polythiocarbonate dynamic networks and their potential as solid-state electrolytes for lithium metal batteries

Thomas Habets^a, Jorge L. Olmedo-Martínez^b, Rafael del Olmo^b, Bruno Grignard^a, David Mecerreyes^{*b,c}, Christophe Detrembleur^{*a}

^a Center for Education and Research on Macromolecules (CERM), CESAM Research Unit, University of Liege, Sart-Tilman B6a, Quartier Agora, 4000 Liege, Belgium.

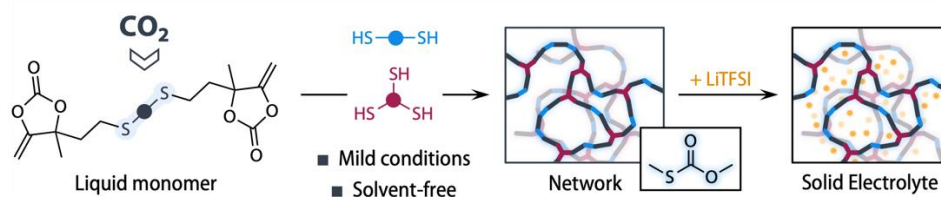
E-mail: christophe.detrembleur@uliege.be

^b POLYMAT, University of the Basque Country UPV/EHU, Avenida Tolosa 72, Donostia-San Sebastián, Gipuzkoa, Spain.

^c IKERBASQUE, Basque Foundation for Science, Plaza Euskadi 5, Bilbao 48009, Spain

E-mail: david.mecerreyes@ehu.es

Abstract



Poly(monothiocarbonate)s are an interesting class of sulfur-containing materials whose application as solid polymer electrolytes was barely studied, certainly due to the elusive production of diversified polymer architectures. Herein, a new liquid CO₂-sourced bis(α-alkylidene cyclic carbonate) monomer was designed at high yield to allow its one-step and solvent-free copolymerization with thiols to produce linear and cross-linked polymers in mild conditions. The influence of the monomer structure on the thermal properties and the ionic conductivity of linear polymers was assessed. The polymer network showed to be thermally re-processable owing to the dynamic nature of the monothiocarbonate bonds. A solid polymer electrolyte was easily obtained from the cross-linked material when combined with LiTFSI salt. The solid polymer electrolyte was characterized by an ionic conductivity reaching $6 \times 10^{-6} \text{ S.cm}^{-1}$ at room temperature with a lithium transference number of 0.37 and a wide electrochemical stability window (4.0 V vs Li⁰/Li⁺) valid for lithium cycling. This work thus reports an attractive valorizing

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approach for carbon dioxide to deliver under mild operating conditions poly(monothiocarbonate)-containing novel covalent adaptable network CAN materials of high potential for energy applications, especially as solid electrolytes for batteries.

Introduction

Sulfur-containing polymers have caught interest of researchers and material manufacturers by virtue of their attractive properties, rendering them particularly suitable for a high diversity of applications such as engineering plastics, optics and optoelectronics, adhesives, or electrolytes^[1]. Intensive research in this field is evidenced by the large panel of recently developed polymer scaffolds embedding sulfur atoms in their backbone^[2]. Poly(monothiocarbonate)s (PMTCs) is an appealing class of these polymers as the sulfur atom integrated in the carbonate unit thoroughly modifies their chemical and physical properties^[3,4] compared to their polycarbonate analogues. The main synthetic pathways relying on the use of harmful reagents and/or the need to eliminate acidic condensate^[5-7] have quickly dropped out of sight as researchers focused on a more promising route: the chain-growth copolymerization of epoxides and carbonyl sulfide (COS)^[8]. This approach delivers defect-free PMTCs at room temperature with metal-free catalysts from a diversity of commercial epoxides^[9]. The main drawback of this polymerization method is the need to carry out the reaction in COS-pressurized autoclaves and in dry conditions, and the range of produced polymers is limited to linear chains.

Recently, some of us pioneered the use of CO₂-sourced bis(α -alkylidene cyclic carbonate)s (bis α CC) monomers to prepare a large palette of new polymers (polycarbonates, polyurethanes, and polythiocarbonates) in unprecedented mild conditions^[10,11]. Following studies by us and other research groups have largely expanded the scope of these important families of polymers^[12-22]. More specifically, this chemistry allowed to access linear PMTCs through the step-growth copolymerization of bis α CC with dithiols in the presence of a base catalyst under ambient conditions^[11]. The versatility of this toolbox was further validated through the one-step synthesis of copolymers containing both urethane and thiocarbonate linkages from the terpolymerization of dithiols and diamines with bis α CC.^[23]

Solid polymer electrolytes (SPEs) are materials that have been widely studied with the purpose of replacing liquid electrolytes in lithium batteries, which would make them safer, avoiding the loss of flammable electrolyte by leakage or the growth of lithium dendrites. The most studied polymer for this application is polyethylene oxide (PEO), due to its great capacity to dissolve lithium salts.^[24] However, it has certain

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disadvantages, such as crystallization that restricts ionic conductivity, and a decrease in mechanical properties depending on the concentration of lithium salt in the system.^[25] Polycarbonates have been studied as another polymeric matrix in SPEs for lithium batteries^[26–28], as they have shown good ionic conductivity, electrochemical stability and a higher transport number than in the case of PEO. The carbonate group shows weaker coordination with lithium cations compared to the ether groups, which is reflected in increased electrochemical properties.^[29]

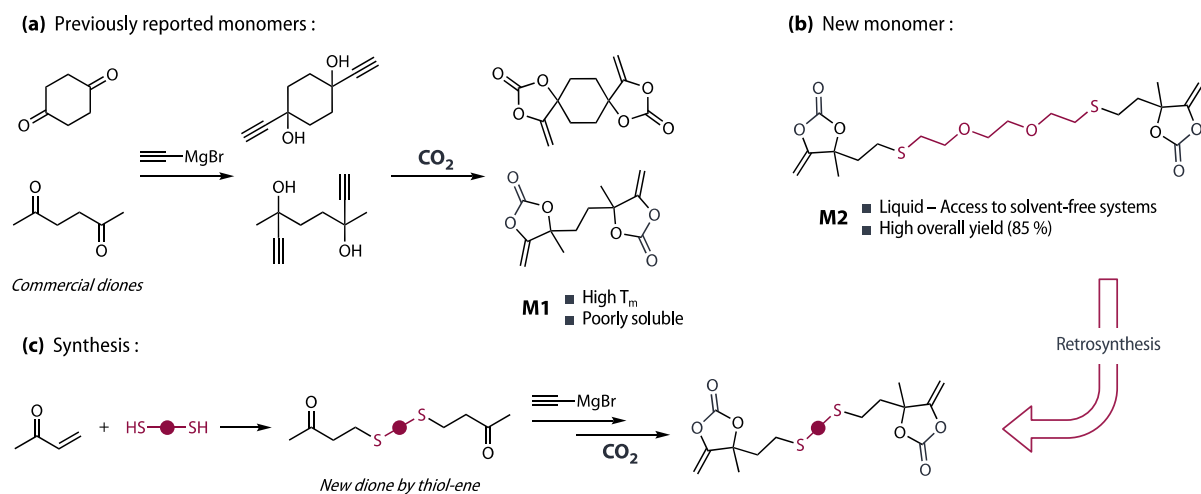
In the case of polythiocarbonates, Cao, *et al.* reported a first study on PMTCs as SPEs in which they prepared block copolymers from PMTCs and PEO doped with various amounts of LiTFSI to simultaneously increase ionic conductivity and mechanical properties of the resulting electrolyte. Many systems were studied and ionic conductivity values in the order of 10^{-4} S.cm⁻¹ at room temperature were obtained. However, the best candidates were containing high amounts of PEO in their chains and the mechanical properties were underperforming other block copolymers scaffolds, e.g. containing polystyrene (PS). Moreover, no further electrochemical studies were performed.^[30] This only contribution concerning the use of PMTCs as SPEs in the literature attests for the lack of applicative studies of these polymers compared to conventional polycarbonates, certainly due to their more difficult preparation.

The overall goal of this work is to report the first facile preparation of a poly(monothiocarbonate) network in mild conditions, that presents a covalent adaptable network (CAN) behavior, and to assess its potential as solid electrolyte for Li-Ion batteries. CANs are very interesting materials since they present properties like recyclability, reprocessing and self-healing possibilities which are of great interest for materials applied in batteries.^[31] To reach this objective, a novel CO₂-based liquid bis α CC monomer was designed for allowing straightforward one-step and solvent-free synthesis of the cross-linked polymer. The CAN behavior of the cross-linked polymer network was shown and the mechanical properties of the reprocessed material were studied. Various PEO-free PMTCs were prepared and subjected to ionic conductivity tests to evaluate the influence of the polymer structure on the ionic conductivity and the performance of the polymer network as a solid-state battery for Li-ion batteries was assessed.

Results and discussion

Monomer design

Although numerous studies were describing the palette of available polymers from bis α CC, only little effort was yet devoted to the synthesis of monomers with higher solubility and lower melting points. The synthesis of these monomers can be achieved by the addition of ethynyl magnesium bromide on a diketone, thus affording a bispropargylalcohol which is further quantitatively reacted with CO₂ to furnish the monomer (Scheme 1a). So far, only two monomers from commercially available diones were synthesized by our group: 1,6-hexanedione^[10] and 1,4-cyclohexanedione-based^[11] monomers. However, they were characterized by limited solubility and high melting points, avoiding developing solvent-free formulations. Lamb et al. recently developed new bispropargylic alcohols through the addition of solubilizing groups on the double bond^[22]. Although these compounds were characterized by T_m ranging from 105 to 200 °C, this approach is an appealing way to potentially access liquid monomers, however total yields starting from the dione were not exceeding 22%. Schaub et al. synthesized monomers starting from 1,4-butanediol and bisepoxides, affording two liquid bis α CCs with overall yields of up to 70%^[20]. However, the compounds were unsubstituted α CCs whose relative reactivity is unknown compared to our previous developed monomers and the synthesis was only proposed at the 1 mmol scale.



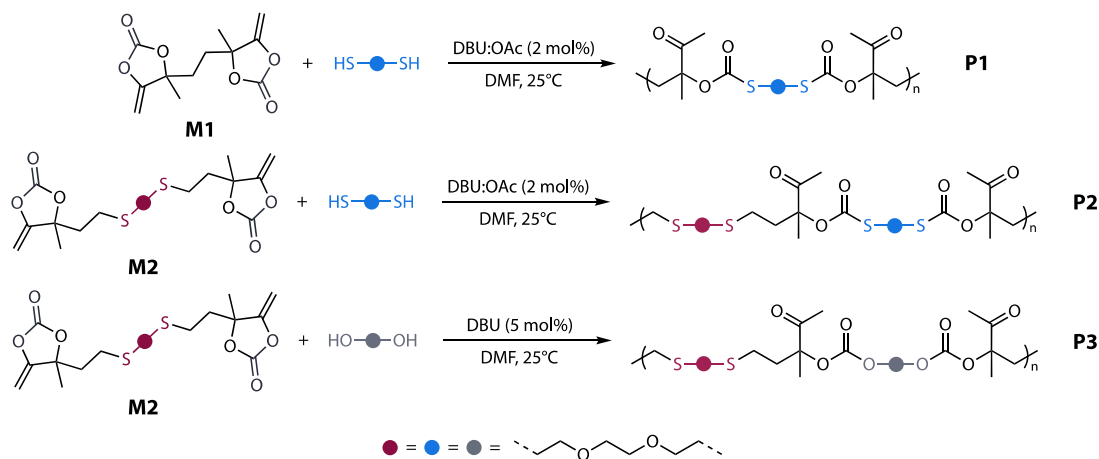
Scheme 1 – Synthetic approach toward bis α CC. (a) Previously reported monomer made from 1,6-hexanedione^[10] and 1,4-cyclohexanedione^[11]. (b) Structure of the new liquid monomer. (c) Design of a new dione to tune the structure of bis α CC by a retrosynthetic approach.

To tune the structure of the monomer, a retrosynthetic approach has led to design a new dione with a flexible segment (Scheme 1b-c). To do so, methyl vinyl ketone (MVK) is an ideal cheap and available synthon containing a ketone group directly conjugated to a terminal alkene. The electron-attractor nature of the ketone makes the compound very

reactive toward thiols through the thia-Michael addition. With the aim to get a novel dione, a dithiol was reacted with MVK in the presence of a low amount of DBU (2 mol%) as base catalyst. To provide flexibility to the backbone, the cheap dithiol 2,2'-(Ethylenedioxy)diethanethiol (DMDO) was selected, affording the new dione in high isolated yield (96 %). The compound was then subjected to the same reactions as the commercial diones (addition of ethynyl magnesium bromide followed by CO₂ coupling), providing a liquid bis α CC **M2** with an overall isolated yield of 85 % (Scheme 1c). The reaction was scaled up to provide nearly 60 g of monomer in one batch. All characterizations (¹H-, ¹³C-NMR and IR) confirmed the chemical structure of the monomer (Figures S5-7).

Synthesis and characterization of PMTCs

We then proceeded to the synthesis of PMTCs by the step-growth copolymerization of bis α CC monomers **M1** and **M2** with the dithiol DMDO to provide **P1** and **P2**. The two monomers **M1** and **M2** were here employed to deliver structurally different PMTCs in order to evaluate the influence of the monomer structure (and thus flexibility) on the ionic conductivity of the polymer material. The syntheses were carried out in DMF at 25°C in the presence of 2 mol% of DBU acetate (DBU:OAc) as base catalyst. As described in a previous work, the thiolysis of bis α CC can lead to two types of linkages: monothiocarbonate and cyclic carbonate-co-thioether ones^[11]. The selectivity toward both units was tuned through the choice of the catalyst. Here, the use of DBU:OAc provided **P1** and **P2** with a selectivity in monothiocarbonate linkage of 91% and 93%, respectively. The structures of the polymers were confirmed by ¹H- and ¹³C-NMR spectroscopy (Figures S8-12) and the linkage selectivity was determined by integration of characteristic resonance as described in SI.



Scheme 2 – Reactions for the polymerization toward **P1**, **P2** and **P3**.

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$^1\text{H-NMR}$ spectra revealed the characteristic ketone methyl of the monothiocarbonate linkage at around 2.14 ppm for both polymers. The cyclic carbonate linkage was evidenced by the resonance of the methylene neighboring the sulfur atom at 2.92 ppm compared to 3.02 ppm for the monothiocarbonate moiety. Both **P1** and **P2** have shown decent molar masses of nearly 20000 g/mol in M_w as determined by SEC (Table 1 & Figure S15).

The thermal properties of the two polymers were determined by differential scanning calorimetry (DSC). As expected, they were both amorphous with T_g s of 8 and -10 °C for **P1** and **P2**, respectively (Table 1). This demonstrates the high impact of the flexible segment within the new monomer **M2**, decreasing the T_g of the polymer of nearly 20 °C compared to the polymer made from **M1**.

As a fair comparison between polythiocarbonates and polycarbonates, **P3** was prepared by the copolymerization of bis α CC **M2** with triethylene glycol (TEG), a diol mimicking the dithiol used in this study. The reaction was carried out in DMF at 25 °C in the presence of 5 mol% of DBU as catalyst. The so-produced polymer was characterized by an even lower T_g of -19 °C (Table 1). It is however not clear if the difference in T_g between **P2** and **P3** is due to the thiocarbonate/carbonate linkage or the presence of a little amount of rigid cyclic linkages in **P2**. The three synthesized polymers also presented a high thermal stability, with a degradation temperature at 5wt% ($T_{\text{deg},5\%}$) around 240°C for the polythiocarbonate, and around 260°C for the polycarbonate (Table 1).

Table 1 – Molecular and thermal properties of the polymers **P1**, **P2** and **P3** (after purification).

Polymer	M_n (g/mol)	M_w (g/mol)	D	$T_{\text{deg},5\%}$ (°C)	T_g (°C)	Cyclic linkage (%)
P1	8700	19800	2.27	245	8	9
P2	9300	19500	2.09	238	-10	7
P3	16600	32800	1.98	262	-19	0

Evaluation of the ionic conductivity of PMTCs

Encouraged by the drop in T_g induced by **M2**, rich in typical Li conducting groups (ether and thioether bonds)^[32–35], the three polymers **P1-3** were evaluated as solid polymer electrolytes (SPEs). For this purpose, the materials were mixed with 30 wt% LiTFSI in acetonitrile prior to solvent removal.

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The anhydrous ionic conductivity of the SPEs was measured by electrochemical impedance spectroscopy (EIS) in a temperature range of 25 to 100 °C. As shown in Figure 1a, the installation of additional thioether and ether groups within the polymer backbone is highly favorable for the conductivity of **P2** ($1.88 \times 10^{-6} \text{ S.cm}^{-1}$) which is 2.5 times higher at 25 °C than **P1** ($7.38 \times 10^{-7} \text{ S.cm}^{-1}$). The ionic conductivity of **P3** ($2.09 \times 10^{-6} \text{ S.cm}^{-1}$) was very similar to **P2**, indicating that thiocarbonates or carbonates linkages seem to have only slight impact on the ionic conductivity. The amount of cyclic carbonate linkage in **P1** and **P2** is rather low (< 10 mol%) and is thus expected to benefit to ionic conductivity as already highlighted by our group^[36]. Although **P3** was characterized by a lower T_g enabling high motion within the chains, the initial value of -19 °C was readily increased to -2 °C by addition of 30 wt% of LiTFSI. Figure 1b shows the second heating cycle for the polymers as a function of the lithium salt concentration. It is observed that the T_g increases with increasing salt concentration in the electrolyte. This phenomenon is related to a higher concentration of cations and charged ionic agglomerates that limit the movement of the polymer chains^[37,38]. Upon addition of the salt, T_g s of **P2** and **P3** become rather similar.

This study highlights that careful tuning of the polymer structure through systematic monomer design allows to reach higher ionic conductivities. Using this strategy by making the monomer **M2** containing flexible groups, decent ionic conductivity could be reached without using long PEO chains which generally induced crystallization. Switching from monothiocarbonate to carbonate linkages did not seem to have major impact on the ionic conductivity of the electrolyte.

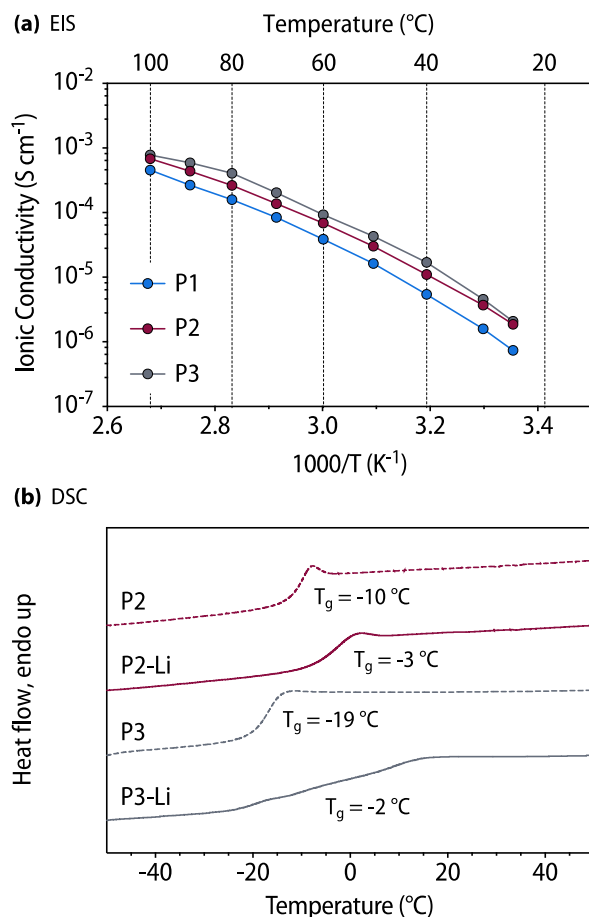


Figure 1 – (a) Ionic conductivity as a function of temperature for the polymers **P1**, **P2** and **P3** with 30 wt% LiTFSI, (b) DSC curves of the second heating for **P2**, **P3**, and **P2-Li** and **P3-Li** containing both 30 wt% of LiTFSI.

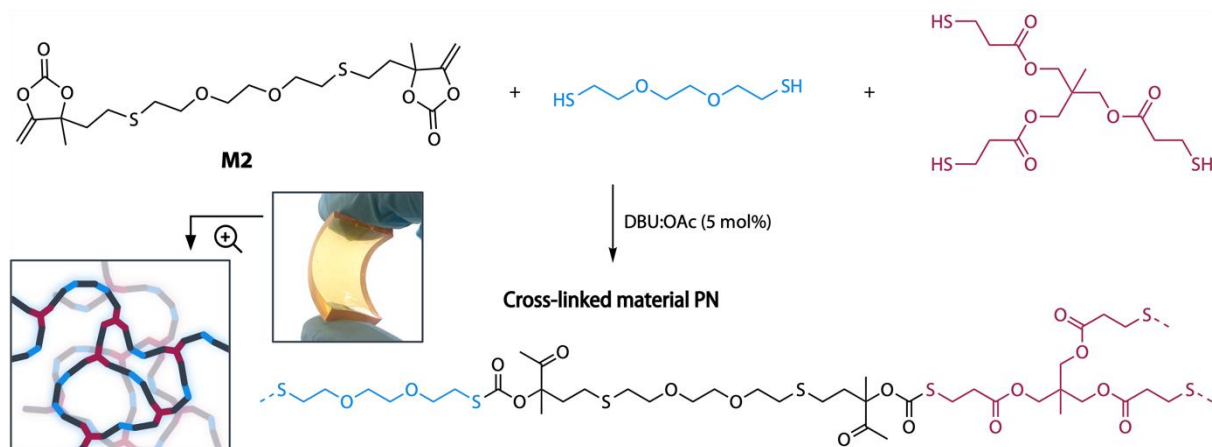
Solvent-free synthesis of a PMTC network

Thanks to the highly flexible segment in **M2**, the liquid monomer can be used for solvent-free formulations. After optimization of the conditions, the polymer network **PN** was easily synthesized by mixing **M2**, the dithiol, and a trithiol in a 1 : 0.5 : 0.33 molar ratio (Scheme 3). For a further application as solid-state electrolyte for batteries with enhanced mechanical properties, the network was designed to mimic the reported polymer **P2** while adding sufficient cross-linker to reach desired mechanical properties. The method for producing **PN** is straightforward: the components are mixed together with the catalyst (DBU:OAc) at room temperature and the homogeneous viscous mixture is transferred into a silicon mold. The polymer is then cured at 50°C for 22h to yield a very flexible self-standing film (Scheme 3). It is noteworthy that the polymerization was performed without any solvent, under air, and in mild curing temperatures. This method

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is also scalable and up to 10 g of **PN** was produced in one batch, highlighting the robustness of this chemistry to easily provide PMTC networks.

Although solution polymerizations were carried out at room temperature, no curing was observed in these conditions for the solvent-free system. It was hypothesized that solvents influenced the reaction. However, a full understanding of these effects is out of the scope of this paper. After optimization, it was found that a slight increase of temperature (25 to 50 °C) was enough to provide curing without affecting the type of polymer linkages.



Scheme 3 – Reaction for the polymerization of **M2**, the dithiol, and the trithiol to furnish the cross-linked material **PN**.

The network was characterized by ATR-IR spectroscopy, which showed a nearly complete disappearance of the band at 1815 cm^{-1} which belongs to the monomer **M2** carbonyl stretching (Figure S16), attesting for the almost completeness of the reaction. A moderate gel content of 76 % in THF was measured with a swelling degree of 326 %. DSC analysis of the network showed that it was totally amorphous with a low T_g of $-34\text{ }^\circ\text{C}$.

As evidenced in our previous publication, the formation of the thiocarbonate is reversible in the presence of the catalyst^[11] (Figure 2a). Although this might be seen as a drawback as it does not allow to provide full conversion and thus high molecular weight linear chains, this particularity can be exploited to design a dissociative covalent adaptable network (CAN)^[39]. To assess if the network can be re-processed through its reversible bonds, the dynamic nature of **PN** was studied by dynamic mechanical analysis (DMA) and rheology. First, a temperature ramp DMA analysis was performed and the polymer behaved as expected for dissociative-type CANs, displaying a constant rubber plateau

above T_g followed by a drop of the storage modulus starting around 100 °C due to entropically favorable excessive bond dissociation (Figure 2b). Stress relaxations experiments at different temperatures were then performed from 50 to 80 °C. As shown in Figure 2c, **PN** is able to relax following a Kohlrausch–Williams–Watt (KWW) stretched exponential model^[40,41] and relaxation times were extracted out of the data through curve fitting (Table S1 & Figure S17). The material displayed fast relaxation from 4 s at 80 °C to 150 s at 50 °C. An Arrhenius plot was built from the extracted relaxation times at the different temperatures and a linear correlation was observed, rendering possible to calculate a flow energy activation of 111 kJ/mol (Figure 2d).

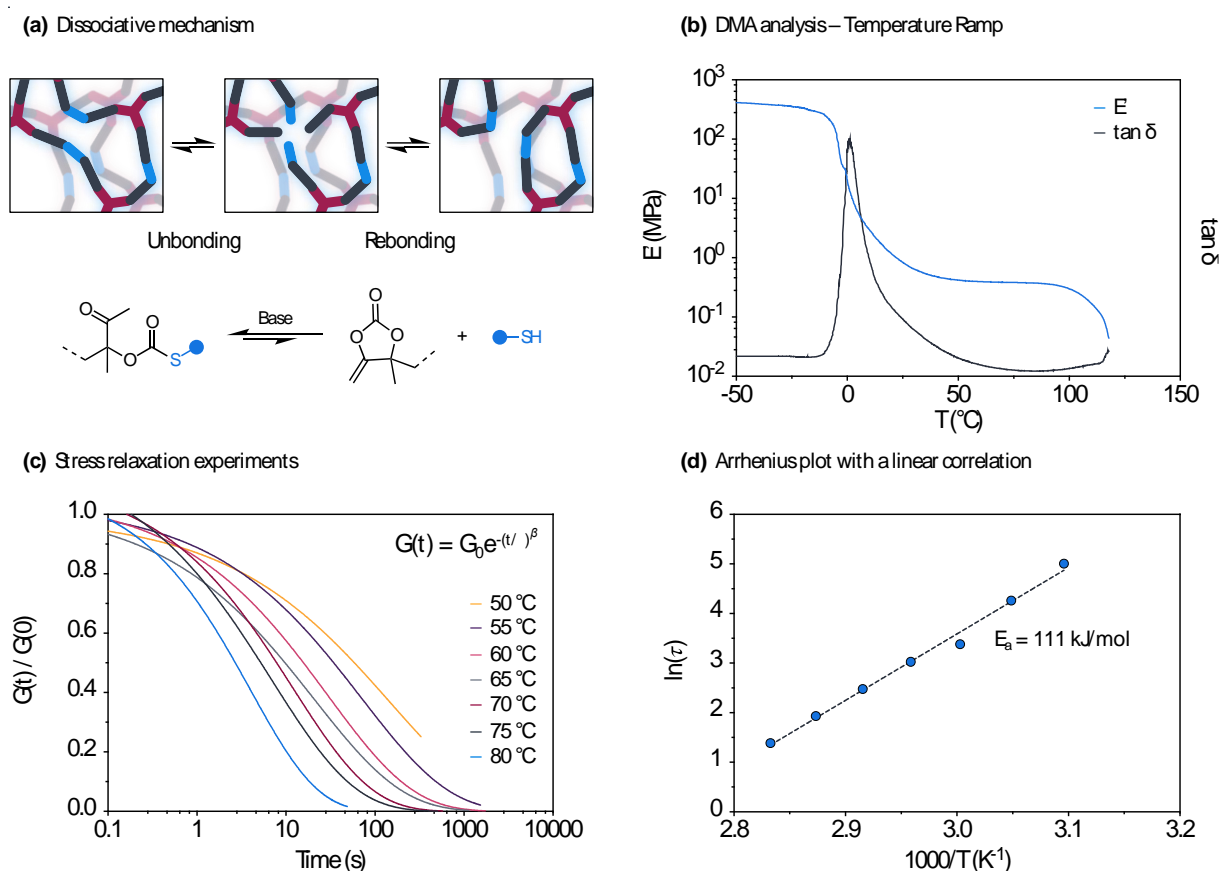


Figure 2 – (a) Dissociative mechanism of the monothiocarbonate linkage in equilibrium with α -alkylidene cyclic carbonate and a thiol, (b) DMA trace of **PN** displaying the $\tan \delta$ and the modulus along an increasing temperature, (c) Stress relaxation fitted curves using the stretched exponential model at different temperatures, (d) Arrhenius plot from the extracted relaxation times of **PN** showing a linear correlation.

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The mechanical properties of **PN** were then evaluated by stress/strain experiments. The material was thus cut in pieces and reprocessed by hot pressing at 70 °C for 15 min. The flat film was cut into rectangular pieces prior DMA analysis. **PN** featured a Young's modulus of 0.51 ± 0.04 MPa, a stress at break of 0.24 ± 0.04 MPa, and a strain at break of 134 ± 16 %, indicating that the polymer is a very flexible material (Figure S18).

Preparation and electrochemical characterization of SPE membranes

As the linear polymers were promising materials for solid-state electrolytes but were lacking decent mechanical properties, the crosslinked material **PN** was evaluated for this application. This **PN** had thus to be loaded by a Li salt, here LiTFSI, in order to impart it ion conductivity. However, adding this salt to the previously described solvent-free formulation inhibited the crosslinking reaction. This was certainly due to strong binding of a high amount of lithium metal to DBU, known to be a good ligand for metal complex catalyzed reactions^[42,43]. To solve this issue, we took advantage of the reprocessing ability of **PN** to prepare the SPE membranes through a facile protocol. The polymer was first reprocessed by hot pressing at 70 °C for 10 min to the desired shape and precise thickness. The material was then immersed in a solution of LiTFSI in acetonitrile for 12h prior evaporation of the solvent, yielding a self-standing SPE membrane loaded by 30 wt% of Li salt. For comparison, a membrane was prepared by direct cut out of the raw material after synthesis without reprocessing. However, only a larger material thickness of 1.33 mm could be obtained compared to 0.65 mm for the reprocessed material. For sake of clarity, this material will be named **CPN** (crude **PN**).

Similarly to **P2**, the **PN**-SPE was characterized by EIS and DSC. Following the same trend, the T_g of **PN** increased when introducing LiTFSI in its matrix, passing from -34 to -15 °C. However, this value is lower than the SPE made of **P2**, which was characterized by a T_g of -3 °C. This higher mobility was highlighted by a higher ionic conductivity at room temperature (5.89×10^{-6} S.cm⁻¹ for **PN** vs 1.88×10^{-6} S.cm⁻¹ for **P2**). However, the ionic conductivity of **P2** was similar to the one of **PN** at 60 °C and superior at higher temperatures, certainly due to the restricted mobility of **PN** containing covalent cross-links. **CPN** was characterized by a very similar ionic conductivity compared to **PN**, showing negligible effect of reprocessing (Figure S19).

The electrochemical stability of the electrolyte as a function of the applied potential is an important parameter for the direct application of this material. Figure 3c shows the linear sweep voltammogram (LSV) for the **PN** 30 wt% LiTFSI electrolyte. When scanning toward more anodic values, an increase in current is observed, attributed to the electrolyte decomposition at the interface with the electrode. The electrolyte was stable up to 4 V, enabling its use in standard lithium iron phosphate batteries. Another key parameter for the electrolyte in batteries is the lithium-ion transference number (t_{Li^+}),

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which is directly related to the fraction of the ionic conductivity that is given by the movement of lithium. Figure S20 shows ac impedance and dc polarization for the lithium-ion transference number measurements for **PN**-Li containing 30 wt% of LiTFSI electrolyte. Using the Bruce-Vincent method^[44] a lithium transport number of 0.37 was obtained. The value reported for PEO/LiTFSI systems is around 0.2, although this value is highly dependent on the LiTFSI concentration and temperature at which the measurement is made. In this case, the increase in the lithium transport number value might be related to the presence of carbonyl groups^[45].

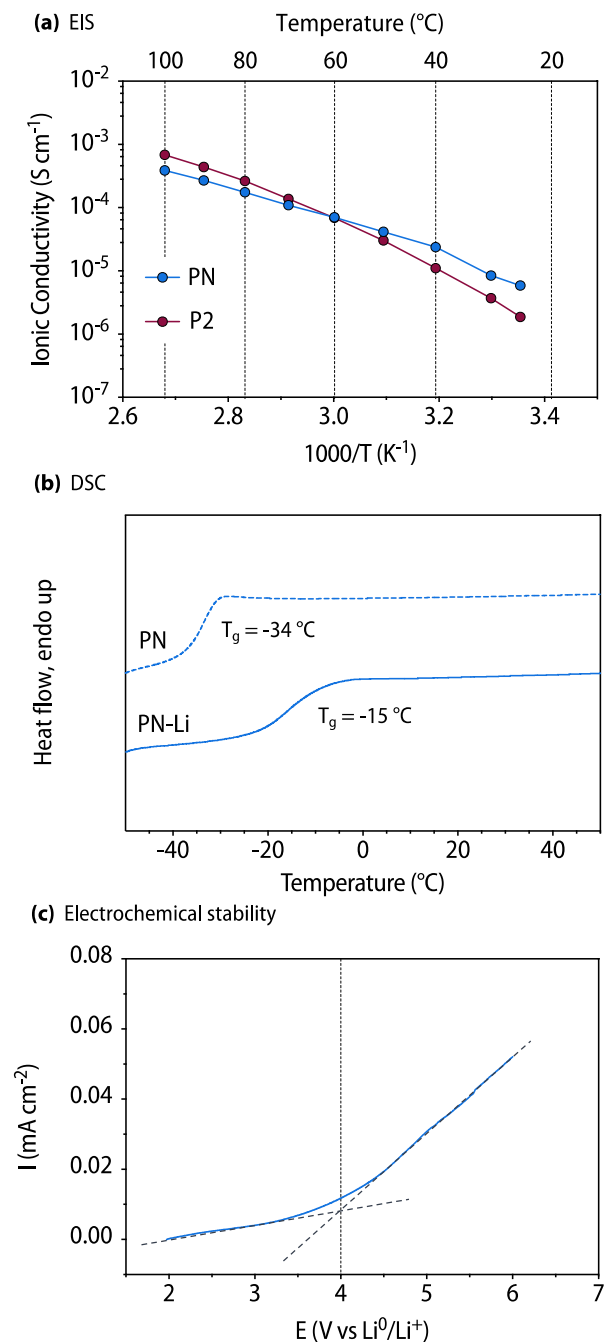


Figure 3 – (a) Ionic conductivity as a function of temperature for the polymers **P2** and **PN-Li** with 30wt% LiTFSI, (b) DSC curves of the second heating for **PN** and **PN-Li** containing 30 wt% of LiTFSI, (c) Electrochemical stability window of **PN-SPE** obtained by CV at scan rate of 10 mV s⁻¹.

The behavior of the polymer electrolyte against lithium is commonly studied by performing plating and stripping tests on a symmetrical lithium cell at different current densities. Figure 4 shows the cell polarization as a function of time for the **PN** and **CPN** electrolytes at 80 °C. For the two studied current densities (0.05 and 0.10 mA cm⁻²), it was observed that the overpotential in both electrolytes is higher when a higher current density is used. The cells were cycled for 180 h showing a slight increase in the overpotential with time. Interestingly, **PN** has shown drastically lower overpotential as compared to **CPN** though their ionic conductivity was similar (Figure S19). The reduced thickness of the SPE (0.65 mm for **PN** and 1.33 mm for **CPN**) is known to be critical for high battery performance as it imparts the system with reduced internal resistance^[46]. The ability to re-process the polymer network into membranes of controlled thickness is thus desirable to reach optimal performances for the electrolyte in lithium batteries. These materials have shown to be stable with lithium metal which opens their application in lithium batteries.

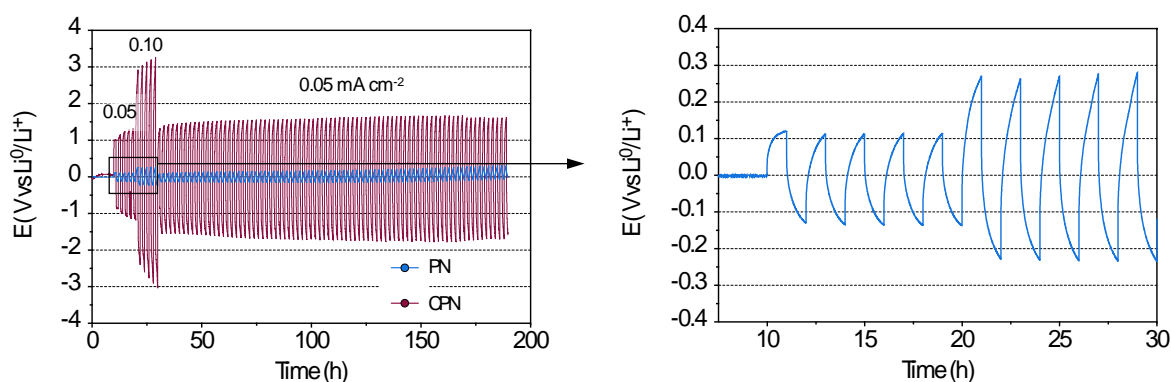


Figure 4 – Potential as a function of time for symmetrical lithium cells from **PN** and **CPN** cycled at 0.05 and 0.1 mA cm⁻² at 80 °C.

Conclusion

This work described a facile route toward cross-linked CO₂-sourced poly(monothiocarbonate)s and their potential as solid polymer electrolytes for Li-batteries. A new liquid bis(α -alkylidene cyclic carbonate) monomer was designed and easily synthesized in high yields following an up-scalable process by valorizing CO₂ as a carbon feedstock. Linear polymers were first synthesized and characterized to assess the impact on this new monomer on the thermal properties and the ionic conductivity. In contrast to previously reported poorly soluble monomers, the liquid monomer could be used in solvent-free formulation to deliver a cross-linked material in a simple one-step

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fashion under mild curing conditions. Owing to the dynamic character of the monothiocarbonate linkages, the covalent adaptable nature of the network was probed and the covalently cross-linked polymer could be re-processed into membranes for solid polymer electrolytes. The SPE was characterized by EIS to measure the ionic conductivity of **PN** reaching $5.89 \times 10^{-6} \text{ S.cm}^{-1}$ at room temperature with a $t_{\text{Li}^+}=0.37$. The electrochemical stability of the material (4.0 V vs Li^0/Li^+) was high enough to be applicable in commercial lithium iron phosphate batteries. Finally, the stability against lithium metal was probed with almost 200 h of stable cycling in lithium symmetrical cells at 0.05 mA cm^{-2} . This paper thus describes the first route to poly(monothiocarbonate)s-containing CAN networks under solvent-free and mild conditions that have a potential to be used as solid electrolytes in batteries. Current works are focusing on the optimization of the polymer structure to improve the ion conductivity and on the recycling of the final product by exploiting the dissociative behavior of the material.

Experimental section

Synthesis of dione 8,11-dioxa-5,14-dithiaoctadecane-2,17-dione (DO2)

To a mixture of DMDO (28.7 g, 0.15 mol, 1 eq.) and a catalytic amount of DBU (228 mg, 1.5 mmol, 0.01 eq.) in chloroform (125 mL) was added dropwise MVK (25.2 g; 30.4 mL, 0.36 mol, 2.4 eq.) under continuous stirring in an ice bath. The reaction was then driven in air for 30 min at rt. The mixture was diluted with 450 mL of chloroform and extracted with 3 x 600 mL of water. The organic layer was dried over MgSO_4 and filtered. The solvent was then removed under vacuum to yield a white solid (46.5g, isolated yield 96%); mp = 30 °C; ^1H NMR (400 MHz, DMSO-d_6) δ 3.55 (t, $J = 6.4 \text{ Hz}$, 4H), 3.52 (s, 4H), 2.76-2.62 (m, 12H), 2.1 (s, 6H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 207.4, 70.7, 70.0, 43.6, 31.2, 30.2, 26.0. See figures S1 and S2 for ^1H - and ^{13}C -NMR spectra, respectively.

Synthesis of bispropargylalcohol 3,18-dimethyl-9,12-dioxa-6,15-dithiaicosa-1,19-diyne-3,18-diol (BPA2)

Ethynylmagnesium bromide solution (800 mL, 0.5 M in THF, 0.4 mol, 3.1 eq.) was added in a two-necked round-bottom flask under nitrogen atmosphere. **DO2** (41.86 g, 0.13 mol, 1 eq.) dissolved in a minimal amount of THF was added dropwise to the solution. After stirring for 24h at room temperature, the reaction was quenched by the addition of a saturated ammonium chloride (NH_4Cl) solution (260 mL). The formed precipitate was removed by centrifugation followed by filtration. Diethylether (300 mL) was added to the filtrate. The aqueous phase was extracted with diethylether (3 x 300 mL). The combined organic phases were dried on MgSO_4 and filtered. The solvent was removed under vacuum. The viscous oil was mixed with a small amount of diethylether

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and purified by flash chromatography onto silica (eluent: diethylether). **BPA2** was collected as a yellow viscous oil after evaporation of the solvent (48.2 g, isolated yield 95%); ^1H NMR (400 MHz, DMSO- d_6) δ 5.38 (s, 2H), 3.56 (t, J = 6.8 Hz, 4H), 3.53 (s, 4H), 3.27 (s, 2H), 2.63 (m, 8H), 1.77 (m, 4H), 1.35 (s, 6H); ^{13}C NMR (100 MHz, DMSO- d_6) δ 88.9, 73.5, 70.6, 70.0, 66.2, 44.2, 31.1, 30.2, 27.1. See figures S3 and S4 for ^1H - and ^{13}C -NMR spectra, respectively.

Synthesis of bis α CC 4,4'-(6,9-dioxa-3,12-dithiatetradecane-1,14-diyl)bis(4-methyl-5-methylene-1,3-dioxolan-2-one) (**M2**)

BPA2 (48.2 g, 0.129 mol, 1 equiv.), DBU (0.98 g, 6.45 mmol, 0.05 eq.), CuI (1.23 g, 6.45 mmol, 0.05 eq.) and MeCN (25 mL) were added in a 250 mL high pressure autoclave. The reactor was charged with 40 bar of CO₂ at 25 °C. After 24h, CO₂ was discharged by depressurization of the reactor. The content of the autoclave was dissolved in a minimum amount of CH₂Cl₂ and the mixture was purified by flash chromatography onto silica (eluent: CH₂Cl₂/diethylether 80/20). The solvent was evaporated and the viscous oil was dissolved back in CH₂Cl₂. Chelex resin (200 mg / g of mixture) was added to trap residual copper and the mixture was stirred at rt for 4h. The resin was filtered and stored to be recycled. The solvent was removed under vacuum to yield a yellowish oil **M2** (59.6 g, isolated yield 93 %); ^1H NMR (400 MHz, DMSO- d_6) δ 4.87 (d, J = 4 Hz, 2H), 4.69 (d, J = 4 Hz, 2H), 3.56 (t, J = 6.6 Hz, 4H), 3.51 (s, 4H), 2.68 (t, J = 6.6 Hz, 4H), 2.54 (m, 4H), 2.14 (m, 4H), 1.60 (s, 6H); ^{13}C NMR (100 MHz, DMSO- d_6) δ 156.9, 151.2, 87.3, 86.8, 70.8, 70.0, 39.7, 31.1, 25.9, 25.7. See figures S5 and S6 for ^1H - and ^{13}C -NMR spectra, respectively.

General synthetic procedure of the linear polymers P1 and P2

A bis α CC (**M1** or **M2**; 2 mmol; 1 eq.) was added to a reaction tube together with the dithiol DMDO (2 mmol; 1 eq.), DBU:OAc (0.04 mmol; 0.02 eq.) and DMF (1 mL). The tube was stirred at 25°C. After 24h, the mixture was diluted and dialyzed in acetone overnight. The solvent was removed under vacuum and the viscous oil was then dried overnight under vacuum at 60 °C. The molecular characteristics and thermal properties of the polymers are summarized in Table 1.

Synthetic procedure of the linear polymer P3

Bis α CC **M2** (2 mmol; 1 eq.) was added to a reaction tube together with the diol TEG (2 mmol; 1 eq.), DBU (0.1 mmol; 0.05 eq.) and DMF (1mL). The tube was stirred at 25°C. After 24h, the mixture was diluted and dialyzed in acetone overnight. The solvent was removed under vacuum and the viscous oil was then dried overnight under vacuum at

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60 °C. The molecular characteristics and thermal properties of the polymer are summarized in Table 1.

Preparation of the poly(thiocarbonate) network

Bis α CC **M2** (15.68 mmol; 1 eq.), the dithiol DMDO (7.84 mmol; 0.5 eq.), the trithiol trimethylolpropane tris(3-mercaptopropionate) (5.17 mmol; 0.33 eq.) and DBU:OAc (0.78 mmol; 0.05 eq.) were added to a vial and stirred for 30 min under air. The viscous mixture was transferred into a silicon mold and was placed in an oven at 50 °C under air. After 22h, a well-defined film is removed from the mold.

Preparation of the solid polymer electrolytes

The electrolytes were prepared by solvent casting method. **P1**, **P2** and **P3** were dissolved in acetonitrile and 30 wt% LiTFSI were added, then placed in a silicon mold and the solvent was allowed to evaporate at room temperature. Subsequently, the electrolytes were dried under vacuum for 12 h before measurements by EIS and DSC. Data are shown in Figure 1.

In the case of **PN** with 30 wt% LiTFSI, an acetonitrile solution of 30 wt% LiTFSI with respect to the weight of the membrane was prepared and this solution was allowed to adsorb onto the polymer for 12 h. The solvent was then removed under vacuum at 30 °C. EIS and DSC data are shown in Figure 3.

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