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Potential of polymethacrylate pseudo crown ethers as solid state polymer electrolytes†

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The association of kinetic studies, DFT calculations and ¹H–⁷Li NMR analyses allowed the control of the *cyclo*-ATRP of PEG₉DMA and the production of polymethacrylate pseudo crown-ethers of various molar masses. Their potential to act as a solid-state polymer electrolyte in Li-ion batteries has been highlighted and may come from the supramolecular organization of the *cyclo*-PEG forming a Li⁺ diffusion channel.

Lithium-ion batteries (LIBs) operate by transferring electrons from a lithium insertion compound to a host intercalation material upon charging, with a concomitant migration of Li ions between the two electrodes *via* an electrolytic medium, and *vice versa* for discharging.¹ The nature of the electrolyte is a critical component to improve the LIB performances. Solid polymer electrolytes (SPEs) are becoming increasingly attractive for LIBs due to their excellent properties such as safety and flexibility.² Since Wright's discovery of ionic conductivity in poly(ethylene oxide) (PEO) complexes with alkali metal salts^{3,4} and Armand's suggestion of a PEO conductor as a material of interest for the development of electrochemical devices,⁵ polymer electrolytes have been extensively investigated as promising candidates to prepare thinner, lighter and safer LIBs. Optimizing the lithium diffusion into a polymer matrix requires a detailed description at the microscopic level of the structure of the polymer-ion complexes. Theoretical and

experimental studies indicate that the Li ion diffusion results from a subtle interplay between the PEO chain dynamics and the Coulomb interactions between cation–anion, cation–chain, and anion–chain.⁶ The Li⁺ migration is typically described *via* a hopping mechanism in which the charge hops between trapping centers with the help of the segmental dynamics in the amorphous phase of the PEO-based complex.⁷ Interestingly, ionic conductivities have also been measured in crystalline polymer matrices yielding a directional motion of Li⁺ ions well separated from the anionic counterparts.⁸

Macrocyclic polyethers, or crown-ethers (CEs), are known to solvate cations by expelling the associated anions out of the coordination sphere. In 1981, Newman already raised the possibility of using CEs to improve the lithium conductivity, stating that weakly associated CE/Li⁺X[−] complexes may exhibit fast cation conduction.⁹ Moreover, the ability of the crown ether rings to stack, forming diffusion channels, may considerably improve the cation motion rendering CEs even more attractive for the development of ionic conductive materials.^{9,10} The limited research made on poly(CE) points to very poor ion-conductivities (σ) at r.t. (10^{-10} S cm^{−1} < σ < 10^{-8} S cm^{−1})¹¹ which may arise from the architecture of the poly(CE), with either an inappropriate CE cavity or an inherent incapacity for the CEs to form stable diffusive channels. Considering that the inability of CE rings to self-assemble might come from the presence of the flexible arm linking the CEs to the poly(meth)acrylate backbone, a series of “arm-free” polymethacrylate pseudo crown ethers has been prepared to favor the formation of ion-channels by stacking of macrocycles.¹⁰ To that end, we revisit here the cation template-assisted polymerization method developed by Sawamoto¹² by adapting it to a controlled radical cyclo-polymerization strategy (Scheme 1).

In order to promote an efficient diffusion of the lithium cation inside the channels formed by the association of the adjacent crown-ether macrostructures, the size of the poly(ethylene glycol) dimethacrylate (PEGDMA) used as a macromonomer is of primary importance.¹³ Accordingly, PEG₉DMA (carrying 9 –CH₂CH₂O– repeating units) has been selected since the crown-ether

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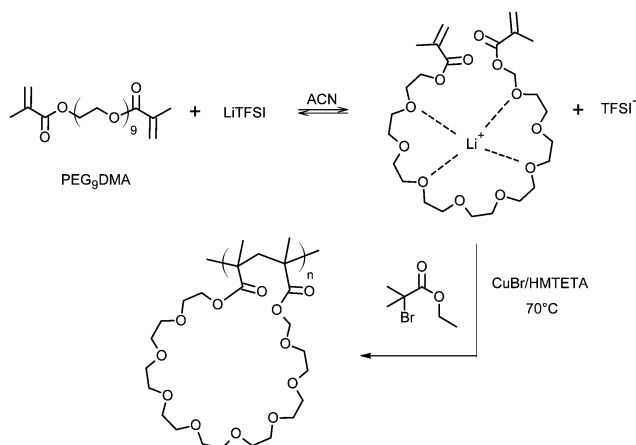
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Scheme 1 Cation template-assisted cyclopolymerization of poly(ethylene glycol) dimethacrylate (the LiTFSI salt is omitted in the final polymer structure).

generated allows an electrostatic interaction with Li⁺ but presents a low efficiency of complexation.¹³ Prior to the cation template-assisted cyclopolymerization, the ability of the monomer to interact with the lithium cation was evaluated by ¹H and ⁷Li NMR using bis(trifluoromethane)sulfonimide lithium (LiTFSI). Acetonitrile (ACN) was selected due to its high dielectric constant¹⁴ and its ability to dissolve electrolyte salts. Using the residual ACN signal as an internal reference, a single set of resonances is observed upon the addition of LiTFSI, with the ¹H chemical shifts of PEG₉DMA moving all downfield with respect to their original positions as the LiTFSI:PEG₉DMA ratio is increased from 0.1 to 2.0 (Fig. S2 in the ESI†). The ¹H resonances shift to different extents, ranging from 0.003 to 0.093 ppm. Simultaneously, the ⁷Li resonance moves downfield by 0.48 ppm in the same titration range (Fig. S3, ESI†). Within this range, the chemical shift changes appear to vary linearly as a function of the LiTFSI:PEG₉DMA ratio. The presence of a direct interaction between the lithium ion and the PEG chain was demonstrated by heteronuclear NOE spectroscopy (HOESY) on the system with a 2.0 LiTFSI:PEG₉DMA ratio (Fig. S1, ESI†). In this spectrum, clear ¹H-⁷Li NOE contacts can be found between the lithium ion and the various CH₂ groups of the PEG chain but not with the methacrylate signals, thus indicating a proximity only with the former. Taken together, these data reveal a dynamic interaction around the equilibrium characterized by a fast exchange on the ¹H and ⁷Li NMR time scales whereby lithium ions selectively interact with the crown ether part of the PEG₉DMA macromonomer.

The cyclopolymerization of PEG₉DMA has been realized by atom transfer radical polymerization (ATRP) in ACN at 70 °C using ethyl α -bromoisobutyrate (EBI) as the initiator and a catalytic complex of CuBr and HMTETA ([EBI]₀ = [CuBr]₀ = 2[HMTETA]₀). Polymerizations were performed for a [PEG₉DMA]₀ of ca. 0.15 M in the presence of LiTFSI. To assess the impact of the lithium salt content on both control and kinetics, a series of reactions was performed by varying the initial amount of LiTFSI ($0 \leq [\text{LiTFSI}]_0/[\text{PEG}_9\text{DMA}]_0 \leq 2$) while keeping constant all

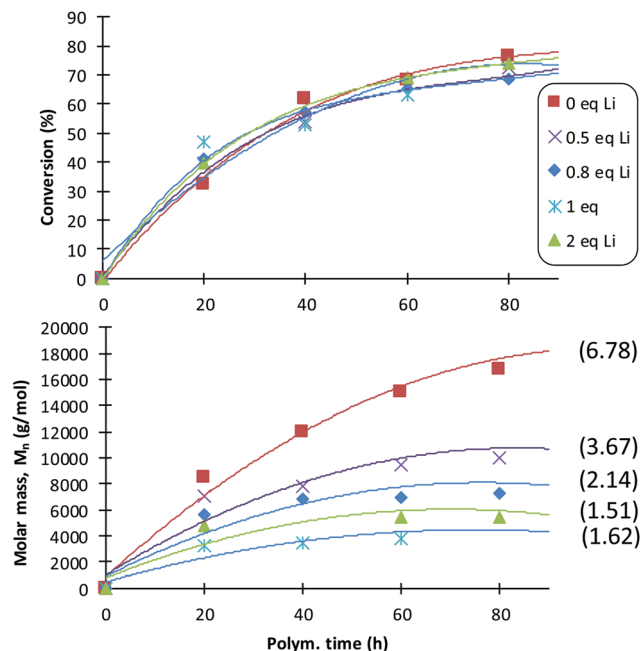


Fig. 1 Influence of the LiTFSI initial content (here in equivalents with respect to [PEG₉DMA]₀) on conversion (top) and molar mass (bottom). Dispersities of the crude final polymers are shown in parentheses.

other parameters. The targeted degree of polymerization ($DP = [\text{PEG}_9\text{DMA}]_0/[\text{EBI}]_0$), representing the number of *cyclo*-PEG chains per polymethacrylate backbone, was initially set at 10. The resulting molecular weight and conversion data indicate that the salt only slightly affects the kinetics, but it has a tremendous impact on the control of the reaction (Fig. 1). Using a default of LiTFSI clearly leads to cross-linking reactions (gelation) which increase considerably both the molar mass and the dispersity ($2 < D_M = M_w/M_n < 6.8$). By using a minimum of 1 eq. of lithium salt per PEG₉DMA, the experimental molar mass (determined by SEC) increases proportionally to the degree of conversion and the polymerization proceeds homogeneously with no gelation. When 1 eq. of lithium salt is used, the relatively good control of the process is deduced from the fact that the experimental molar mass ($M_{n,SEC} = 4300 \text{ g mol}^{-1}$, $D_M = 1.62$) is in close agreement with the theoretical one (conv. ~ 0.7 , $M_{n,th} = 4100 \text{ g mol}^{-1}$).

Interestingly, the control of the process is refined for a [LiTFSI]₀-to-[PEG₉DMA]₀ initial ratio of 2, as attested by the decrease in the final dispersity ($D_M \sim 1.5$). To better understand the role of the amount of LiTFSI on the dispersity, molecular dynamics simulations (see the ESI† for details) have been performed on two extreme cases, *i.e.*, a PEG₉DMA macromonomer in the absence or presence of 2 lithium cations.

Analysis of the trajectories of molecular dynamics runs at room temperature (Fig. 2) reveals that, in the absence of the salt, the monomer molecule is quite flexible, as demonstrated by the large fluctuations (from 4 Å to 36 Å) of the distance between the reactive methacrylate groups, *i.e.*, between the methylene carbons of the methacrylate functions. Introducing two equivalents of lithium cations induces strong changes in

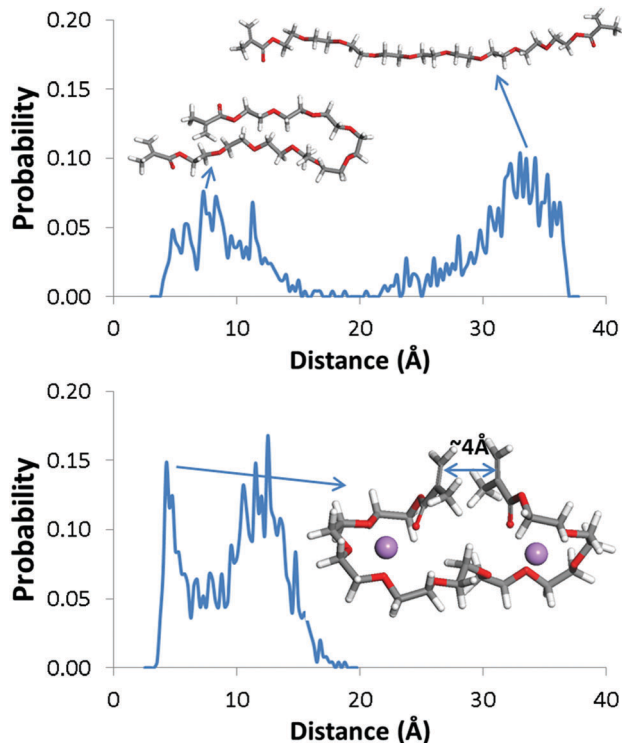


Fig. 2 Distribution profiles of the distance between the two reactive groups of a PEG₉DMA molecule, isolated (top) and complexed with two (bottom) lithium cations together with illustrations of characteristic structures, as extracted from the molecular dynamics trajectories. The size of the lithium cations (in purple) has been adapted for clarity.

the three-dimensional structure of the complex. To avoid electrostatic repulsions between the lithium atoms, the PEG segment surrounds them through interactions with its ether groups, in agreement with the absence of ¹H-⁷Li NOE signals. Interestingly, in these conformations, the reactive methacrylate end groups get closer to each other (from 4 Å to 20 Å) and therefore should favor the cyclisation processes.

Polymerizations were then realized for higher polymerization degrees (DP = 50 and 100, [LiTFSI]₀/[PEG₉DMA]₀ ~ 1.5), followed by ¹H-NMR and SEC analyses. Conversions were limited to *circa* 70–75% to prevent deleterious reactions. The number-average molecular weights increased with the targeted DPs while dispersities were kept below 1.7. Table 1 summarizes the molecular characterizations of samples purified from residual PEG₉DMA (Fig. S4, ESI[†]).

Table 1 Molecular characterizations of P(cycloPEG₉DMA) produced by Li⁺ template-assisted cyclopolymerization of PEG₉DMA

Entry	DP _{exp.} ^a	M _n SEC ^b (g mol ⁻¹)	D _M ^b	T _g ^c (°C)	T _g -Li ^d (°C)
1	8	4300	1.5	-14	-22
2	35	7200	1.6	-14	-19
3	70	9600	1.7	-15	-10

^a Determined from the conversion. ^b Determined by SEC analysis in THF at 35 °C with PEO calibration. ^c Measured by DSC analysis on a pristine polymer. ^d Measured by DSC analysis on the polymer-LiTFSI complex ([EO]₀/[Li]₀ = 20).

It is generally agreed that ion-transport above the glass transition temperature (T_g) is dependent on the segmental motion of polymer chains. To maximize the ionic conductivity, the polymer hosts should be flexible and amorphous and should present a low T_g value.¹⁵ Unlike P(CE)-salt mixtures,¹¹ the addition of LiTFSI on P(cycloPEG₉DMA) ([EO]₀/[Li]₀ = 20) is accompanied by a variation of the T_g value depending on length of the polymer (Table 1 and Fig. S5–S10, ESI[†]). Generally, the incorporation of a lithium salt into a PEG-based macrostructure is accompanied by an increase of the T_g value due to the good complexation of the cation by the ethylene oxide units and the increase of rigidity. In the present case, it seems that the separation of both the lithium cation and the TFSI anion (by the effective complexation of the Li⁺ by the pseudo crown ether) is compensated by a plasticization of the mixture from the TFSI anions. If the plasticization is important for a low molar mass P(cycloPEG₉DMA), its effect is less and less pronounced for higher molar mass structures. Both the low T_g values and the absence of crystallinity prompted us to assess the conductive character of the three samples. Fig. 3a shows the Nyquist plot from a representative electrochemical impedance spectroscopy (EIS) experiment realized on the P(cycloPEG₉DMA)₈ complex at 293 K; the response is typical of an electrolyte behavior. The measurements on the three investigated systems at different

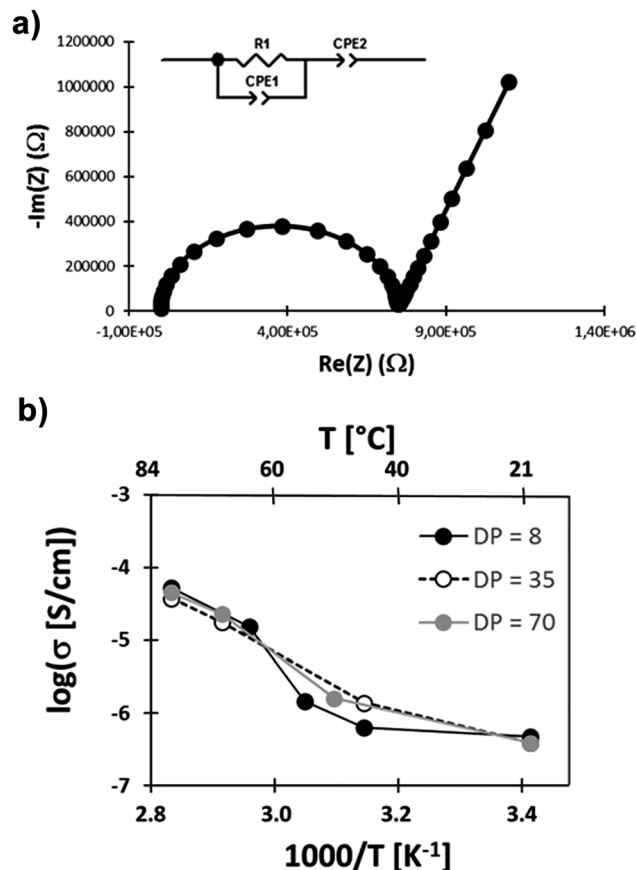


Fig. 3 (a) Nyquist plot P(cycloPEG₉DMA)₈ complex at 293 K (equivalent circuit modeling in the inset). (b) Arrhenius plots of the conductivities.

temperatures are presented as an Arrhenius plot in Fig. 3b. As expected, the ionic conductivities increase as the temperature increases due to the increased mobility of the polymer chain segments in the solid polymer electrolytes. As compared to both DPs 35 and 70, the ionic conductivity of the DP 8 presents a curved evolution. This peculiar behavior (out of the scope of the present communication) might come from the viscosity of oligoPEG which follows a Vogel–Tamman–Fulcher (VTF) model. As reported, oligoPEG of 400 g mol^{-1} (quite similar to the one used here) presents a viscosity-to-temperature curve characterized by a kink for a $1000/T$ of $3\text{--}3.1 \text{ K}^{-1}$ (Fig. S11, ESI†).¹⁶

The measured values are in the range of the conductivities obtained for efficient solid polymer electrolytes,¹⁷ and are, as expected, higher than the ionic conductivities of the corresponding doped polymers carrying linear ethylene oxide dandling groups.¹⁸ For example, doped P(MMA-*r*-OEM) presents a conductivity of $2.8 \times 10^{-8} \text{ S cm}^{-1}$ at r.t., which is significantly lower than that in the present case. To prove that this difference is due to the organization of the crown-ether functions which are sufficiently large to welcome the lithium cation and let it diffuse, a comparison with a P(*cyclo*PEG₄DMA) complex has been realized. Since the crown ether cavities of P(*cyclo*PEG₄DMA) are much smaller than those of P(*cyclo*PEG₉DMA), the lithium cation is theoretically too much stabilized and should not diffuse so well. To that end, a P(*cyclo*PEG₄DMA)₁₅ complex has been prepared, characterized ($M_n = 1600 \text{ g mol}^{-1}$, $D_M = 1.32$, $T_g\text{-Li} \sim 0.9 \text{ }^\circ\text{C}$) and compared to P(*cyclo*PEG₉DMA) (Fig. S12, ESI†). As expected, the conductivities are much lower proving indirectly that the supramolecular association of P(*cyclo*PEG₉DMA) is much better to produce a diffusion pipe in which the lithium cation may diffuse. Note however that since the dispersion of micro- or nanoparticles (including SiO₂,¹⁹ Al₂O₃,²⁰ TiO₂,¹⁹ zirconia particles^{21,22} as well as zeolites²³) in PEO based solid electrolytes is effective to enhance both ionic conductivity and mechanical properties, this could be a future option to raise the ambient conductivities.

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