On the impact of the type of anion on the properties of solid-state electrolytes

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ABSTRACT

Solid-state batteries are a valuable option for sustainable energy storage. Their performance is strongly dependent on the ionic conductivity of the solid-state electrolyte (SSE). The mechanism of ion conduction in solid polymer electrolytes has been extensively studied in terms of flexibility of the polymer chains and their interactions with mobile cations that hop between conduction sites carrying the charge. The role of the counterion (i.e. anion) interacting with both the polymer and the cation has not been explored in detail. In this study we show however, that the anion can severely impact the conduction as well. The effect of the anion (I⁻, SCN⁻, BF₄⁻ and PF₆⁻) on the thermal, structural and electrical properties of a solid polymer electrolyte (15C5BA polymer) was investigated. The results clearly show that the nature of the anions can be used as a parameter to actually tune the properties of the polymer electrolyte.

1. Introduction

The transition towards a sustainable future combined with environmental awareness requires the development and implementation of energy efficient and environmentally friendly technologies. In this context energy storage plays a crucial role, with solid state batteries showing great promise as energy storage devices [1–3]. Solid state batteries rely on solid state electrolytes (SSEs) like polymers or inorganic materials. Due to their solid nature, SSEs do not suffer from leakage, are thermally and mechanically stable and are an environmentally safe alternative to liquid electrolytes [4,5]. The applicability of SSEs is often limited by their generally lower ionic conductivity compared to their liquid counterparts, especially in the case of solid polymer electrolytes [6]. Fast ionic conduction is an essential property to expand the relevancy and operating window of these type of materials. The mechanism of ion conduction in SSEs has been extensively studied and it is best described as ions hopping from one conduction site to another [5,6]. This hopping mechanism is heavily influenced by the activation energy (E_a) necessary for the ion to hop between sites [7]. A lower E_a implies a lower energy barrier and favours fast ionic transport. This activation energy is a consequence of the interactions arising between the ions and the matter of the matrix of the solid electrolyte [5]. Ion hopping is enhanced in the case of favourable interactions between the mobile ion and the vacant site. To achieve fast ion conduction, careful choice of the matrix of the SSE is thus of central importance.

Solid polymer electrolytes based on poly(ethylene oxide) (PEO) are widely known to give rise to complexation of alkali metal ions [8] by means of ion-dipole interactions of the mobile charge carrying cations and the ether linkages of the SSE polymer backbone. This complexation behaviour serves as driving force for the ions to move from one conduction site to another. Unfortunately, the formation of favourable interactions between SSE and ions is not the only requirement to achieve high ionic conductivities. The mobility of the ions in the polymer matrix is in fact, of key importance as well. In the case of PEO-based solid electrolytes these are often limited by the high degree of crystallinity of the polymer [9]. This locks the ions in the polymeric crystal lattice and prevents their motions and hence, restricts effective ion conduction [4]. For this reason, new polymers that have favourable ion-dipole interactions like PEO while still allowing for polymer chain flexibility have been developed [9]. In this field, crown-ether containing polymers were found to be promising candidates as SSEs [9–13] due to the inherent selectivity of the crown-ether moiety for alkali metal ions combined with the enhanced flexibility of the polymeric chains.

Even though research efforts have been directed to the comprehension of the ion conduction mechanism and to the development of appropriate SSEs, very limited attention has been devoted to the

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understanding of the influence of the nature of the anions dissolved in the SSE polymer matrix on the morphological properties and ionic conductivity of that polymer matrix. Often, the focus lays on the behaviour of the cation carrying the charge (e.g. Li+ or Na+) in the solid polymer electrolyte as that is responsible for the generation of power [14–17].

The counter ion though, also has an effect on the transport properties of the solid polymer electrolyte and the nature of the counterion (i.e. anions) on the ion conductivity is often overlooked, although it does impact the ultimate battery performance. While the focus is on the cation hopping between one conduction site to another, its dissociation from the anion that precedes this, can thus have a severe influence on the ionic conductivity. Controlling the interaction of the anions with the polymeric SSE matrix is thus an important parameter as well to tune cation conduction and with that, battery performance [18,19]. It goes without saying that the design of an SSE cannot be fully rationalized without the fundamental understanding of the effect of both the cations as well as the anions on the ion conductivity.

For this reason, in this work we show how the type of anion influences the properties of the SSE. We report the preparation of a new polymer containing crown-ether functionalities (15-crown-5) and amicdic groups and its complexation with a series of sodium salts (NaI, NaSCN, NaBF4, NaPF6). The presence of the ether linkages in this new polymer allows for favourable interactions with the sodium ions thus forming the conduction sites. The amide functionalities instead, interact with the anions of the salts and play a determining role in defining the entity of the ionic conductivities of the systems. Unlike systems that have been studied before in which either ether linkages or amide functionalities are present in the polymeric structure, in our system the concurrent presence of these functionalities guarantees for the systematic study of the effect of different anions. The polymers prepared are characterized and evaluated in terms of thermal properties, crystallinity and ionic conductivity.

2. Experimental

2.1. Characterization methods

Nuclear magnetic resonance spectroscopy (NMR) spectra were recorded at room temperature on a Bruker, FT-NMR spectrometer AVANCE III HD-Nanobay (400 MHz, Bruker Ultrashield magnet, BBFO Probehead, BOSS1 shim assembly) in deuterated chloroform. Chemical shifts are given in ppm with respect to tetramethyl silane (TMS, 0 ppm) as internal standard.

Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS) was performed on a Bruker Autoflex Speed MALDI-MS instrument using DCTB (2-[(2E)-3-(4-tert-butylphenyl)-2-methylprop-2-enylidene] malononitril) as matrix. Attenuated total reflection Fourier transform infrared spectroscopy (ATR FT-IR) spectra were recorded at room temperature on a Varian Cary 3100 FT-IR spectrometer equipped with a golden gate attenuated total reflection (ATR) sampling accessory. Scans were taken over a range of 4000–650 cm−1, with a spectral resolution of 4 cm−1 and 50 scans per spectrum.

Elemental analysis was performed by Mikrolab Kolbe (Oberhausen, Germany).

Differential scanning calorimetry (DSC) measurements were recorded in hermetic T-zero aluminium sample pans using a TA Instruments Q2000 DSC equipped with cooling accessory. The DSC measurements were performed, using approximately 5 mg of compound, with three cycles of heating and cooling at a rate of 2 °C/min with an isothermal equilibration of 3 min after each heating or cooling ramp. The transition temperatures were determined from the third heating and cooling cycle using TRIOS DSC software. Prior to the measurement, the samples were dried in a vacuum oven overnight at 120 °C.

Thermal gravimetric analysis was performed using a Perkin Elmer TGA 4000. Samples were heated from 40 to 500 °C using a heating rate of 10 °C/min under a constant nitrogen flow of 20 mL/min.

Polarising optical microscopy (POM) was performed using a Leica DM 2700 M optical microscope equipped with two cross polarizers with the sample in between a Linkam hot-stage THM5600 with a Linkam TMS94 controller and a Leica DFC420C camera. The samples were heated up till melting and cooled down at 2 °C/min.

XRD profiles were recorded on a Guinier-Cu ultra-low divergence source producing X-ray photons with a wavelength of 1.54 Å and a flux of 1 × 108 photons s−1. Diffraction patterns were collected using a Pilatus 300K silicon pixel detector with 487 × 619 pixels of 172 µm2 placed at a sample to detector distance of 91 mm. Temperature was controlled with a Linkam HFSX350 heating stage and cooling unit. Measurements were performed on bulk samples.

The ionic conductivity (σ) of the polymers was evaluated by performing impedance measurements using a potentiotstat (Biologic VMP-300). A frequency range from 7 MHz to 10 Hz at 10 mV sinus amplitude with 6 measurement points per decade was applied. Data were collected from a symmetrical Swagelok-type cell consisting of two stainless steel electrodes screwed together with Swagelok pipe fittings. The diameter of each circular electrode was of 1 cm. From the impedance measurements the bulk resistance was extracted and the ionic conductivity (σ [S cm−1]) was calculated using the equation below in which R (Ω) is the bulk resistance, A (cm2) is the area of the electrode and l (cm) the thickness of the polymer electrolyte:

\[
\sigma = \frac{I}{RA}
\]

2.2. Materials and synthesis

2.2.1. Materials

Methyl gallate, 11-Bromo-1-undecene, thionyl chloride, triethylamine, trimethylolpropane tris(3-mercaptopropionate) and potassium carbonate were purchased from SigmaAldrich. 4′-Amino benzob-15-crown-5-ether was purchased from TCI chemicals Europe. Irgacure 819 was supplied by Ciba. All reagents were used as supplied without further purification. All solvents were obtained from Biosolve.

2.2.2. Synthesis of 15C5BA monomer

The synthesis of the 15C5BA monomer was performed according to previously reported literature [20]. The preparation of the 15C5BA monomer was performed as follows. 4-amino benzob-15-crown-5 (1 eq) was added in a round bottom flask with two necks. An inert atmosphere was created in the reaction flask by performing three vacuum/nitrogen cycles. The solid was then dissolved in approximately 20 mL of dry DCM. The reaction mixture was kept in an ice bath at 0 °C under magnetic stirring for 5 min. To this solution NBr2 (1.1 eq) was added and the system was left stirring for 15 min. After this time, a solution of compound 3 (1.1 eq) in approximately 10 mL of dry DCM was added dropwise to the reaction flask under magnetic stirring. Stirring was continued under an inert atmosphere subsequently at 0 °C for 2 h. After this time the system was brought to room temperature and left reacting for 16 h. The crude product was extracted three times with H2O (3 × 40 mL). The organic phase was subsequently dried with Na2SO4 and filtered via gravimetric filtration. The excess DCM was removed with
rotary evaporation. The brown sticky solid obtained was further purified by recrystallization in the minimum amount of warm EtOAc (~15 mL). This mixture was cooled down in the fridge overnight (~16 h) and the solid product obtained was separated via Buchner filtration obtaining compounds 15C5BA as a pale grey solid with a yield of 74%. ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): δ (ppm) = 1.30–1.50 (m, 36H), 1.69–1.86 (m, 6H), 1.98–2.09 (m, 6H), 3.70–3.80 (m, 8H, 2 x O-(CH₂crown)²-O), 3.85–3.93 (m, 4H, 2 x O-(CH₂crown)²-O-), 3.99–4.04 (m, 6H, 3 x O-CH₂-CH₂), 4.09–4.20 (m, 2H, CH₂crown(CH₂crown-)), 4.88–5.04 (dd, 6H, J = 10 Hz and 16 Hz, 3 x CH₂=CH), 5.74–5.87 (ddtt, 3H, J = 7 Hz, 10 Hz and 17 Hz, 3 x CH₂=CH-CH₂), 6.83–6.85 (d, J = 9 Hz, 2H, O-C₂H₂-CH₂-C-amide), 7.04 (s, 2H, 2 x CH₃ gallate), 7.48 (s, 1H, O-C₂H₂-C-amide), 7.67 (bs, 1H, NH amide). ¹³C NMR (1 MHz, CDCl₃, 25 °C, TMS): δ (ppm) = 165.92, 153.69, 149.95, 146.44, 141.94, 139.65, 132.66, 130.38, 115.28, 114.59, 112.97, 110.71, 110.71, 106.23, 74.00, 71.57, 71.49, 71.07, 70.92, 69.93, 69.33, 34.29, 34.26, 30.77, 30.11, 30.02, 30.00, 29.91, 29.83, 29.82, 29.65, 29.60, 29.43, 29.40, 26.52, ATR FT-IR (Neat, cm⁻¹): 3260, 3076, 2922, 2851, 1751, 1638, 1582, 1516, 1427, 1341, 1231, 1119, 993, 909, 845, 721. (MALDI-TOF): [M + Na⁺] calcd. for C₉₅H₇₆NO₇: 914.61; found: 914.65 [20].

2.2.3. Preparation of polymeric films

A mixture of 15C5BA monomer (1 eq), trimethylpropane tris(3-mercaptopropionate) (1eq), photoinitiator (Irgacure 819 0.5 wt%) and inhibitor (TBHQ, 0.1 wt%) was dissolved in dichloroethane (DCE). The solvent was allowed to evaporate overnight by flushing the system with nitrogen through a needle. Remaining traces of solvent were removed by placing the system under vacuum for 2 h at room temperature. Glass plates (3 x 3 cm) were first washed with water and soap, then rinsed with water. After drying with anti-scratch paper towels, the glass plates were immersed in isopropanol and sonicated for 30 min. After this time the glass cells were rinsed with acetone, air dried for 10 min and treated in a UV ozone photoreactor (Ultra Violet Products, PR-100, 20 min) to activate the glass surface. The surface of the glass plates was then modified by spin-coating a 1H,1H,2H,2H-perfluorodecyltriethoxysilane solution (1 vol% solution in ethanol) onto the activated glass substrate for 45 s at 3000 rpm followed by curing for 10 min at 100 °C. To obtain a cell with a defined gap thickness, two glass plates were then glued together with a UV active glue and spacer beads (25 μm). The 15C5BA monomer mixture was heated till melting (~120 °C) and the glass cell prepared was filled with the monomer mixture by capillary forces. After that, the polymer film was gently removed from the glass cell by opening it with a razor blade and peeling off the film.

2.2.4. Complexation of the 15C5BA films with sodium salts

A 15C5BA film was placed in a bottle containing 10 mL of DCM. At this point, the film was allowed to swell for 10 min, at room temperature in the solvent. A solution in MeOH (5 mL) of the chosen sodium salt (50 wt% over the film weight) was prepared and added to the bottle containing the 15C5BA film. The system was shaken (60 rpm) overnight at room temperature. After that, the polymer film was gently removed from the solvent mixture and allowed to shrink in air for 2 min. The system was then washed first with 2 mL of water and then with 2 mL of MeOH. The 15C5BA complexed polymeric film prepared was dried overnight in a vacuum oven at 70 °C.

3. Results and discussion

3.1. Synthesis and polymerization of 15C5BA monomer

15-crown-5 ether moiety containing monomer was chosen for its Na⁺ selectivity and synthetized according to literature [20]. The size of the 15-crown-5 moiety and the ion-dipole interactions of the polyether segments with Na⁺ allow for its preferential complexation with sodium over other alkali metal ions [21]. The successful synthesis was confirmed by ¹H NMR, FT-IR and Maldi-TOF analysis as reported in our previous work [20].

The polymerization of the 15C5BA monomer was performed employing the three double bonds present in the structure of the molecule. The double bonds reacted with a trithiol (trimethylolpropane tris(3-mercaptopropionate)) in an equimolar amount to ensure good crosslinking of the system (the molecular structure of the polymer is visible in Fig. S1). This thiol-ene reaction was photoactivated and performed in solid state to obtain polymeric films without the need of further casting/processing of the polymer. FT-IR confirms good conversion of the double bonds (Figure S2.1).

3.2. Complexation of 15C5BA with sodium salts

The 15C5BA polymer is complexed with different sodium salts (NaI, NaSCN, NaBF₄, NaPF₆) to evaluate the effect of the anions on the order and properties of the material. The polymeric films were first placed in DCM and allowed to swell to create more flexibility in the polymer chains. This ensures that the 15-crown-5 moieties are more easily accessible to the sodium salts and allow the complexation. FT-IR, elemental analysis, TGA, DSC, POM and WAXS/MAXS analysis of the films complexed with different sodium salts are discussed in the following paragraphs. All these methods confirm the successful complexation.

3.2.1. ATR FT-IR and elemental analysis

The complexation of the ions and their interaction with the amide functionalities of the 15C5BA polymer was confirmed by ATR FT-IR (Fig. 1).

The signals attributed to the amide functionalities present in the native polymer (NH at 3260 cm⁻¹ and C=O at 1638 cm⁻¹, Fig. 1, black line) appear as sharp peaks. The stretching frequency at which they fail is diagnostic for the presence of H-bonds between the amides in the polymer matrix (a magnified version of the spectra can be found in SI, Figure S2.2). After complexation (Fig. 1, NaI, NaSCN and NaBF₄ complexes) these signals become broader and shift to higher wavenumbers. This behaviour suggests the formation of a different type of interaction arising between the amides in the polymer matrix and the sodium salts. This is due to the breaking of the H-bonds and the formation of intermolecular interactions with the anions (I⁻, SCN⁻, BF₄⁻) due to their chaotropic character [20]. The polymer complexed with NaPF₆ does not experience the breaking of the H-bonds between the amides due to the non-coordinating character of PF₆⁻ [22–24]. As a consequence, the IR spectrum looks comparable to that of the native polymer. Confirmation of the successful inclusion of the ions in the polymer matrix is given by the signal at ~2200 cm⁻¹ in the spectrum of the complex with NaSCN, and at ~840 cm⁻¹ for the spectrum of the complex with NaPF₆. Those two signals are diagnostic for the respective anions (SCN⁻ and PF₆⁻).

Quantitative evidence of the presence of the sodium salts in the 15C5BA polymeric matrix was obtained through elemental analysis (Table 1). With elemental analysis, the actual amount of sodium in the polymer (experimental) was determined and this was correlated to the theoretical amount based on crown ether – ion coordination (theoretical).
Despite the use of an excess amount of sodium salts in the complexation stage, none of the polymers prepared achieved a 1:1 complexation between Na\(^+\) and the crown-ether moieties present in the polymeric structure. This can be due to incomplete swelling of the polymer films resulting in lack of space for the ions to access the interacting sites. The lowest Na\(^+\) intake is observed for the system complexed with NaPF\(_6\) and this can be related to the large size of the anion (Table 1). The Na\(^+\) uptake for the other salts used show very similar values and does not seem to be related to the size of the respective anions. This suggests that the underlying mechanism of incorporation of the sodium salts in the polymer matrix is not exclusively dependent on the size of the anions. As observed also from the FT-IR analysis, it is thought that the ease of formation of interactions between the anions and the amidic functionalities of the 15C5BA polymer is related to the nature of the anions used and their coordinating ability and with that to the amount of ion uptake.

Obviously, the concentration of the ions has an influence on conductivity in general [28, 29], with higher concentrations usually giving stronger effects. For the systems investigated in this study, all have very similar ion concentrations (as proven by elemental analysis, Table 1), except for the system with PF\(_6\), making the effects described below probably even more pronounced when this anion would be present at a similar concentration as the other anions.

### 3.2.2. Thermogravimetric analysis (TGA)

The TGA results obtained are presented in Fig. 2.

All systems studied are thermally stable till \(\sim 250^\circ\)C. For the native polymer the degradation starts at \(\sim 350^\circ\)C (Fig. 2, black curve) and no other relevant thermal events are observed. Except for the system complexed with NaPF\(_6\), all the other complexed polymers show different behaviour compared to the native one. More in detail, the polymers complexed with NaI or NaSCN experience the start of the decomposition at a lower temperature (\(\sim 250^\circ\)C; Fig. 2, blue and green curves) compared to the other polymers prepared. This is attributed to the weakening of the H-bonds between the amidic functionalities of the 15CSBA polymer and to the formation of new interactions with the counterions of the sodium salts (I\(^-\), SCN\(^-\)) [20]. The presence of H-bonds in the structure of a molecule is indeed known to increase the thermal stability of the system compared to a situation in which there is no interaction [30]. In the case of I\(^-\) and SCN\(^-\), their high H-bonding ability allows them to interfere with the H-bonds in the native polymer, to break them and to form new but similar type of interactions with the polymer.
polymer chains. Those interactions are less strong compared to the ones present in the native polymer because of the ability of the amide groups to act both as an H-bond donor and acceptor \cite{31,32}. The lower strength of the interactions between the amidic functionalities in the polymer chain and the $I^-$ or SCN$^-$ ion is responsible for the lower thermal stability of the polymers complexed with these sodium salts compared to the native polymer.

In addition to this, the polymers complexed with NaI or NaBF$_4$ show another thermal event at $\sim400^\circ$C (Fig. 2, blue and orange curve). This can be attributed to the decomposition of the sodium salts from the crown-ether cavity \cite{33}. As a matter of fact, a similar thermal behaviour is observed after complexation of the 15C5BA monomer with all the sodium salts (Fig. S3). For the polymer complexed with NaBF$_4$, the start of the degradation appears at a similar temperature as the native polymer ($\sim350^\circ$C). This behaviour is explained by the lower coordinating ability of BF$_4^-$. Unlike $I^-$ and SCN$^-$, BF$_4^-$ does not possess free electron pairs and this leads to the formation of even weaker interactions with the polymer chains. As reported in our previous work \cite{20}, in this case the H-bonds between the amide functionalities are not fully destroyed hence the thermal stability of the system complexed with NaBF$_4$ is not seriously affected. Nevertheless, like for the complexes with NaI and NaSCN, the appearance of another thermal event at $\sim440^\circ$C is observed and can be attributed to the decomplexation of Na$^+$ from the crown-ether moiety.

Finally, the thermogram obtained for the system complexed with NaPF$_6$ (Fig. 2, purple curve) closely resembles the result obtained for the native polymer. This differs from the TGA of the complexed 15C5BA monomer with NaPF$_6$ (Fig. S3) for which the same thermal event is observed. In the case of the polymer, it is hypothesized that the even lower coordinating ability of PF$_6^-$ compared to the other anions examined in this study, prevents it from strongly interacting with the amide groups of the polymer backbone thus, resulting in a limited effect on the thermal properties of the 15C5BA polymer.

3.2.3. Polarized optical microscopy

The effect of complexation of the 15C5BA polymer was studied in terms of birefringence with POM analysis. Fig. 3 shows the POM image of the 15C5BA native polymer (Fig. 3a) and that of the NaSCN complexed polymer (Fig. 3b).

Fig. 3 shows the absence of birefringence for the native 15C5BA polymer. This is attributed to the amorphous nature of the system. In case of the native polymer, potentially, alignment of the polymeric chains, hence crystallinity, could be generated by the formation of an ordered array of H-bonds between the amidic functionalities. However, this is not observed, probably due to the fast polymerization promoted by the use of equimolar amounts of cross-linking agent and 15C5BA monomer and by the high polymerization temperature close to the clearing point of the 15C5BA monomer (Figure S5.1). This lack of order, hence lack of crystallinity, makes the 15C5BA polymer optically isotropic i.e. non-birefringent.

After complexation with the different sodium salts, birefringence is visible as the formation of small spherulitic domains in the POM images (Fig. 3b, see also SI section 4). This indicates that the sodium salts allow the amorphous 15C5BA polymer to achieve sufficient order to be able to show optical anisotropy. The swelling of the polymer in DCM contributes to the flexibility of the polymeric chains therefore, allowing sodium salts to access the complexation sites. In this context, the formation of the ion-dipole interactions between the crown-ether moieties and Na$^+$, the presence of intermolecular interactions between the functionalities of the polymer (H-bond and $\pi-\pi$ stacking) and the interaction between the anions of the sodium salts and the amidic functionalities of the polymer act as a switch from optical anisotropy to molecular order.

3.2.4. Differential scanning calorimetry (DSC)

DSC analysis is used to evaluate the glass transition temperature ($T_g$) of the polymers studied and to address the polymer chain flexibility before and after complexation with the sodium salts. Fig. 4 shows the DSC thermogram of the native polymer. The DSC thermograms of all other polymers can be found in section 4 of the supporting information.

The thermogram of the native polymer clearly shows a glass transition but does not exhibit any crystallization peak ($T_c$). This indicates that the native polymer is in its amorphous state in the studied temperature range. This result is in agreement with the optical anisotropic behavior visible in the POM image. Furthermore, a $T_g$ around $10^\circ$C is detected suggesting that the native polymer is in its rubbery state at room temperature. As previously reported in literature \cite{4,9}, a $T_g$ below room temperature (i.e. the solid polymer electrolyte in its rubbery state) guarantees enough chain flexibility for the ions to be sufficiently mobile in the polymer matrix to enhance conductivity.

The $T_g$ of the native polymer and all polymer complexes obtained

![Fig. 3. POM images taken at room temperature of a) native 15C5BA polymer b) 15C5BA polymer complexed with NaSCN. The direction of the polarizers is indicated in the lower left corner of the image.](image-url)
from the thermal analysis is summarized in Table 2.

While the presence of the sodium salts as additives in the polymer is expected to have an effect on the \( T_g \) [34], differences in the degree of polymerization and/or cross-linking of the polymers will also affect the obtained values [35-38], making a fair comparison based on absolute values difficult. For this reason, rather than evaluating the magnitude of the different \( T_g \) values found, it is only relevant to acknowledge that all the systems studied are in their rubbery state at room temperature. Regardless of the sodium salt complexed by the crown-ether functionality, the flexibility of the polymeric chains is maintained.

Although the entity of the \( T_g \) can be misleading in understanding the differences between the polymers prepared in this work, the presence of additional thermal events observed in the thermograms of the polymers complexed with the sodium salts (Figure S5.2) can give further insights. Though, as shown in Figure S5.2 besides the presence of a \( T_g \), additional peaks are visible in the thermal traces of the systems complexed with NaI, NaBF₄ and NaPF₆. These can be attributed to melting/re-crystallization of the polymer [39,40]. Interestingly, these phase transitions are known to take place only for crystalline or semi-crystalline polymers [39,40]. This indicates that the presence of the salts promotes the formation of a more ordered array of molecular chains compared to the native polymer. The concurrent presence of a \( T_g \) and of melting peaks suggests that the polymers complexed with NaI, NaBF₄ and NaPF₆ are semi-crystalline. The complexation of the amorphous polymer with those salts triggers the formation of a more ordered phase hence the appearance of the small melting peaks at the DSC. As demonstrated in our previous work [20], by breaking the H-bonds between the amidic functionalities of the 15C5BA monomer, the anions can promote the formation of positional order of the molecules.

In the case of the systems complexed with NaI, NaBF₄ and NaPF₆, the results are in agreement with the ones obtained with the POM analysis showing spherulitic domains after complexation. For the polymer complexed with NaSCN instead, only a \( T_g \) is visible in the thermogram. Even though this polymer shows birefringence, suggesting also in this case the formation of some crystalline regions, the presence of a melting peak is not observed in its thermogram. This can be due to the lower temperature at which the thermogram is analysed: since the polymer complexed with NaSCN starts degrading at a lower temperature compared to the other polymers (Fig. 2), its DSC could not include the range in which the melting/re-crystallization peaks are found for the other polymers.

### 3.2.5. Medium and wide-angle x-ray scattering

Medium and wide-angle x-ray scattering measurements (MAXS and WAXS) were performed to study the morphological change after complexation of the 15C5BA polymer with the sodium salts. Fig. 5 shows the WAXS data of the native 15C5BA polymer and that of the system complexed with NaI.

The WAXS data of the native polymer show the appearance of several broad scattering signals. These indicate that the native polymer presents short range atomic order that is typical for amorphous systems [41,42].

As shown in our previous work [20], 15C5BA monomers are prone to form intermolecular H-bonds. Those interactions also occur in the native polymer being responsible for a certain degree of atomic order. After complexation with the sodium salts also the diffractogram of the complexed polymer shows the appearance of broad scattering features (Fig. 5, see SI section 5 for the other polymers). However, compared to the native 15C5BA polymer, a clear shift in the first scattering signal is observed in all cases after the complexation with sodium salts (Table 3). This shift demonstrates that the distance between the diffracting planes of the lattice of the polymers (d spacing) significantly increases upon complexation with the sodium salts clearly confirming the successful insertion of the sodium salts between the 15C5BA polymer chains.

In fact, the formation of a host-guest interaction between the 15-crown-5 ether moiety of the polymer and Na⁺, together with the non-covalent interactions between the amidic functionalities and the anions of the sodium salts (I⁻, SCN⁻, BF₄⁻ and PF₆⁻) separates the diffracting planes of the polymer lattice compared to the native polymer. It is worth to mention that the entity of the shift in the d spacing cannot simply be explained by sterical effects generated by the size of the anions involved in the interactions (Table 3). If this would be the case, the increase in the d spacing would be proportional to the Ionic radius of the anions.

Finally, it is remarkable to observe that the d spacing of the native polymer remains comparable before and after swelling the system in pure solvent (Figure S6.1), confirming once more the presence of the ions dispersed in the matrix.

### 3.3. Ionic conductivity

It goes without saying that the observed interactions and effects will ultimately impact the ionic conductivity of the polymer electrolyte. To address this, ionic conductivity (\( \sigma \)) measurements were performed to evaluate the influence of the complexation with the different sodium

![Fig. 5. WAXS diffractograms recorded at room temperature of the native 15C5BA polymer (black line) and the NaI complexed polymer (blue line). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)](image-url)

<table>
<thead>
<tr>
<th>Polymer</th>
<th>d spacing (Å⁻¹)</th>
<th>Ionic radius (Å⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Native polymer</td>
<td>35.990</td>
<td>-</td>
</tr>
<tr>
<td>NaI complexed</td>
<td>52.537</td>
<td>2.06 [25]</td>
</tr>
<tr>
<td>NaSCN complexed</td>
<td>49.157</td>
<td>2.13 [25]</td>
</tr>
<tr>
<td>NaBF₄ complexed</td>
<td>45.409</td>
<td>2.29 [25]</td>
</tr>
<tr>
<td>NaPF₆ complexed</td>
<td>49.159</td>
<td>2.54 [27]</td>
</tr>
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</table>

Table 3 d spacing for the first scattering signals in the diffractogram of the 15C5BA native polymer and the polymer complexed with the sodium salts and the ionic radii of the corresponding anions.
The complexation with the sodium salts clearly induces higher ionic conductivities in the polymer compared to the native polymer. For NaI, NaSCN and NaBF₄ complexes, this is an increase of more than an order of magnitude. These findings are in agreement with the WAXS/MAXS results. Indeed the structural and morphological changes observed in the organization of the polymers do have effect on the mobility of the ions within the polymeric lattice and with that on the ion conduction in the polymers. The looser the packing of the structure in which the ion is intercalating, the lower the energy barriers that prevent the movement of the ions in the lattice [43]. In essence, a larger $d$ spacing between the polymeric planes results in a higher mobility of the ions. This is clearly visible for the polymer complexed with NaI and NaSCN for which the highest $d$ spacing corresponds to the highest ionic conductivity. The polymer complexed with NaBF₄ deviates from this trend: even though this polymer has the lowest $d$ spacing (Table 3), this does not translate into the lowest ionic conductivity. This is instead, related to another effect that influences the ion conduction. Ion conduction is attributable to ions (Na⁺) hopping between preferred and vacant sites [43]. This depends on the free volume available for the ions to move and on the formation of interactions between the ions and the receiving sites (Na⁺ and crown-ether) relative to the interactions between the ions and the leaving site. However, it is also known that the ionic conductivity is also influenced by the dissociation of the cations from the anions [44] and the simultaneous migration of the latter in the electrolyte [28].

In our work the interaction between the anions and the amic functionalities present in the polymer matrix (demonstrated in the AT-FT-IR section) has indeed a clear effect on the mobility of Na⁺: I⁻ and SCN⁻ possess higher coordinating ability [23] (Fig. 6) and interact strongly with the amides in the 15C5BA structure [20]. The formation of these interactions between the anions and the polymer matrix helps the dissociation from Na⁺, lowering the migration of the anions. This translates into a higher ionic conductivity of the system. On the contrary, BF₄⁻ and PF₆⁻ are known to be poorly coordinating and interact less strongly with the amides. This disfavours the dissociation of the anion from Na⁺ and induces lower ionic conductivity.

The influence of the interaction between the anions of the sodium salts and the polymeric matrix is so relevant that even though BF₄⁻ gives rise to the lowest $d$ spacing, its higher coordinating ability overrules this resulting in an ionic conductivity even higher than that of the system complexed with NaPF₆. Moreover, even though similar concentrations of Na⁺ are found for the systems complexed with NaSCN and NaBF₄ (Table 1), the system containing BF₄⁻ shows a significantly lower ionic conductivity. Further evidence of this concept is obtained by looking at the behaviour of the systems containing SCN⁻ and PF₆⁻. Despite their very similar $d$ spacing, the system with SCN⁻ has a much higher conductivity than the system with PF₆⁻. This is clearly due to the very different coordinating ability of these two anions (Fig. 6): SCN⁻ is a much stronger coordinating ion than PF₆⁻ [23,45]. This results in a higher ionic conductivity (1.5 times higher) for the polymer complexed with NaSCN and a higher mobility of Na⁺ ions due to the lower interactions with their anions, which in turn, interact with the 15C5BA polymer matrix.

4. Conclusions

In this work we systematically studied the effect of the type of anion (I⁻, SCN⁻, BF₄⁻ and PF₆⁻) on the properties of a solid polymer electrolyte (15C5BA polymer) and evaluated its effect on the thermal, structural and electrical properties of the polymer electrolyte. The results clearly prove the impact of the nature of the anions on the relevant properties of the polymer electrolyte. Complexation with different sodium salts (NaI, NaSCN, NaBF₄ and NaPF₆) has in all cases an evident positive effect on the distance between the planes of the polymer lattice. This was confirmed with MAXS and WAXS analysis and it gives rise to an enhanced mobility of the ions as confirmed also by the higher ionic conductivity found compared to the native polymer. The higher coordinating ability of the anions I⁻ and SCN⁻ gives stronger interactions with the amides in the polymer structure and ultimately leads to faster ion conduction. The effect of the different anions is particularly evident when comparing the complexes with NaSCN and NaPF₆. Even though they give rise to similar $d$ spacing, the interactions between the anions (SCN⁻ and PF₆⁻) and the polymer matrix allow the system containing SCN⁻ to have an ionic conductivity almost 1.5 times higher than for the system containing PF₆⁻.

Our results show that the choice for a specific polymer electrolyte should thus not only be based on the polymer itself but also on its interactions with the anion. Moreover, knowing the importance and consequences of the effects described in this manuscript, the type of anion could even be used as a method to tailor and preferably enhance the conductivity of the polymer electrolyte.

CRediT authorship contribution statement

Anna Casimiro: Conceptualization, Methodology, Validation, Formal analysis, Investigation, Writing – original draft, and, Writing – review & editing, and, Visualization. Kitty Nijmeijer: Supervision, Writing – review & editing, Project administration, and, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

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References


