



## Lithium conducting ionic liquids based on lithium borate salts

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### ABSTRACT

The simple reaction of trialkoxyborates with butyllithium resulted in the obtaining of new lithium borate salts:  $\text{Li}\{\text{CH}_3(\text{OCH}_2\text{CH}_2)_n\text{O}\}_3\text{BC}_4\text{H}_9$ , containing oxyethylene substituents (EO) of  $n = 1, 2, 3$  and  $7$ . Salts of  $n \geq 2$  show properties of room temperature ionic liquid (RTIL) of low glass transition temperature,  $T_g$  of the order from  $-70$  to  $-80$  °C. The ionic conductivity of the salts depends on the number of EO units, the highest conductivity is shown by the salt with  $n = 3$ ; in bulk its ambient temperature conductivity is  $2 \times 10^{-5} \text{ S cm}^{-1}$  and in solution in cyclic propylene sulfite or EC/PC mixture, conductivity increases by an order of magnitude. Solid polymer electrolytes with borate salts over a wide concentration range, from 10 to 90 mol.% were obtained and characterized. Three types of polymeric matrices: poly(ethylene oxide) (PEO), poly(trimethylene carbonate) (PTMC) and two copolymers of acrylonitrile and butyl acrylate p(AN–BuA) were used in them as polymer matrices. It has been found that for systems of low salt concentration (10 mol.%) the best conducting properties were shown by solid polymer electrolytes with PEO, whereas for systems of high salt concentration, of the polymer-in-salt type, good results were achieved for PTMC as polymer matrix.

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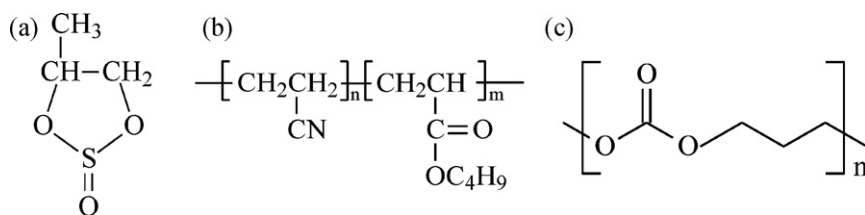
### 1. Introduction

Reversible lithium and lithium-ion batteries have a prominent place on the market of novel power sources, but still research is carried out on enhancing the parameters obtained, such as: capacity, power and current density, lifetime connected with the number of charge/discharge cycles at the possibly lowest mass of the device. In a majority of presently produced batteries, lithium salt solutions in polar organic solvents, mainly cyclic and linear carbonates (propylene carbonate, ethylene carbonate, dimethyl carbonate) or their mixtures, are used [1].  $\text{LiPF}_6$  is most often used as the salt; it is characterized by relatively high ionic conductivity and is not corrosive against current collectors, but, as known, is thermally and hydrolytically unstable. HF evolves from its decomposition, which acts destructively on the chemical cell components [2,3]. During the recent few years several new solutions of lithium salts have been proposed, which could replace  $\text{LiPF}_6$ , such as: whole class of imide salts [4,5], orthoborate [6,7], salts containing superweak aluminate anion [8], phosphorus salts –  $\text{LiPF}_6$  derivatives [9,10] or chelate-type ones [11], and recently proposed imidazole salts [12]. However, none of these solutions found universal commercial application. Application works concerning the properties of lithium and lithium-ion batteries involving various types of electrolytes indicate that seeking of systems of high diffusion coefficients and

high cation transference numbers should become the leading trend in further works on electrolytes [13,14]. Low lithium transference numbers ( $t_+$ ) indicate a dominating participation in the charge transfer of anions, which do not undergo irreversible electrode reactions, resulting in salt concentration polarization limiting the high-power performance of rechargeable lithium-ion batteries. In the literature examples can be found on the application of additives capable of complexing anions, such as supramolecular compounds [15], and derivatives of Lewis acids properties [16,17], or the anions can be completely immobilized by chemical bounding with the polymer matrix, however in this case, due to the strong interaction of ions in polyelectrolytes, a considerable decrease in ionic conductivity is observed [18,19].

The synthesis of lithium salts comprising anions of molecular masses characteristic for oligomers is a combination of the idea of new salts and polyelectrolytes [20–22]. Such a type of electrolytes has been called “ionic melts electrolytes”. The ionic conductivity of these derivatives is high, which results from combining the low lithium salt network energy with the relatively low viscosity of oxyethylene substituents and high concentration of lithium cations. The system containing an oxyethylene fragment and sulfonyl group can be an example of an oligomeric lithium salt described in the literature; for this type of salt of formula  $\text{PEO}350\text{-SO}_3\text{Li}$  the lithium transference number  $t_+ = 0.7\text{--}0.8$  at  $20$  °C [23]. Another example of a salt is based on a similar idea, with the only difference that the salt contains an imide anion with an oxyethylene fragment, of which the ambient temperature ionic conductivity achieved was of the order of  $10^{-6} \text{ S cm}^{-1}$  [24–26].

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**Scheme 1.** Chemical structure of: (a) cyclic propylene sulfite (CPS), (b) acrylonitrile with butyl acrylate copolymer [(p(AN-BuA))] and (c) poly(trimethylene carbonate) (PTMC).

Interesting results connected with enhanced safety and electrochemical performance of Li-ion batteries are achieved for electrolytes involving ionic liquids, which can effectively replace typical carbonate solvents. The introduced ionic liquids, due to their ionic structure, facilitate dissociation of the lithium salt and participate in ions transport. Derivatives based on salts of the 1-ethyl-3-methylimidazolium (EMI) cation were widely studied because of their low viscosity, high conductivity and ability to dissolve lithium salts [27], but they have poor stability toward Li metal [28], and therefore current research is focused on increasing the cathodic stability of the salts [29] or applying other cations as: pyrazolium [30], quaternary ammonium [31] or *N*-alkyl-*N*-methylpyrrolidinium cations [32].

This work is concerned with the synthesis of new borate salts of an oligomeric structure from the simple reaction of trialkoxyborates, containing oligooxyethylene groups as substituents, with an alkyllithium compound. Trialkoxyborates are known derivatives, which can be obtained in the reaction of boron trioxide with an appropriate alcohol [33]. Another known method leading to the obtaining of oxyethylene glycol borate oligomers consists in the reaction of  $\text{BH}_3$  and tetrahydrofuran complex with oxyethylene monoether glycol [34]. It was found that selected obtained salts show properties of room temperature ionic liquids (RTILs). The ionic conductivity of the obtained borate salts was studied, in the neat form and in solutions in polar solvents. The obtained salts were used also as components of polymer electrolytes involving various polymer matrices: poly(ethylene oxide) (PEO), poly(trimethylene carbonate) (PTMC) and acrylonitrile and butyl acrylate copolymers.

## 2. Experimental

### 2.1. Reagents

$\text{B}_2\text{O}_3$  (Aldrich), oxyethylene glycol monomethyl ethers [(EO), ethylene oxide repeat unit:  $-(\text{CH}_2\text{CH}_2\text{O})_n-$  where  $n=1, 2, 3, 7$ ; Aldrich] were dried over sodium, then distilled and stored over molecular sieves in argon atmosphere, butyllithium (BuLi, 2.0 M solution in hexane, Aldrich) was used as supplied. The solvents acetonitrile (Aldrich), hexane (Merck), toluene (Aldrich), propylene carbonate and ethylene carbonate (Aldrich) were dried according to standard methods and stored over molecular sieves in argon atmosphere. Cyclic propylene sulfite (CPS) was obtained according to the procedure described earlier [35] in the copolymerization of propylene oxide with sulfur dioxide catalyzed by pyridine and then

decomposed in the presence of trimethylchlorosilane  $(\text{CH}_3)_3\text{SiCl}$ . Poly(trimethylene carbonate) was obtained *via* ring-opening polymerization of six-member cyclic carbonate (trimethylene carbonate) [36], the copolymers of butyl acrylate (BuA, Fluka) and acrylonitrile (AN, Aldrich) [p(AN-BuA)] with molar ratio AN:BuA 5:1 and 2:1 were obtained by radical polymerization in the presence of azobutyronitrile as initiator [37] (Scheme 1). Poly(ethylene oxide) (Aldrich,  $M_w = 5 \times 10^6 \text{ g mol}^{-1}$ ) was dried at  $50^\circ\text{C}$  for 24 h under vacuum.

### 2.2. Instruments and methods

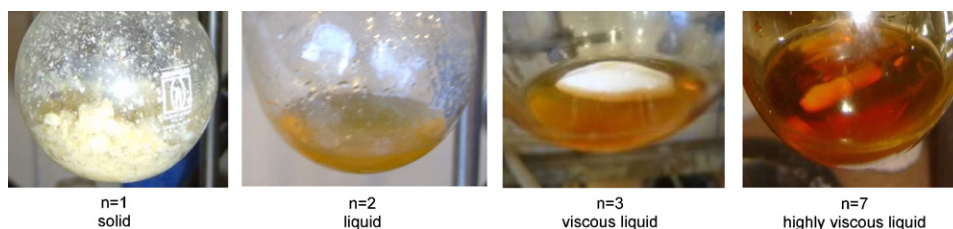
The chemical structure of  $\text{Li}[(\text{RO})_3\text{BBu}]$ , where  $\text{R} = -(\text{CH}_2\text{CH}_2\text{O})_n\text{CH}_3$ ,  $n=1, 2, 3, 7$  was characterized by  $^1\text{H}$  (Varian 400 MHz) and  $^{11}\text{B}$  NMR referenced to pirazabol (2.6 ppm in  $\text{C}_6\text{D}_6$ ) (Varian 128.3 MHz) in solutions in  $\text{CD}_3\text{CN}$ . DSC was carried out on TA Q200 calorimeter in hermetically sealed pans for volatile samples under a nitrogen flow. The measurements were conducted from  $-100$  to  $300^\circ\text{C}$  with heating rate of  $10^\circ\text{C min}^{-1}$ . The glass transition temperatures were determined from the Modulated Differential Scanning Calorimetry MDSC thermogram during heating cycle with heating rate of  $20^\circ\text{C min}^{-1}$ .

The electrolytes were prepared under an inert gas using syringes for transferring liquid substances and solid components were weighed in a dry-box. The liquid electrolytes were obtained by dissolving  $\text{Li}[(\text{RO})_3\text{BBu}]$  in anhydrous polar solvents in desired proportion and in the case of solid electrolytes by dissolving in acetonitrile the salt and polymeric matrix: PEO, p(AN-BuA)] or PTMC. Then, acetonitrile was removed under reduced pressure. Ionic conductivity of the electrolytes was determined from the impedance measurements carried out in cells with stainless steel electrodes using VMP3 potentiostat/galvanostat (Bio-Logic, France) in the frequency range from  $10 \mu\text{Hz}$  to  $500 \text{ kHz}$  when the influence of temperature was studied in the range from  $20$  to  $80^\circ\text{C}$ .

## 3. Results and discussion

### 3.1. Synthesis and characterization of lithium alkyltrialkoxycarbonates $\text{Li}[\text{Bu}(\text{RO})_3\text{B}]$

In the first step of the salt synthesis, trialkoxyborates were obtained from  $\text{B}_2\text{O}_3$  and respective oxyethylene glycol monomethyl ethers with removal of the produced water in the form of an azeotrope with toluene [33], according to the reaction



**Fig. 1.** Pictures of  $\text{Li}\{[\text{CH}_3(\text{OCH}_2\text{CH}_2)_n\text{O}]_3\text{BC}_4\text{H}_9\}$  salts, where  $n=1, 2, 3$  and  $7$ .

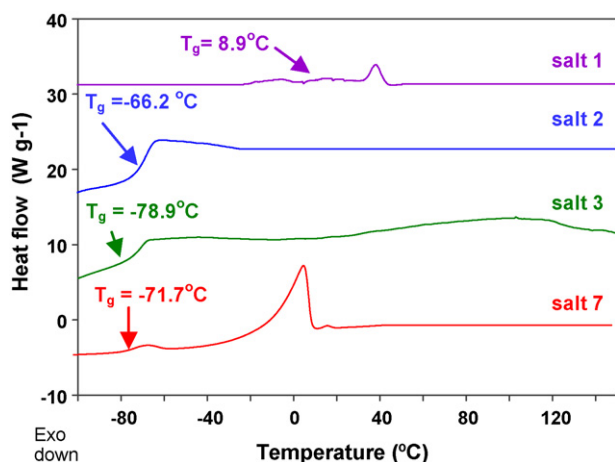
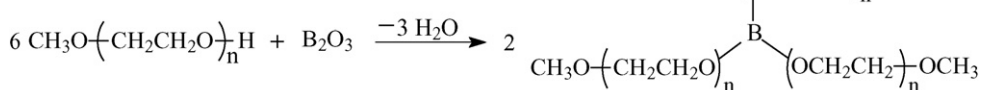
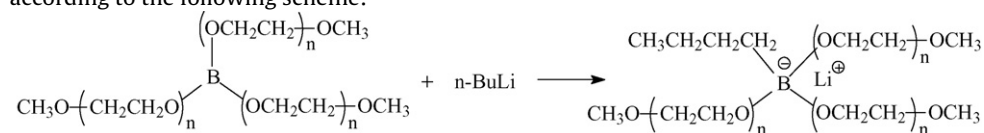


Fig. 2. Thermograms of  $\text{Li}\{[\text{CH}_3(\text{OCH}_2\text{CH}_2)_n\text{O}]_3\text{BC}_4\text{H}_9\}$ , where  $n = 1, 2, 3$  and  $7$  obtained from the IInd cycle of heating.

scheme:



The obtained trialkoxy derivatives of boron were converted into the form of lithium salts in the reaction with  $n$ -butyllithium, according to the following scheme:



$n = 1, 2, 3, 7$

The reactions were performed by gradually dropping the butyllithium solution in hexane to the trialkoxyborane solution in hexane during vigorous stirring and cooling of the reaction mixture due to the strong exothermal effect. After reaction completion the product was washed several times with hexane and dried under reduced pressure. In the case when  $n = 1$ , the product obtained had a crystalline form, and the other salts formed transparent liquids of increasing viscosity with elongation of the oxyethylene substituent. Fig. 1 shows pictures of the salts obtained.

On the basis of DSC measurements the phase transitions temperatures of the obtained salts were determined; the thermograms obtained for the IInd heating cycle are presented in Fig. 2. As can be noticed, the salt with substituent  $\text{R} = -\text{CH}_2\text{CH}_2\text{OCH}_3$  ( $n = 1$ ), characterized by a considerably high glass transition temperature ( $T_g = 8.9^\circ\text{C}$ ), is crystalline and melts at  $76.1^\circ\text{C}$  (in 1st heating cycle). The other salts have low  $T_g$  of the order of  $-66$  to  $-71^\circ\text{C}$ . For  $n = 2$  and  $3$  no tendency towards crystallization is observed, and for the salt of  $n = 7$  the side oxyethylene substituents are long enough to form substances of a regular structure, of melting point  $ca. 7^\circ\text{C}$ .

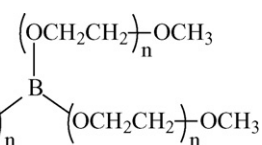
The salts obtained were spectrally characterized with the aid of  $^1\text{H}$  and  $^{11}\text{B}$  NMR. In Fig. 3 is presented the  $^{11}\text{B}$  NMR spectrum recorded for the  $\text{Li}\{[\text{CH}_3(\text{OCH}_2\text{CH}_2)_2\text{O}]_3\text{BC}_4\text{H}_9\}$  salt. The chemical shift of the product signal is in the region characteristic for four-coordinative boron in the anion form and is equal to  $6.54$  ppm. If the reaction is carried out too quickly, not diluting the reagents due to the high reactivity of butyllithium, the derivative containing four butyl groups,  $\text{Li}^+[(\text{C}_4\text{H}_9)_4\text{B}]^-$ , can be formed. In  $^{11}\text{B}$  NMR spectra its chemical shift is at  $ca. -14$  ppm (Fig. 3).

To evaluate the susceptibility of the borate salts obtained towards hydrolysis and oxidation, two types of experiments were carried out. The first one consisted in the contact of the salt with air for a desired time, and in the second method a desired amount of water was added to the salt solution in acetonitrile, or gaseous oxygen was passed through such a solution. About 20 min after exposition of the salt, changes in NMR spectra were observed. After 1 h the changes were distinct – gradual substitution of alkoxy groups with hydroxyl ones took place (the  $^{11}\text{B}$  NMR spectrum obtained is presented in Fig. 4). The passing through of oxygen, even for an hour, does not cause changes in the spectrum. The final products of hydrolysis of the studied salts are  $\text{LiOH}$ ,  $\text{Li}[(\text{OH})_4\text{B}]$  (signal in the  $^{11}\text{B}$  NMR spectrum at  $2.74$  ppm) and alcohols.

### 3.2. NMR analysis of $\text{Li}\{[\text{CH}_3(\text{OCH}_2\text{CH}_2)_n\text{O}]_3\text{BC}_4\text{H}_9\}$ in $\text{CD}_3\text{CN}$ solution

$n = 1$   $^1\text{H}$  NMR:  $\text{BCH}_2$   $-0.346$  to  $-0.242$  ppm (m, 2H),  $\text{CH}_2\text{CH}_2\text{CH}_3$   $0.667$ – $1.376$  ppm (m, 7H),  $\text{OCH}_3$   $3.015$ – $3.181$  ppm (s, 9H),  $\text{OCH}_2\text{CH}_2\text{O}$   $3.181$ – $3.518$  ppm (m, 6H);  $^{11}\text{B}$  NMR:  $5.99$  ppm.

$n = 2$   $^1\text{H}$  NMR:  $\text{BCH}_2$   $-0.225$  to  $-0.116$  ppm (m, 2H),  $\text{CH}_2\text{CH}_2\text{CH}_3$   $0.773$ – $1.541$  ppm (m, 7H),  $\text{OCH}_3$



$3.308$ – $3.459$  ppm (s, 9H),  $(\text{OCH}_2\text{CH}_2)_2\text{O}$   $3.459$ – $3.908$  ppm (m, 12H);  $^{11}\text{B}$  NMR:  $6.54$  ppm.

$n = 3$   $^1\text{H}$  NMR:  $\text{BCH}_2$   $-0.202$  to  $-0.117$  ppm (m, 2H),  $\text{CH}_2\text{CH}_2\text{CH}_3$   $0.821$ – $1.524$  ppm (m, 7H),  $\text{OCH}_3$   $3.268$ – $3.409$  ppm (s, 9H),  $(\text{OCH}_2\text{CH}_2)_3\text{O}$   $3.485$ – $3.757$  ppm (m, 18H);  $^{11}\text{B}$  NMR:  $6.56$  ppm.

$n = 7$   $^1\text{H}$  NMR:  $\text{BCH}_2$   $-0.225$  to  $-0.128$  ppm (m, 2H),  $\text{CH}_2\text{CH}_2\text{CH}_3$   $0.783$ – $1.521$  ppm (m, 7H),  $\text{OCH}_3$   $3.307$  ppm (s, 9H),  $(\text{OCH}_2\text{CH}_2)_{17}\text{O}$   $3.464$ – $4.075$  ppm (m, 42H);  $^{11}\text{B}$  NMR:  $6.56$  ppm.

### 3.3. Ionic conductivity of lithium alkyltrialkoxoborates $\text{Li}[\text{Bu}(\text{RO})_3\text{B}]$

Fig. 5 shows the ionic conductivity of lithium alkyltrialkoxoborates at  $30, 50,$  and  $70^\circ\text{C}$  as a function of the number of oxyethylene units in the alkoxy groups. The salt comprising the  $\text{CH}_3\text{OCH}_2\text{CH}_2$  ( $n = 1$ ) group as the alkoxy substituent is a solid under normal conditions – to carry out measurements it was pressed under pressure to obtain a pellet. The results presented are related to the temperature above the glass transition temperature ( $T_g = 8.9^\circ\text{C}$ ) and below the melting point ( $T_m = 76^\circ\text{C}$ ) of the described salt. Under these conditions the conductivity is low and is equal to  $ca. 8 \times 10^{-8} \text{ S cm}^{-1}$ . As can be noticed, among the derivatives studied by us, the highest conductivity is shown by the salt comprising three oxyethylene units; its ambient temperature conductivity is  $2 \times 10^{-5} \text{ S cm}^{-1}$ . Probably  $n = 3$  is the number of oxyethylene monomeric units, which assures appropriate coordination of the lithium cations forming a structure, in which the distance between

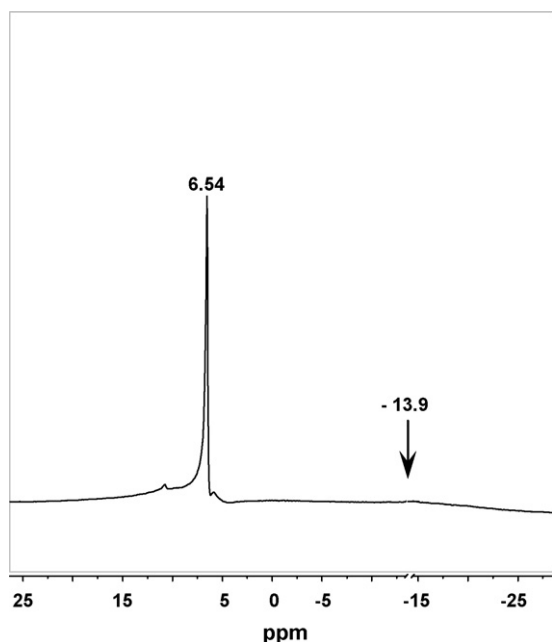


Fig. 3.  $^{11}\text{B}$  NMR spectrum of  $\text{Li}\{[\text{CH}_3(\text{OCH}_2\text{CH}_2)_2\text{O}]_3\text{BC}_4\text{H}_9\}$  in  $\text{CD}_3\text{CN}$  solution at  $30^\circ\text{C}$ .

respective basic centers favors hopping of the  $\text{Li}^+$  ions. Ion transport takes place due to segmental motion of the oxyethylene substituents. This phenomenon is favored by an increase in temperature. Effective complexation of lithium cations by oxyethylene substituents decreases the interaction of  $\text{Li}^+$  cations with the borate anion resulting in an increase in ionic conductivity. Such an effect is not observed for salts of  $n=1$ , for which the low conductivity results probably from the stronger interaction of  $\text{Li}^+$  with salt anions. When the oxyethylene substituent is longer ( $n=7$ ), the conductivity of the salt is smaller than that for  $n=3$ , due to larger energy barriers connected with accepting appropriate conformation of oligoether substituents, the motion dynamics of which affects the lithium cations transport rate. The ion mobility decreases along with a considerable increase in viscosity of this salt. It should be also noted that with the large mass of anions ( $M_w = 1125 \text{ g mol}^{-1}$ ) also their mobility decreases. Moreover, these groups have a tendency towards crystallization and therefore the mode of cation transport within the regular regions changes, similarly as in the PEO matrix [38].

The salt best conducting in bulk, of  $n=3$ , was selected for conductivity measurements of solutions in aprotic solvents. CPS, PC and a mixture of EC with PC in equiweight proportion were used as solvents. The obtained ionic conductivity data as a function of salt concentration is presented in Fig. 6.

Among the solvents used, CPS showed the best properties as a conducting medium, affording the highest conductivity values over a wide concentration range. This results from the fact that CPS is characterized by high polarity favoring dissociation of the salt and at the same time the solutions have the lowest viscosity. The maximum conductivity values obtained for the EC/PC mixture are comparable to that with solutions in CPS, however, they occur at higher salt concentrations and in a much narrower range. The lowest conductivities are shown by solutions in PC (Fig. 6). At  $30^\circ\text{C}$ , in the best solvent (CPS), the conductivity is  $1.2 \times 10^{-4} \text{ S cm}^{-1}$ . A probable explanation of the presented differences in ionic conductivity of the borate salt solutions in the solvents studied is their different effect on the viscosity of solutions and on the connected with it ion mobility. At very low salt concentrations the differences in viscosity are low, similarly at very high salt concentrations, whereas at

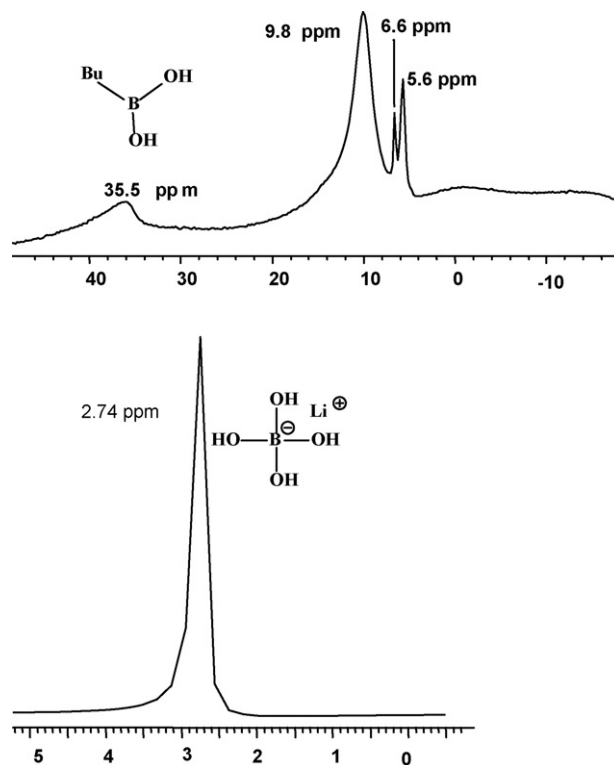


Fig. 4.  $^{11}\text{B}$  NMR spectrum of products of  $\text{Li}\{[\text{CH}_3(\text{OCH}_2\text{CH}_2)_2\text{O}]_3\text{BC}_4\text{H}_9\}$  hydrolysis in  $\text{CD}_3\text{CN}$  solution at  $30^\circ\text{C}$ .

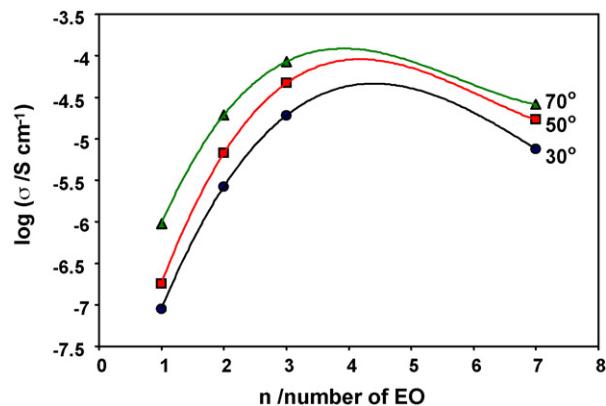


Fig. 5. Isotherms of ionic conductivity at  $30$ ,  $50$ , and  $70^\circ\text{C}$  of  $\text{Li}\{[\text{CH}_3(\text{OCH}_2\text{CH}_2)_n\text{O}]_3\text{BC}_4\text{H}_9\}$ , for  $n=1, 2, 3$  and  $7$ .

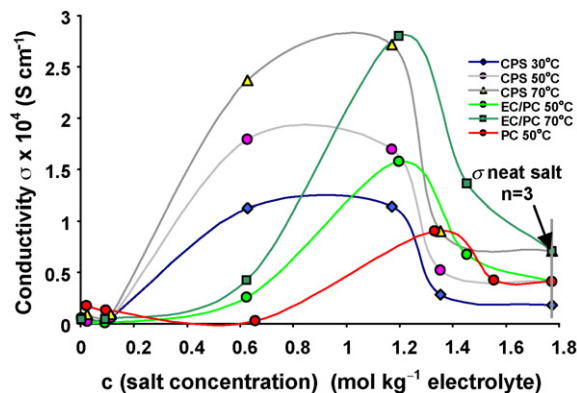


Fig. 6. Ionic conductivity solutions of  $\text{Li}\{[\text{CH}_3(\text{OCH}_2\text{CH}_2)_3\text{O}]_3\text{BC}_4\text{H}_9\}$  in various solvents such as CPS, PC and EC/PC as a function of salt concentration.

**Table 1**

Temperature of phase transitions of solid electrolytes containing PEO and 10 mol.% of  $\text{Li}[(\text{RO})_3\text{BBu}]$ , where  $\text{R} = -(\text{CH}_2\text{CH}_2\text{O})_n\text{CH}_3$ ,  $n = 1, 3$  and  $7$  obtained from DSC measurements.

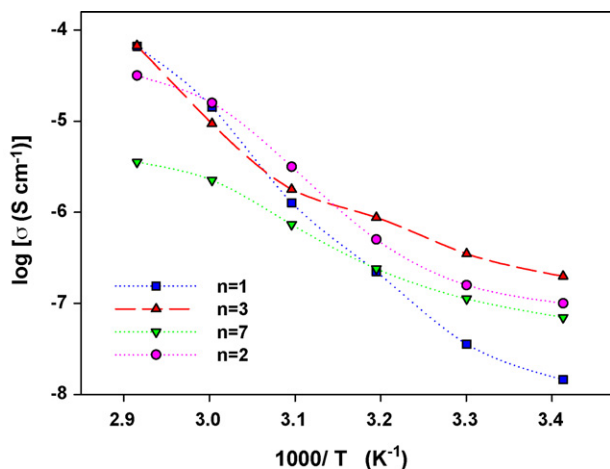
Type of salt $n$	$T_g$ ( $^\circ\text{C}$ )	$T_m$ ( $^\circ\text{C}$ )	Degree of PEO crystallinity (%)
1	-71.3	72.0	50.8
3	-80.4	66.0	46.5
7	-78.1	-6.6; 66.7	47.6

a certain concentration range the viscosity of solutions was lower for CSP than that in the case of other solvents. Solutions of many other salts, e.g.  $\text{LiPF}_6$  give higher conductivities by over an order of magnitude. However, it should be noted that in this case due to the bulkiness of anions, their mobility is probably considerably limited. For example, for lithium aluminate salts containing oligoether groups, high lithium transference numbers, reaching the value of  $t_+ = 0.78$ , were obtained [20]. Therefore, limited anion mobility may be an explanation of the lower salt ionic conductivity.

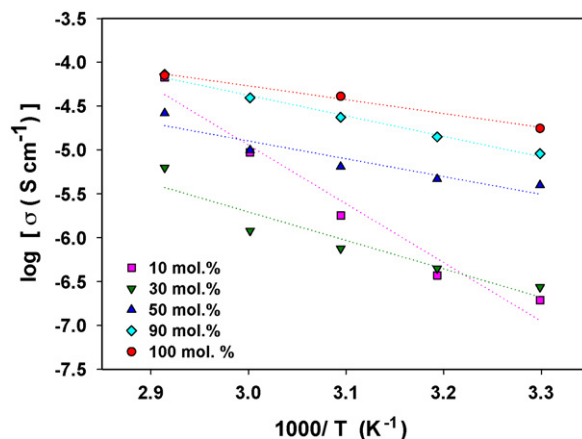
#### 3.4. Characterization of polymer electrolytes with lithium alkyltrialkoxyborates $\text{Li}[\text{Bu}(\text{RO})_3\text{B}]$

Solid polymer electrolytes involving PEO as the polymer matrix and 10 mol.% of lithium alkyltrialkoxyborates containing groups with  $n = 1, 2, 3$  or  $7$  oxyethylene monomeric units (EO m.u.) were obtained. In Table 1 is shown the temperature of phase transitions obtained from DSC measurements. As can be noticed, the addition of salt, also of ion liquid properties ( $n = 3$  and  $7$ ) in an amount of 10 mol.% does not limit the PEO crystallization, and the share of crystalline phase determined from the 1st heating cycle is about 50%. These electrolytes are characterized by low glass transition temperature, in the range of  $-70$  to  $-80$   $^\circ\text{C}$ .

Fig. 7 presents the results of ionic conductivity measurements. As can be noticed, the greatest differences in conductivity occur in the temperature range below the melting point of the PEO crystalline phase. Similarly as in liquid systems, the electrolyte with the salt of  $n = 3$  shows the best conducting properties, and that of  $n = 1$  the worst. The salt comprising 7 EO m.u. conducts much weaker than in comparison to that of the neat salt. The considerable limitation of anion mobility due to their greatest mole mass is probably an explanation of this. In the polymer matrix composed of polyether chains of analogous chemical structure, tangling of them with oligoether substituents takes place, which additionally immobilizes the salt anions, resulting in a decrease in ionic conductivity.



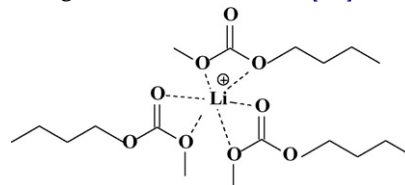
**Fig. 7.** Ionic conductivity of polymer electrolytes containing PEO and 10 mol.% of  $\text{Li}\{[\text{CH}_3(\text{OCH}_2\text{CH}_2)_n\text{O}]_3\text{BC}_4\text{H}_9\}$  with  $n = 1, 2, 3$  and  $7$ .



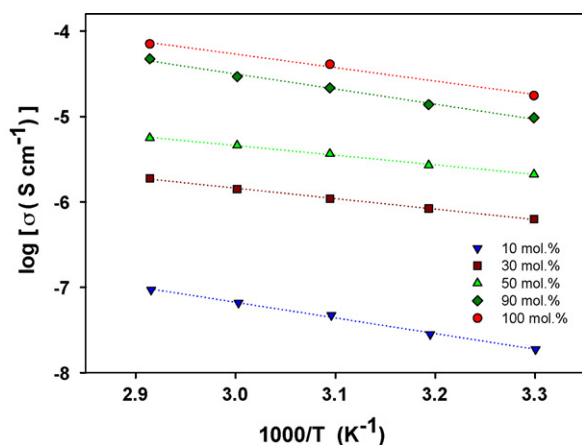
**Fig. 8.** Ionic conductivity of polymer electrolytes containing  $\text{Li}\{[\text{CH}_3(\text{OCH}_2\text{CH}_2)_3\text{O}]_3\text{BC}_4\text{H}_9\}$  and PEO in various proportions from 10 to 90 mol.% and as a reference the conductivity of the neat salt.

Fig. 8 presents the ionic conductivity of polymer electrolytes containing  $\text{Li}\{[\text{CH}_3(\text{OCH}_2\text{CH}_2)_3\text{O}]_3\text{BC}_4\text{H}_9\}$  and PEO in various proportions from 10 to 90 mol.% and as a reference the conductivity of the neat salt is presented. The dependences presented in the figure show how the mode of ion transport changes depending on the salt concentration. At 10 mol.% a typical “polymer-in-salt” is present, for which the effect of temperature is very clear, which is connected with a gradual decrease in the crystalline phase content and increase in the mobility of PEO chains, on which the ion migration depends. At 30 mol.% of the salt, the salt dissociation probably recedes and the share of ion pair and higher associates increases [39,40] and the conductivity decreases. In the literature we can find suggestions that the concentration dependences of conductivity are attributable to a decrease in anion mobility with decreasing free volume [41]. With an increase in salt concentration the percolation threshold is reached and due to the possibility of contact of ion agglomerates and formation of paths, the ionic conductivity increases, at 90 mol.% of the salt it is slightly lower than that of neat salt.

In order to show the effect of the polymer matrix structure on the conductivity of electrolytes involving a borate salt, the synthesis of electrolytes has been carried out utilizing the polymer of an aliphatic carbonate structure: poly(trimethylene carbonate) at analogous salt concentrations as for PEO. The results are presented in Fig. 9. In the case of this matrix, at low salt concentrations (10 mol.%) the conductivity is much lower than that for PEO. The ability of ion transport below the percolation threshold for polycarbonates is much weaker than that in the case of PEO, for which the distances between the lithium cations coordination centers are optimal. It can be assumed that by analogy for polymers containing ester groups, interaction of carbonate groups with lithium cations takes place causing dissociation of the salt [42].



At high salt concentrations the conductivity gradually approaches that of the neat salt. The activation energy determined from the Arrhenius plot, both for low (10 mol.%) and high concentrations is relatively low and close to the value determined for the neat salt ( $E_a = 0.313$  eV) shown in Table 2.  $E_a$  are clearly lower than the energies determined for systems with PEO, especially at low salt concentrations.



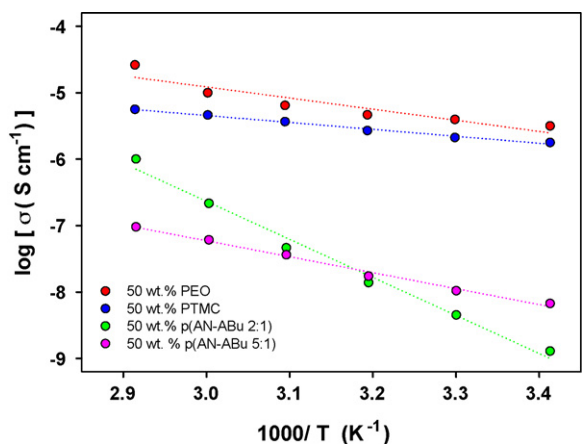
**Fig. 9.** Ionic conductivity of polymer electrolytes containing  $\text{Li}\{[\text{CH}_3(\text{OCH}_2\text{CH}_2)_3\text{O}]_3\text{BC}_4\text{H}_9\}$  and poly(trimethylene carbonate) (PTMC) in various proportions from 10 to 90 mol.% and as a reference the conductivity of the neat salt.

**Table 2**

Activation energy determined from Arrhenius plots for electrolytes containing  $\text{Li}\{[\text{CH}_3(\text{OCH}_2\text{CH}_2)_3\text{O}]_3\text{BC}_4\text{H}_9\}$  and various polymer matrices.

Salt content (mol.%)	Polymeric matrix	$E_a$ (eV)
100	–	0.313
10	PTMC	0.353
50		0.207
10	PEO	0.972
30		0.644
50		0.332
50	p(AN–BuA) 2:1	1.136
50	p(AN–BuA) 5:1	0.476

**Fig. 10** compares three types of polymeric matrices: PEO, PTMC and two copolymers of acrylonitrile and butyl acrylate p(AN–BuA) of AN to BuA molar ratio equal 2:1 and 5:1. The matrices were compared with each other using 50 mol.% of the salt  $\text{Li}\{[\text{CH}_3(\text{OCH}_2\text{CH}_2)_3\text{O}]_3\text{BC}_4\text{H}_9\}$ . At this concentration the highest ionic conductivity was shown by the system with PEO, slightly worse conducting properties are shown by that with PTMC. Acrylonitrile copolymers are considerably worse matrices. The percolation threshold is probably reached earlier in the case of PTMC and PEO than in other case. The low enthalpy of melting of the



**Fig. 10.** Ionic conductivity of polymer electrolytes containing  $\text{Li}\{[\text{CH}_3(\text{OCH}_2\text{CH}_2)_3\text{O}]_3\text{BC}_4\text{H}_9\}$  and as polymeric matrix: poly(ethylene oxide) (PEO), poly(trimethylene carbonate) (PTMC) and two acrylonitrile and butyl acrylate copolymers p(AN–BuA) of AN to BuA molar ratio equal 2:1 and 5:1.

PEO crystalline phase on the DSC thermograms ( $\Delta H = 15 \text{ J g}^{-1}$ ) indicates a small, 5% share of the PEO crystalline phase, which provides good conditions for ion transport. The electrolyte involving PTMC is amorphous and highly plasticized, which might be an explanation of the good conductivity. The electrolytes containing p(AN–BuA) copolymers are stiff membranes, and at 5:1 composition of the monomeric units partial inhomogeneity of the system is observed. The activation energies for these electrolytes are higher than that for the other matrices, especially the system with the copolymer at 5:1 composition is characterized by high  $E_a$  equal 1.14 eV (Table 2).

#### 4. Conclusions

The obtained lithium borate salts show interesting physical properties, constituting at  $n \geq 2$  room temperature ionic liquids of low glass transition temperature,  $T_g$  of the order from  $-70$  to  $-80$  °C. The optimal conducting properties among the borates studied is shown by the salt containing  $n = 3$  EO units in the alkoxy group, for which the ambient temperature ionic conductivity in bulk is  $2 \times 10^{-5} \text{ S cm}^{-1}$ . Cyclic propylene sulfite appeared to be a good low molecular weight solvent for the borate salts, and PEO showed the best properties from among the studied polymer matrices at low salt concentration, however, for polymer-in-salt type systems, polycarbonate seems to be an interesting matrix. The lower conductivity of salts of longer oxyethylene segment results probably from the low mobility of this anion caused by the high molecular mass and possibility of tangling of the substituents with the polymer matrix. To prove the low mobility of the salt anions, studies are currently being carried out on the lithium cation transference numbers.

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