

The effect of receptor–polymer matrix compatibility on electrochemical properties of PEO-based polymer electrolytes containing supramolecular additives

Part 2. Ionic transport study

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Abstract

Poly(ethylene oxide)–lithium salt composite electrolytes containing two different derivatives of calix[4]arene were tested as anion complexing agents for I^- and $CF_3SO_3^-$. Both calix[4]arene derivatives studied have identical anion coordination groups but they have different compatibility with the polymer matrix obtained by chemical linking of the oligo(ethylene oxide) chains to one of the studied calixarenes. The impedance spectroscopy studies showed that the addition of the anion receptor significantly changes the conductivity. The character of this changes strongly depends on the receptor used while the electrochemical stability of these two calixarene receptors measured by cyclic voltammetry is similar. It was also proved that addition of the anion receptor strongly changes the polymer matrix morphology and thermal behavior. By the comparison with the liquid systems which electrical properties were similar to the polymer matrix, we can assume that these changes are a result of anion–receptor interactions.

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1. Introduction

The PEO-based membranes containing a salt dissolved in the polymer matrix are well-developed but still not well-defined materials and their properties have been studied for over three decades [1–3]. The idea of application of these materials as electrolytes in batteries is nearly 30 years old [4,5]. Their name solid polymer electrolytes (SPEs) or polymer electrolytes define their main advantages: very good processability, no danger of leak, possibility of production of very thin films and, thus, enhancement of the energy density of the battery in which SPE could be applied, as well as excellent mechanical and chemical resistance. Moreover, for SPE-containing batteries, there is no need of the additional electrode separator and, thus, the construction of this type battery is simpler in comparison with batteries containing liquid or gel organic electrolyte.

Since the SPEs application in lithium batteries have been proposed, the main limitation of their application in batteries was due to their poor ionic conductivity σ and low lithium cation transference number t_{Li^+} . As a result, the batteries in which SPE was applied as electrolyte are characterized by a high and unstable bulk resistance. To overcome these problems, several strategies, including application of different polymers such as poly(ethylene imine), poly(ethylene sulfide) or poly(propylene oxide) [6–9], addition of ceramic (Al_2O_3 or SiO_2) or polymeric fillers (as poly(*N,N*-dimethylacrylamide)) [10–14], ionic liquids [15–18] or plasticizing agents [19–21] as well as synthesis of polymeric blends [22–25] were used. Up to now, none of the above-mentioned strategies was able to simultaneously improve both important transport properties (overall conductivity and lithium transference number). Additionally the increase of the electrical properties cannot be often realized without losing such advantages of simple PEO–lithium salt system as thermal, mechanical and electrochemical stability.

The addition of anion receptors (supramolecular compounds), which interact with anions by several hydrogen bonds,

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to the PEO-based electrolytes resulted in the improvement of their conducting properties. Enhancement of the lithium cation transference number was observed and, simultaneously, the ionic conductivity of the electrolyte was not significantly lower in comparison to the not modified ones [26,27]. This change should be related to the anion–receptor complex formation, and, in result, the improvement of salt dissociation with simultaneous lowering of the anion mobility. However, preparation of the membranes which have such interesting conducting properties required several adaptations in typical SPE's synthetic routes due to incompatibilities in polymer–receptor–salt–solvent system from which SPE foils are cast. Receptors often do not dissolve in acetonitrile (ACN) from which SPE foils are usually cast and salts do not dissolve in chloroalkanes such as dichloromethane and chloroform. Thus, several procedures were tested to obtain optimized conditions for synthesis of the composite film [28]. The chosen procedure is based on polymer and salt dissolving in CH₃CN with parallel dissolution of the receptor in one of the chlorinated solvents (usually methylene dichloride due to its high volatility). In the next step both solutions were mixed, stirred and the foil was cast from the obtained homogenous liquid. Golodnitsky and Peled [29] proved that there was no difference in the conducting and physicochemical properties of the receptor free membranes obtained by casting from ACN and obtained through the strategy proposed by us, however, the proposed procedure was much more complicated and its repeatability might be worse. Moreover, also in the solid state the partial anion receptor precipitation, in several cases, was observed [29] due to the limited solubility of the supramolecular compound in both solid PEO crystalline and amorphous phase. Thus, the interaction of the receptor and the anions present in the polymeric phase can be limited and only a limited amount of the receptor present in the sample is active in anion trapping for higher salt and thus receptor concentrations. Moreover the mechanical properties of the membrane deteriorate through the increased heterogeneity of the system. The consideration of the above mentioned facts led us to the conclusion that anion receptors characterized with better compatibility (solubility) with the PEO-based matrix than previously synthesized 5,11,17,23-tetra-*p-tert*-butyl-25,27-bis(*N-p*-nitrophenylureidobutoxy)-26,28-dipropoxycalix[4]arene (**Cx2**) should be synthesized and applied.

In the case of **Cx2**, modifications in both rims can be applied. However, the modification in the narrow rim can influence the receptor coordination properties negatively as it was proved previously by Parzuchowski et al. [30]. Taking this into account, we focused on synthesis of a **Cx2**-like receptor modified with poly(ethylene oxide) chains in the wide rim. The new receptor (**Cxg**) proposed by us, contains identically located anion coordinating groups as **Cx2** but with wide rim modified with two oligo(ethylene oxide) chains chemically linked to the receptor molecule. This type of changes in the structure of the receptor should improve the properties of the anion receptor-containing composite by the improvement of the matrix–receptor compatibility without any influence on the anion trapping properties of the receptor. This property is achieved through the presence of the

side chains of chemical structure identical as the polymer matrix.

2. Experimental

2.1. Synthesis of receptors

The synthesis and preparation of **Cx2** was conducted as described in [26].

The synthetic route leading to the **Cxg** compound is depicted in Figs. 1 and 2. Calixarenes: **C1**, 5,11,17,23-tetra-*t*-butyl-25,26,27,28-tetrahydroxy-calix[4]arene [31–34], **C2**, 25,26,27,28-tetrahydroxycalix[4]arene [35], **C3**, 25,27-dipropoxy-26,28-dihydroxycalix[4]arene [36], **C4**, 25,27-dipropoxy-26,28-diallyloxy-calix[4]arene [37], **C5**, 5,17-diallyl-25,27-dipropoxy-26,28-dihydroxy-calix[4]arene [37,38] were synthesized according to the literature procedures. The spectral characteristics of the obtained compounds and their melting points matched to the literature data. The next synthetic steps of the calix[4]arene derivatives **C6–C9** (see Fig. 1) and the intermediate oligo(ethylene oxide) compounds **P1–P2** (see Fig. 2) were originally developed by our group and are described below. All the operations (except of **C8** synthesis) were conducted in the atmosphere of nitrogen. The **C8** step was realized in open air conditions as one of the reagents (hydrazine hydrate) contains water. All the solvents (benzene, toluene, dimethylformamide (DMF), tetrahydrofuran (THF), ethyl acetate, dichloromethane, hexane fraction from petroleum, all pure), NaOH and MgSO₄ (both pure) were supplied by POCH. DMF and THF were dried prior to use. Hydrazine hydrate (reagent grade), *N*-(4-bromobutyl)phthalimide, 1,2-ethanedithiol (both purum), 1-hydroxycyclohexylphenyl ketone (Irgacure 184, 99%), poly(ethylene glycol) methyl ether (*M*_w = 350), allyl chloride (99%), 4-nitrophenyl isocyanate (98%) and NaH (95%) were supplied by Aldrich. For UV-induced reactions, a medium-pressure mercury lamp PLK Type 5 (80 W) characterized with the following wavelength ranges: 100–280 nm (maximum 10% absorption), 280–315 nm (minimum 30% absorption), and 315–380 nm (minimum 50% absorption) was used.

2.1.1. Synthesis of 5,11-diallyl-25,27-bis[(*N*-4-phthalimidobutoxy)-26,28-dipropoxy-calix[4]arene (**C6**)

The solution of 2.4 g (4 mmol) of **C5** in 60 cm³ of the DMF–THF (1:4) mixture and 0.6 g (25 mmol) of NaH was stirred for 1 h at room temperature. After that 5.8 g (21 mmol) of *N*-(4-bromobutyl)phthalimide was added. Then, the reaction was carried out for another 24 h at 70 °C. The reaction progress was controlled by thin layer chromatography (TLC) (eluent: ethyl acetate/hexane 1:3). After the reaction was finished, 40 cm³ of water was added and the product was extracted with CH₂Cl₂. The solution was dried with MgSO₄ and evaporated to dryness. The residue was purified using column chromatography (ethyl acetate–hexane 1:3). After removal of the solvents, 2.1 g of **C6** were obtained (53%).

¹H NMR (400 MHz, CDCl₃), δ (ppm): 7.78–7.76 (m, 4H, ArH–Pht), 7.69–7.67 (m, 4H, ArH–Pht), 6.56 (s, 4H, ArH),

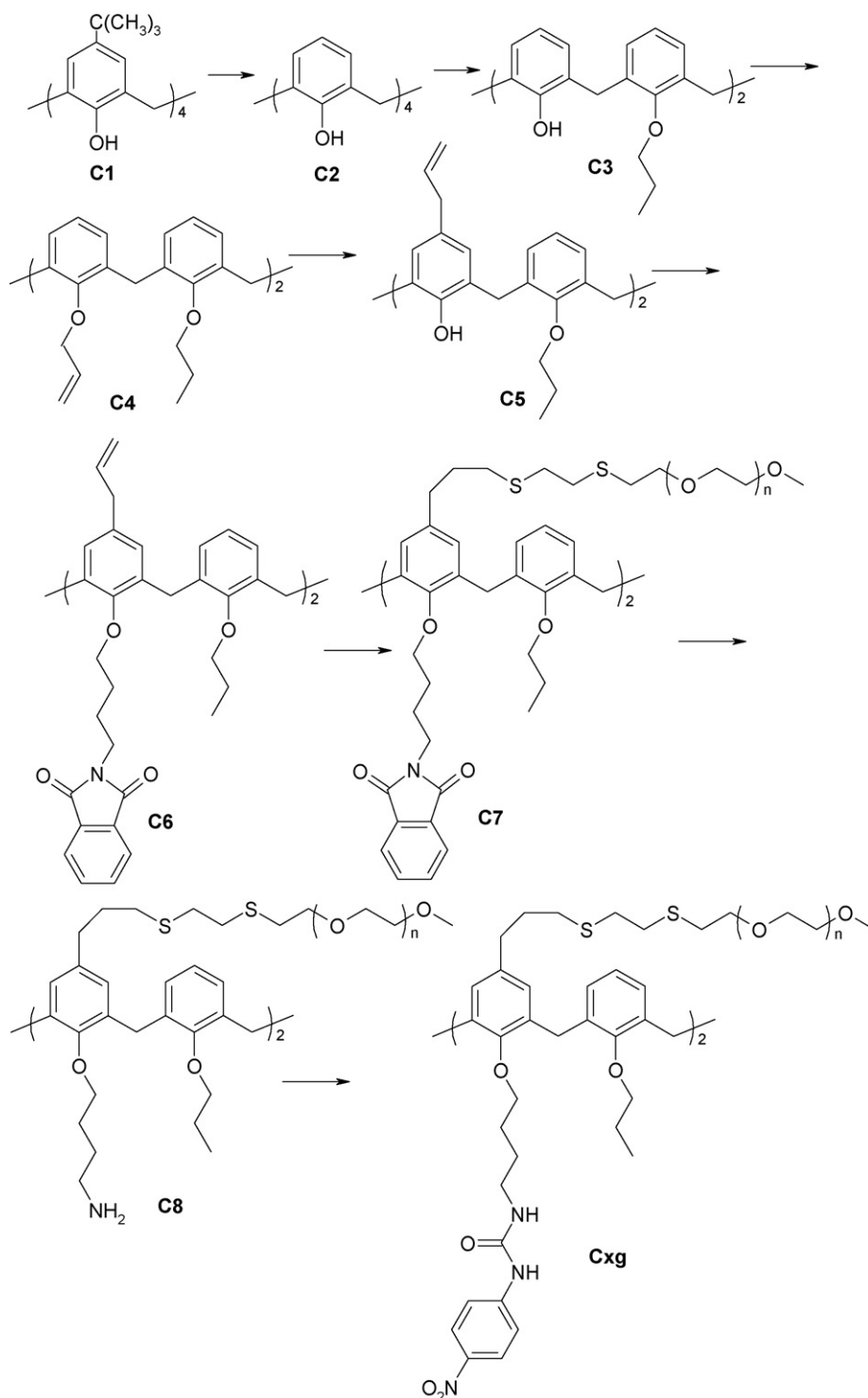


Fig. 1. Cxg synthetic scheme. Part 1. Main synthetic route.

6.45 (m, 6H, ArH), 5.89–5.83 (m, 2H, $CH=CH_2$), 5.00–4.95 (m, 4H, $=CH_2$), 4.39 (d, 4H, $ArCH_2Ar$, ax, $J=13.2$ Hz), 3.94 (t, 4H, CH_2N , $J=7.6$ Hz), 3.79–3.72 (tt, 4H, OCH_2 , $J=7.6$ Hz), 3.12 (m, 4H, $ArCH_2CH$), 3.11 (d, 4H, $ArCH_2Ar$, eq, $J=13.2$ Hz) 1.98–1.94 (m, 4H, OCH_2CH_2N), 1.92–1.86 (m, 4H, $OCH_2CH_2CH_2$), 1.82–1.71 (m, 4H, CH_2CH_3), 0.98 (t, 6H, CH_3 , $J=7.6$ Hz).

2.1.2. Synthesis of poly(ethylene glycol) allylmethyl ether (PI)

The solution of 16 g (0.4 mol) of NaOH in the mixture of 40 ml benzene and 28 g (80 mmol) of poly(ethylene glycol) methyl ether ($M_w = 350$) was heated up to 60 °C. Then, to this solution 19.5 ml (0.24 mol) of allyl chloride was added dropwise during 1.5 h. The mixture was stirred for 20 min at the same tem-

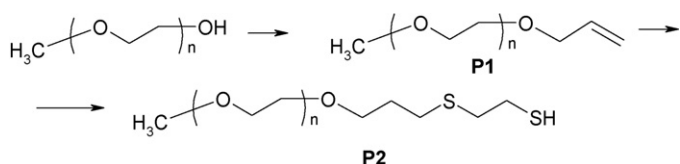


Fig. 2. **Cxg** synthetic scheme. Part 2. Intermediate oligo(oxyethylene) compounds.

perature. This was followed by the addition of 7 g (0.175 mol) of NaOH and 10 ml of benzene. Then, 13 ml (16 mol) of allyl chloride was added dropwise within 0.5 h. After this, the reaction was conducted for another 2 h at 60 °C. The reaction mixture was cooled down to room temperature, filtered, washed with 5% hydrochloric acid and dried over anhydrous MgSO_4 . Benzene and volatile impurities were distilled off under vacuum yielding 30 g of poly(ethylene glycol) allyl ether ($M_w = 390$) (93%).

2.1.3. Synthesis of P2

The 1 g (1.7 mmol) of **P1** and 0.324 g (3.45 mmol, 0.288 cm³) of 1,2-ethanedithiol was dissolved in 5 cm³ of ethyl acetate. Then 0.04 g (0.196 mmol) of photoinitiator Irgacure 184 was added. Then, the reaction mixture was UV irradiated for 20 min. After that the solvent was distilled off yielding 1.1 g of **P2** (96%).

¹H NMR (400 MHz, CDCl_3), δ (ppm): 3.65–3.63 (m, 42H, $-\text{CH}_2\text{O}-$), 3.55–3.52 (m, 2H, CH_2OCH_3), 3.37 (s, 3H, OCH_3), 2.75–2.70 (m, 2H, SCH_2CH_2), 2.63–2.59 (m, 2H, $\text{CH}_2\text{CH}_2\text{SH}$), 1.87–1.83 (m, 2H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{O}$).

2.1.4. Synthesis of C7

To 0.3 g (0.303 mmol) of **C6** dissolved in 5 ml of ethyl acetate 0.449 g (0.666 mmol) of **P2** and 0.023 g (0.113 mmol) of photoinitiator Irgacure 184 were added. Then, the reaction mixture was irradiated by UV for 20 min. The removal of the solvent yielded 0.38 g of **C7** (76%).

¹H NMR (400 MHz, CDCl_3), δ (ppm): 7.78–7.76 (m, 4H, ArH–Pht), 7.71–7.68 (m, 4H, ArH–Pht), 6.58–6.36 (m, 10H, ArH), 4.38 (d, 4H, ArCH_2Ar , $J = 12.8$ Hz), 3.96–3.94 (m, 4H, OCH_2), 3.75–3.71 (m, 4H, CH_2N), 3.66–3.63 (m, 42H, $-\text{CH}_2\text{O}-$), 3.60–3.52 (m, 4H, OCH_2), 3.38 (s, 6H, OCH_3), 3.10 (d, 4H, ArCH_2Ar , $J = 12.8$ Hz), 2.85–2.44 (m, 16H, SCH_2), 1.98–1.94 (m, 4H, $\text{OCH}_2\text{CH}_2\text{N}$), 2.04–1.66 (m, 24H, $-\text{CH}_2-$), 0.99 (t, 6H, CH_3 , $J = 7.6$ Hz).

2.1.5. Synthesis of C8

The mixture of 0.3 g (0.18 mmol) of **C7** and 2.5 cm³ (50 mmol) of hydrazine hydrate in 11 cm³ of ethanol was heated under reflux for 12 h. Then, the product was precipitated with water and extracted with CH_2Cl_2 . The organic layer was washed with water and dried with MgSO_4 . The solvent was distilled off yielding 0.24 g (94%) of **C8**. The product was immediately used in the next reaction.

¹H NMR (400 MHz, CDCl_3), δ (ppm): 6.87–6.10 (m, 10H, ArH), 4.38 (d, 4H, ArCH_2Ar , $J = 12.8$ Hz), 4.26–3.94 (m, 4H, OCH_2), 3.75–3.71 (m, 4H, CH_2N), 3.60–3.52 (m, 4H, OCH_2), 3.10 (d, 4H, ArCH_2Ar , $J = 12.8$ Hz), 1.98–1.94 (m, 4H,

$\text{OCH}_2\text{CH}_2\text{N}$), 2.86–2.45 (m, H, $-\text{CH}_2-$), 2.71 (s, 6H, OCH_3), 2.04–1.66 (m, H, $-\text{CH}_2-$), 0.99 (t, 6H, CH_3 , $J = 7.6$ Hz).

2.1.6. Synthesis of Cxg

To the vigorously stirred solution of 0.14 g (0.1 mmol) of calixarene **C8** in 12 cm³ of toluene 0.036 g (0.22 mmol) of 4-nitrophenyl isocyanate was added. The reaction was carried out for 24 h at room temperature. Then the viscous yellow liquid was separated and washed twice with 10 cm³ of toluene. The residue of solvent was removed by distillation under reduced pressure. The yield of calixarene **Cxg** was 78% (0.1265 g).

¹H NMR (400 MHz, $\text{DMSO}-d_6$): δ (ppm): 9.22 (s, 2H, NH), 8.10 (m, 4H, ArH), 7.59 (d, 4H, ArH), 6.59–6.45 (m, 12H, ArH, NH), 4.31 (d, 4H, ArCH_2Ar , $J = 12.4$ Hz), 3.85–3.82 (m, 4H, OCH_2), 3.72–3.68 (m, 4H, CH_2N), 3.49–3.48 (m, 42H, $-\text{CH}_2\text{O}-$), 3.42–3.40 (m, 4H, OCH_2), 3.20 (s, 6H, OCH_3), 3.20 (bs, 4H, ArCH_2Ar , eq), 2.85–2.44 (m, 16H, SCH_2), 1.98–1.94 (m, 4H, $\text{OCH}_2\text{CH}_2\text{N}$), 2.04–1.66 (m, 24H, CH_2), 0.99 (t, 6H, CH_3 , $J = 7.6$ Hz).

2.2. Membrane sample preparation

All preparative operations were performed in an argon glove box with humidity level below 3 ppm.

ACN, CH_2Cl_2 (both POCH, for DNA synthesis, water content below 10 and 50 ppm, respectively) were used as received. Both salts (both Aldrich, 99.995% LiCF_3SO_3 –lithium trifluoromethanesulfonate, lithium triflate, and 99% LiI, lithium iodide) and PEO (Aldrich, average $M_w = 5\,000\,000$) were dried for over 72 h at temperature up to 100 °C under high vacuum ($<10^{-4}$ mmHg).

The preparation of the electrolyte samples was conducted as in Ref. [28]. The electrolyte was obtained by casting the mixture of the two separately prepared solutions: salt and PEO in CH_3CN and **Cx2** (or **Cxg**) in CH_2Cl_2 and dried using the procedure described in the reference above. All samples were prepared maintaining ether oxygen atoms to lithium cations molar ratios equal to 20:1. For the **Cxg**-containing ones the oligo(ethylene oxide) chains present in the receptor were counted into the total number of the ether oxygen atoms present in the sample. The salt to receptor ratio was always equal to 3:1.

2.3. Conductivity measurements

The ionic conductivity was determined by the means of impedance spectroscopy. The electrolytes were pressed between stainless-steel blocking electrodes. An Atlas 98HI Frequency Response Analyzer was used in 1 Hz to 100 kHz frequency range. The cell was immersed in a HAAKE DC 50 cryostat to control the measurement temperature in 293–338 K range. A Bernard Boukamp EQ software [39] was used for analyze of the obtained impedance data. The thermal dependency of conductivity for all studied samples was described by the Arrhenius type equation: $\sigma = \sigma_0 \exp(-E_a R^{-1} T^{-1})$.

2.4. DSC measurements

DSC data were collected using a Perkin-Elmer Pyris 1 DSC at a heating rate $20\text{ }^{\circ}\text{C min}^{-1}$ in the -120 to $250\text{ }^{\circ}\text{C}$ temperature range.

2.5. NMR spectra

^1H and ^{19}F NMR spectra were recorded on a computer-interfaced Varian Gemini 200 NMR spectrometer at 200 and 188 MHz, respectively. All measurements were performed at $25\text{ }^{\circ}\text{C}$. The spectra were analyzed using Mestrec 2.3 software. Procedure of the complex formation constant estimation was published previously [40]. In general NMR titration is here used where the chemical shift δ is plotted as a function of the guest (e.g. anion)–host (supramolecular receptor) concentration ratio. The observed changes are related to the complexation process. Equilibrium constant value can be found on the basis of non-linear least square fit of the obtained data.

2.6. Cyclic voltammetry studies

Chronovoltamperometric measurements were performed in a dry-box using Pt disc (1 mm diameter) working electrode, a Ta wire counter electrode and a Ta wire pseudo reference electrode. The usage of the Ta reference was previously tested to give reasonably stable values of reference potential in nonaqueous electrolytes [41]. DMF (Aldrich water free grade) was used as received as a solvent. $(\text{C}_2\text{H}_5)_4\text{NBF}_4$ (Aldrich electrochemical grade, previously vacuum dried) was dissolved in DMF up to 0.1 mol kg^{-1} to create the basic solution. An EG&G PAR 263A computer-interfaced potentiostat was used to collect the data.

3. Results

3.1. Conductivity measurements

Thermal dependences of conductivities for $(\text{PEO})_{20}\text{LiTf}$ and $(\text{PEO})_{20}\text{LiI}$ composites with addition of the anion receptors are depicted in Figs. 3 and 4, respectively. In both cases, we observe that addition of anion receptor results in the lowering of conductivity for temperatures lower than $50\text{ }^{\circ}\text{C}$. At higher temperatures, the conductivity of **Cx2**-containing samples is similar or even

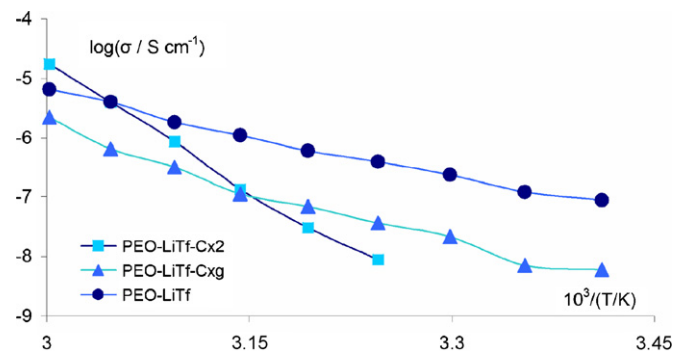


Fig. 3. Thermal dependency on conductivity-systems containing LiTf.

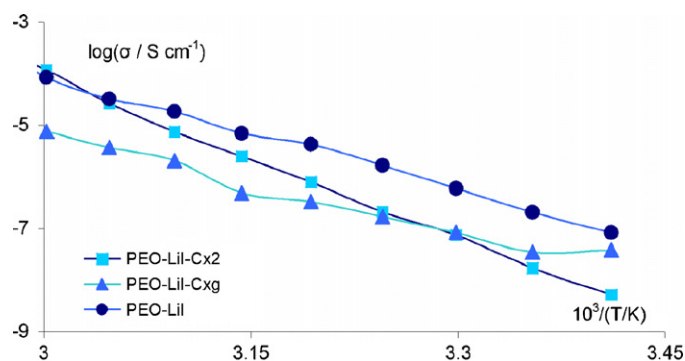


Fig. 4. Thermal dependency on conductivity-systems containing LiI.

higher than conductivity of systems which does not contain the anion receptor. The activation energy (Table 1) of conduction is the highest for systems containing **Cx2**. For LiI containing samples the lowest value was observed for the system containing **Cxg** while for LiTf ones the pristine system is characterized with the lowest E_a . Despite of the last fact the value of the E_a for **Cxg**-containing samples was always far lower than for the **Cx2** ones.

3.2. DSC measurements

A typical DSC trace for the PEO–lithium salt system [42–44] presents two signals: the first one (baseline shift) characteristic for the second order transition, is observed between -40 and $-10\text{ }^{\circ}\text{C}$ and can be assigned to the glass transition, while the second one (endothermic peak) is located between 60 and $75\text{ }^{\circ}\text{C}$ and can be attributed to the melting of the PEO crystalline phase. In the case of **Cx2**- and **Cxg**-containing samples, one can observe an additional exothermic peak, between -15 and $10\text{ }^{\circ}\text{C}$, which can be attributed to the crystallization of the pure PEO and salt–PEO complexes from the amorphous phase present in the sample. The DSC trace for PEO–LiTf–**Cx2** systems, which is typical for all samples containing anion receptor as an additive, is depicted in Fig. 5. Table 2 gathers the transition temperatures, enthalpies of melting and crystallization together with changes in the specific heat capacity (c_p) for the glass transition (Fig. 6).

3.3. NMR spectra

The estimation of anion complexation reaction equilibrium constant (complexation constant) in solid samples by means of NMR spectroscopy, is difficult due to both, technical as well as chemical problems (e.g. ion–ionic pair exchange is much slower

Table 1
Activation energies of the conductivity

System	E_a (kJ mol $^{-1}$)
LiI	153
LiI Cx2	200
LiI Cxg	115
LiTf	89
LiTf Cx2	265
LiTf Cxg	118

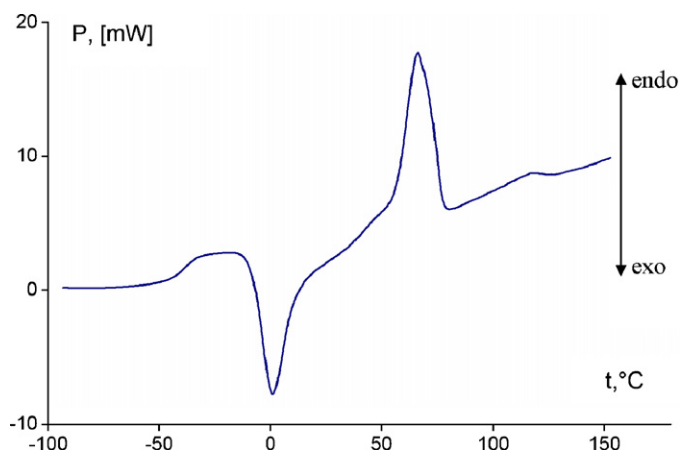
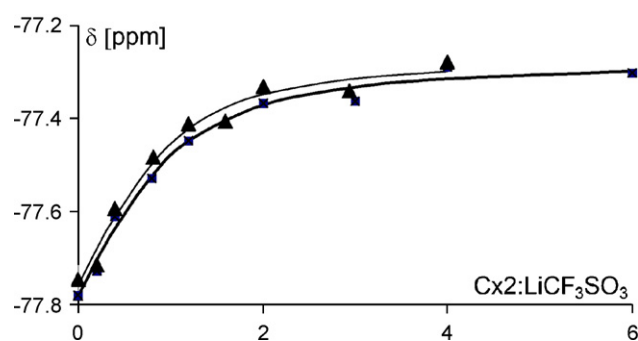
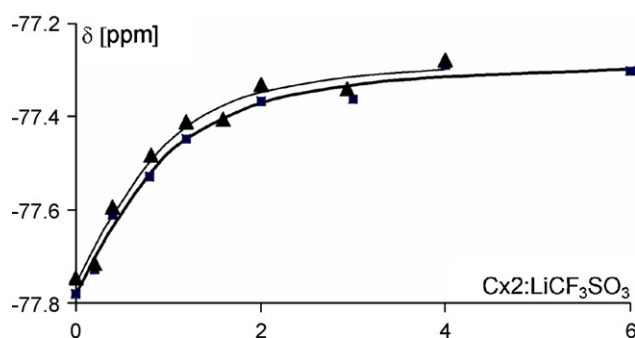


Fig. 5. DSC trace for PEO-LiTf-Cx2 system.

Fig. 6. ^{19}F NMR chemical shift of the CF_3SO_3^- as a function of $\text{Cx2}:\text{LiTf}$ molar ratio in DME ($c_{\text{LiTf}} = 1.15 \text{ mmol (kg DME)}^{-1}$).

in the solid state). In opposition to this, complexation constant estimation in the liquid phase is much easier and is the standard technique applied in supramolecular chemistry studies [45]. Thus, we decided to estimate the anion receptor complexation constant in the solution in which solvent (mixture of 1,4-dioxane and acetonitrile) has the same dielectric constant as PEO ($\epsilon = 5.5$, dioxane: CH_3CN mass ratio 12:1) and its liquid oligomeric analogue PEODME ($\epsilon = 8$, dioxane: CH_3CN mass ratio 48:7). The choice of the solvent mixture was a compromise between the coordination properties (represented by the donor number DN related to the solvent-cation affinity and the acceptor number AN which is responsible for the anion-solvent interactions) and the solvent-receptor interactions inhibiting the anion complexation [40]. As is shown later, the ideal mixture of DME and

Fig. 7. ^{19}F NMR chemical shift of the CF_3SO_3^- as a function of $\text{Cx2}:\text{LiTf}$ molar ratio in dioxane- CH_3CN mixtures having $\epsilon = 5.5$ (squares, $c_{\text{LiTf}} = 5.34 \text{ mmol (kg of the solvent)}^{-1}$) and $\epsilon = 8$ (triangles, $c_{\text{LiTf}} = 5.76 \text{ mmol (kg of the solvent)}^{-1}$).

1,4-dioxane (both solvents have DN and AN almost identical like the PEO matrix) must be replaced with a CH_3CN -dioxane mixture being less ideal from the point of view of the physicochemical parameters but not complexing the supramolecular compound (set of parameters for pure solvents was taken from [46] – dielectric constants and [47,48] – AN and DN numbers).

To overcome problem of chemical shift change as a result of receptor self-complexation and ionic pairs forming, we conducted ^{19}F NMR titration of the anion. A set of solutions was obtained by the mixing of the salt (LiCF_3SO_3) and receptor solutions and pure solvent to maintain both constant salt concentration and appropriate host to guest ratio. We emphasize here that this procedure can be applied only for titration of the fluorine atom-containing salts. Thus, it was impossible to apply this procedure to the LiI-containing systems.

In the recorded spectra we observed only a single peak whose the chemical shift is the weighted average of the chemical shifts δ of the complexed δ_{RA^-} and non-complexed anions δ_{A^-} . To simulate the solid polymeric electrolyte a mixture of dimethoxyethane and dioxane (dielectric constant equal to 5.67) was used [40]. Unfortunately, the registered dependency of the chemical shift on the salt:receptor ratio is not representative and cannot be used for the complexation constant estimation. This observation can be related to the phenomenon of the complexation of the supramolecular additive with the solvent species observed by us previously [41]. In contrast to this, the ^{19}F NMR chemical shift for the LiCF_3SO_3 and Cx2 in dioxane:acetonitrile mixtures as a function of $\text{Cx2}:\text{LiCF}_3\text{SO}_3$ molar ratio are depicted in Fig. 7. From these data we estimated the complexation constants equal to $650 \text{ mol (kg of solvent)}^{-1}$ for

Table 2
Temperatures, specific heat and enthalpies of transitions in the composites

No.	Sample	Glass transition		Recrystallization		Polymer melting	
		T ($^{\circ}\text{C}$)	Δc_p ($\text{J mol}^{-1} \text{ } ^{\circ}\text{C}^{-1}$)	T ($^{\circ}\text{C}$)	ΔH (J g^{-1})	T ($^{\circ}\text{C}$)	ΔH (J g^{-1})
1	PEO	-48.8	0.035	Not observed		71.1	133.2
2	PEO-LiTf	-46.0	0.058	Not observed		60.5	73.7
3	PEO-LiI	-12.5	0.210	Not observed		67.0	81.7
4	PEO-LiTf-Cx2	-38.9	0.396	-8.6	24.2	61.8	72.3
5	PEO-LiI-Cx2	-38.9	0.343	-18.0	21.7	64.4	71.1
6	PEO-LiTf-Cxg	-38.4	0.321	-17.1	14.8	55.9	60.0
7	PEO-LiI-Cxg	-22.8	0.219	16.5	8.0	52.0	43.9

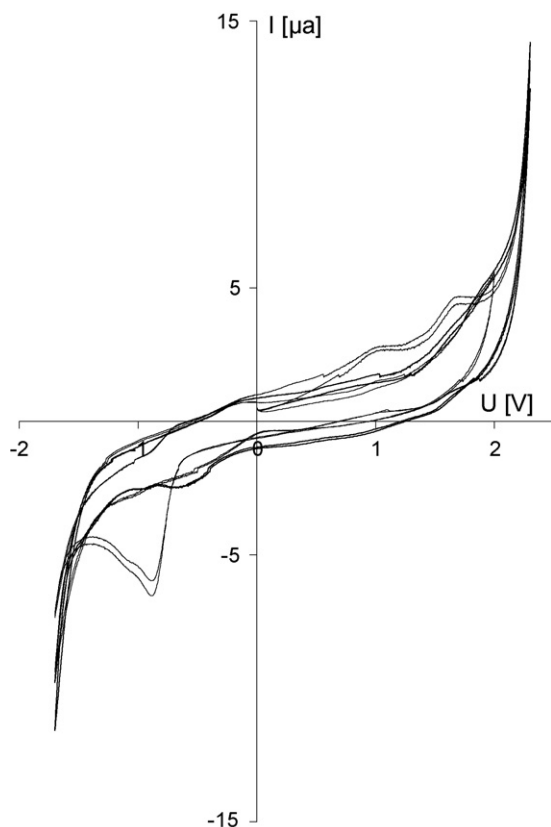


Fig. 8. Chronovoltamperometric traces of the basic solution (dotted line), the **Cx2** compound (dashed line) and the **Cxg** (solid line). Sweeping rate equal to 50 mV s^{-1} .

solvent having $\epsilon = 5.5$ and $700 \text{ mol (kg of solvent)}^{-1}$ for solvent having $\epsilon = 8$, respectively.

3.4. Cyclic voltammetry studies

Fig. 8 shows the comparison of the CV traces for the basic solution (dotted line) the **Cx2** compound (dashed line) and the **Cxg** (solid line). The concentration of the solutions was equal to 10 mg cm^{-3} and 20 mg cm^{-3} , respectively. As the molar mass of the **Cxg** is two times higher than that of **Cx2** the molar concentration of both solutions was the same. A small peak is observed for the **Cx2** compound while the **Cxg** solution behaves identically to the basic solution. To determine whether the peak is related with the tested compound or rather the impurities of the solution an additional portion of **Cx2** was added to it doubling the initial concentration to 20 mg cm^{-3} . The peak current did not increase showing that the observed process is not related to the compound itself (Fig. 9).

4. Discussion

The conductivity of the membrane containing more PEO-compatible receptor **Cxg** is about one order of magnitude lower than in the case of the additive-free one in whole range of temperatures. The measurements for the **Cx2**-containing composites reveals that the activation energy for these system is significantly

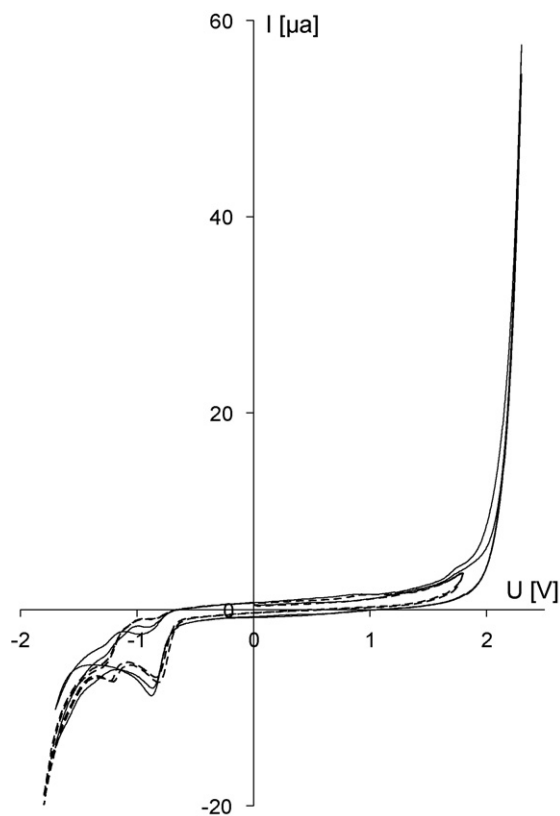


Fig. 9. Chronovoltamperometric the **Cx2** compound 10 mg cm^{-3} (dashed line) and the 20 mg cm^{-3} (solid line). Sweeping rate equal to 25 mV s^{-1} .

higher (i.e. in higher temperatures as 60°C the conductivity is similar, but at room temperature it is lower for more than two orders of magnitude. Both thermal dependences were observed by us previously [26–28], however, we cannot link thermal dependency on conductivity behavior with any physicochemical effect observed in the system.

The NMR titrations showed that **Cx2** interacts with Tf^- anion in the solvent having similar (or even stronger) coordinating properties (see Table 2) as polymeric and solid PEO. This observation points out of the fact that the improvement of the lithium transference number can be a result of the anion–receptor complex forming. The complexation constants measured in two solvent mixtures having different ϵ do not differ significantly (the difference lies in the range of the estimation accuracy). Thus, the differences between complexation, in opinion of the authors, should depend rather on coordinating properties of the electrolyte (donor and acceptor number) than on its ϵ . To additionally judge for this assumption, one must take into consideration that the dielectric constant is a global macroscopic value, while the complexation strength of the electrolyte itself is related to the local ionic affinity of the composition. From the point of view of the samples with low concentration of both salt and the receptor this property is not much affected by the acetonitrile concentration changes in this range. The acetonitrile concentration is in both cases a few orders of magnitude higher than the anion concentration and, thus, the solvation preferences of the anion are not affected.

What is worth stressing, the NMR titrations are, in our opinion, a more accurate tool for complexation constant estimations than, e.g. IR spectra analysis and they can also be applied in the more diluted solutions. On the other hand, the main limitation of this technique arises from the fact that NMR titrations need to be conducted in liquid and in case of ^1H measurements must be performed in deuterated solvent. Moreover, the method is solvent sensitive. One can compare the ^{19}F NMR titration of **Cx2** with LiTf salt for CH_3CN –dioxane solutions with identical data obtained for 1,2-dimethoxyethane (DME)–dioxane mixtures to observe that in the later case the chemical shift change cannot be observed. In the later case the solvent–receptor complex formation inhibits the formation of the anion–receptor ones due to the much higher concentration of the solvent molecules. Further experiments must be conducted to estimate the complexation constant of the neutral solvent molecules with the supramolecular additive. Previously, the similar obstructions were observed in the case of PEO– LiBF_4 composites containing the previously studied receptor (1,1,3,3,5,5-*meso*-hexaphenyl-2,2,4,4,6,6-*meso*-hexamethylcalix[6]pyrrole), where strong discrepancies between solid and liquid polyether based samples were observed in terms of the conductivity and lithium transference numbers. The improvement of the cation transport properties for this receptor (lithium transference number and conductivity) observed for solid systems cannot be confirmed by both the electrochemical data and changes of ^{19}F NMR chemical shift for the LiBF_4 solutions in poly(ethylene glycol) dimethyl ether (PEODME) [49] with and without the anion receptor. Contrary to this, in $\text{CH}_3\text{CN}/\text{CH}_2\text{Cl}_2$ mixtures solutions of the same salt and receptor [40] a significant change of the chemical shift of the fluorine atom can be observed in the ^{19}F NMR spectra.

In the DSC curves, several thermal effects were observed. In the case of receptor-containing samples, the change of the glass transition temperature is dependent on the salt type used. For both compounds the LiI containing electrolytes are plasticized. This observation is consistent with the previous data obtained by our group [26]. To explain the fact that the plasticization is weaker for the **Cxg** receptor one must consider, first of all, the stoichiometry of the samples. The salt to ether oxygen atoms ratio was here calculated taking into consideration both polymer and the receptor oligo(ethylene oxide) chains, thus the molar concentration of the salt in respect to the polymer matrix only is almost two times higher. Additionally, this phenomenon can be also related to the stronger physical cross-linking of the polymer matrix observed for the samples containing receptor with oligo(ethylene oxide) chains which, on one hand, could act as an internal plasticizer but, on the other, can play the role of short bridges cross-linking (via lithium cation or ionic aggregate) the polymer matrix with heavy (and thus immobile) receptor molecules.

For samples containing LiTf the effect observed is opposite. The increase of T_g shows that the addition of the supramolecular additive stiffens the polymer matrix. To discuss this phenomenon, first of all, one must consider that for this system the T_g values are generally much lower. A triflate salt addition leads to only a slight increase of this value which can

be related to both quasi-plasticizing properties of the trifluoromethanesulfonate molecule and ionic equilibria present in the sample. When studying the glass transition in the PEO-based electrolytes one must take into consideration two various effects which can be responsible for the formation of the transient physical cross-linking and, thus, matrix stiffening. The first type of interaction is related to the lithium cation, which is able to interact with oxygen atoms belonging to different polyether chains. This mechanism is widely observed for various SPE systems and can be partially inhibited by the addition of various modifiers. The additional stiffening interaction is specifically related to the presence of the anion receptor, whose interactions with neutral compounds including PEO and their liquid analogs were already described in our previous papers [40,41]. Therefore in the case of the iodide anion the general effect is based on the overruling of the second one by the depletion of the very strong first one. Contrary to the triflate anion, the first effect is rather weak and can be easily depressed by the second one.

5. Conclusions

The electro-, physicochemical as well as conductivity related properties of PEO-lithium salt based composites with addition of two different anion receptors (calix[4]arene derivatives) of similar anion coordinating structure but different compatibility with the polymer matrix were compared showing that the electrochemical stability of these two receptors is very similar. In opposition to this, the ion transport properties as well as the surface micromorphology are strongly dependent on the receptor and salt used. We suggest that it is the effect of different compatibility of these two receptors to the PEO matrix in terms of the phase separation observed for some non-modified receptors. Additionally, for **Cx2** receptor, additional confirmation of its interactions with Tf^- anion was acquired using ^{19}F NMR spectroscopy. Similar values of the complexation constant for both solutions characterized with different dielectric constant prove that this interactions are rather weakly dependent on the salt dissociation degree.

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