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Polyanionic electrolytes with high alkali ion conductivity

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Abstract

We describe the synthesis of chain polymers that contain Lewis base or Lewis acid groups in the backbone that can then be reacted with acidic or basic groups to form polyanions with weak binding sites for alkali cations. We review both ‘base-in-chain’ and ‘acid-in-chain’ approaches to this type of polyanion. When the anionic groups are optimally separated, the conductivities of the polymers are found to be high relative to those of most single ionic conducting polymers and even most non-imide salt-in-polymer electrolytes. The concentration of ionic groups, can be varied using polyethylene glycol links (spacers) of variable length. The conductivity is found to maximize near the value which maximizes the conductivity in simple salt-in-fully amorphous polyether polymers (the number of the ethyleneoxy repeating unit $n = 12$). Finally a novel process, which achieves the same objective by a different route, will be described. This class of weakly coordinating polyanionic electrolyte, in which the coulomb traps for Li^+ are little if at all stronger than the polyether chelation traps, is seen as a promising development in the solid polymer electrolyte field. Except for the case of ‘weak trap’ acid-in-chain polymers, all these electrolytes are unicationic in their conduction.

1. Introduction

The field of solid electrolytes based on the dissolution of salts in polyethers is very heavily researched due to their promise for solid state electrochemical device applications [1]. One of the most successful of these uses lithium bis(trifluoromethanesulfonyl) imide ($\text{LiN}(\text{SO}_2\text{CF}_3)_2$ or LiTFSI) as the dissolved salt in polyethylene oxide and obtains room temperature conductivities as high as $10^{-4.3} \text{ S cm}^{-1}$ [2]. We will keep this figure in mind as a standard for comparison with materials being reported in the present paper.

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A well known disadvantage of the salt-in-PEO type of solid electrolyte is that the lithium is strongly chelated by the basic ether groups in the chain and that, as a consequence, the conductivity is dominated by the motion of the anions. Transport numbers as low as 0.1 have been reported for the Li cations in these media [3], and even in the favourable case of lithium imide, the transport number of Li^+ is estimated to be only 0.2–0.3 [4].

In an attempt to overcome this drawback, the senior author and his group have been utilizing the chain polymers as a dilute component to impart ‘solidity’ [5] to molten alkali metal salt mixtures of high conductivity. The salts are chosen so that the liquid is stable at ambient temperature and, also, the cationic motion is decoupled from the anionic motion. In this case the conductivity is cationic as in the popular ‘superionic glass’ electrolytes [6]. For this to be achieved, the anions must be of the ‘weakly coordinating’ variety and much effort has been made to synthesize new examples of such anions. Unfortunately it has proven extremely difficult to find simple salts of lithium cations that have high stability and remain liquid at room temperature. Those that do, such as the unsymmetrical chlorofluorosulfonyl imide and its dichloro-equivalent [7], prove to have very poor conductivities.

One strategy for overcoming the crystallization problem [8–12], combines aspects of the two approaches, salt-in-polymer and polymer-in-salt, by covalently connecting (tethering) the anions using short polymer chains (‘tethered ions’). This makes the crystallization of the salt almost impossible. While solving the crystallization problem, this approach suffers from the effects of undesirable increases in glass transition temperature and, at least in the initial attempts using sulfonate anions [8], from the loss of good decoupling characteristics. The consequence has been rather poor ambient temperature conductivities [9], though recent developments of this approach by Ohno and co-workers [10–12] have given much improved performance by use of more favourable anionic moieties.

The present approach takes this ‘tethered anion’ strategy one step further by placing favourable anionic moieties in the polymer chain itself. Results are optimized by choosing a concentration of anionic links that maximizes the ionic conductivity. To prepare polymers with favourable (weakly coordinating) anionic moieties, three approaches have been taken. The first (‘base-in-chain’) is to place a basic anion in the chain and then overcome its basicity by reacting the polymer anions with a Lewis acid that is stronger than the Li^+ cation itself [13, 14]. This displaces the Li^+ from the anion site, leaving it free to conduct, unicationally. The second approach (‘acid-in-chain’) [15] is to first synthesize a molecular polymer with Lewis acid groups in the chain and then to react these groups with Lewis base anions provided by an added lithium salt. These attach to the chain at the acid sites, creating a polyanionic polymer in which Li^+ cations are the conducting species. The third approach [16] accomplishes the results of the first approach in a concerted synthetic process that yields an anionic polymer with the best properties of the results of the first two approaches.

1.1. Base-in-chain anionic polymers

We have previously shown [13] that anionic polymers with high conductivities can be obtained by linking anion imide groups by short molecular connecting units of different character to make polymers with negative charges on the chain nitrogen atoms. These anionic polymers, of which an example is $-\text{[SO}_2\text{-N-CO-N-SO}_2\text{]}_n^-$, have poor conductivity in the ‘bare’ state because the imide nitrogens are basic enough to bind the Lewis acid cations (Li^+) rather strongly in the absence of solvent. The binding is weaker than in the case of the pure ionic liquid imide (which is an insulator except at very high temperature), but strong enough to preclude useful Li^+ ion conductivity. However, these systems become good conductors if a stronger Lewis acid than Li^+ is offered to the imide nitrogen. Thus additions of the Lewis acid

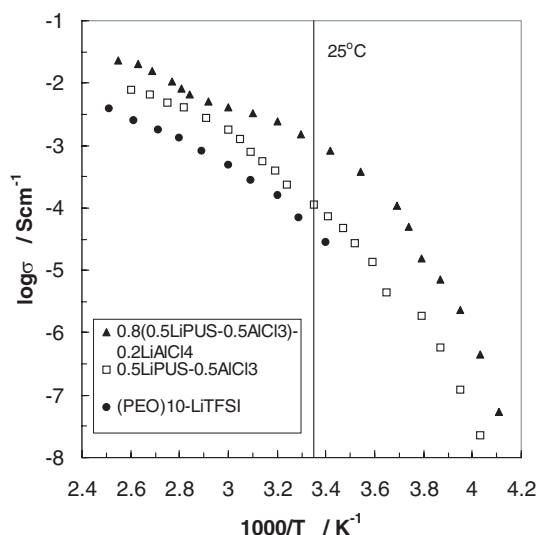


Figure 1. Arrhenius plots of the conductivity of the AlCl_3 complex of lithium polyureasulfonyl imide (LiPUSIm) and a solution with LiAlCl_4 . Note the ambient conductivity, $10^{-3.8} \text{ S cm}^{-1}$ of the pure complex, which is thought to be a sort of polytetrahaloaluminate. The solutions remain non-crystallizing up to $\sim 20 \text{ mol\% LiAlCl}_4$ (the dip at $\sim 60^\circ\text{C}$ is probably due to a trace of crystallization). At $20 \text{ mol\% LiAlCl}_4$ the ambient conductivity is $10^{-2.9} \text{ S cm}^{-1}$ and the conductivity at T_g , $10^{-7.3} \text{ S cm}^{-1}$. The latter value indicates a high level of decoupling of the conducting modes (presumed due to Li^+) from the viscosity, hence high lithium transport numbers. The conductivity of LiTFSI in PEO ($\text{O}:\text{Li}^+ = 10$) is shown for comparison.

AlCl_3 result in very high ionic conductivity, $10^{-3.8} \text{ S cm}^{-1}$, as shown in figure 1 represented by open squares.

These anionic polymers, can be regarded as a polypseudotetrahaloaluminates (since the $-(\text{S}-\text{N}-\text{C})-$ group in the chain acts like a pseudohalide). They not only have the highest conductivities of any chain polymers yet synthesized, but they may also be plasticized with LiAlCl_4 , without loss of single ion conductivity. Unlike normal plasticizers, LiAlCl_4 is incombustible. The conductivity of the most highly plasticized case that remains amorphous at ambient temperature is $10^{-3} \text{ S cm}^{-1}$ [12]. These polyanionic electrolytes also have good electrochemical characteristics, but overall they are not preferred because of the reliance on AlCl_3 (or BF_3) as the complexing agent. The Lewis acid may in principle be lost over time as vapours. Though the escape rate has not been determined, it may be extremely low. The BF_3 -complexed materials have not yet been properly characterized, though their glass transition temperatures are known to be lower than those of the AlCl_3 -complexed systems [14].

1.2. Acid-in-chain polymers and their conversion to polyanions

An alternative synthetic approach is to put the Lewis acid groups into the chain itself, so there can be no question of their loss as a volatile species. The anions are then created by adding the Lewis base as a negatively charged species, i.e. an anion, that is charge-compensated by any cation of choice [15]. This approach permits us to generate chains that range from those with permanent anionic groups within the chain (in which the added base cannot be distinguished from a group that was already present in the molecular chain), to those in which the chain is

better described as a molecular entity with weak anionic traps. One aim is to organize such traps (strong or weak) so that they are of optimized concentration.

We note that an anionic polymer containing anion traps (boroxine rings) in the polymer structure has recently been described [17, 18]. This is a polymeric version of the BEG (boric acid esters of glycols) electrolyte additive described by us in an earlier work [19] and in more detail in a US Patent [20]. In the latter work we described the formation of polyBEG anion trapping polymers but did not pursue them because of their poor conductivities. The best conductivity reported by Mehta *et al* [18] was about $10^{-6.5}$ S cm⁻¹, which is rather poor compared with values found in the present work.

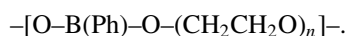
We have described [15] the preparation and properties of the polymers ranging from purely anionic polymers to purely anion-trapping polymers. The performance of these can be further modified by adding molecular or ionic plasticizer components on the one hand, and nanoscopic ceramic fillers, on the other.

2. Experiments

2.1. Synthesis

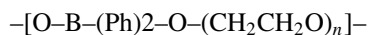
2.1.1. Base-in-chain polymers. The synthesis of polymers containing the imide nitrogen anionic group (as in LiTFSI) has been described in the literature [13] and need not be repeated here. It is straightforward enough, involving refluxing of, for example, urea with sulphonyl chloride, followed by lithiation at the imidic hydrogen by reaction with lithium hydride. The conductivity of the pure polymer is poor, but it increases greatly upon complexing the imide nitrogen with AlCl₃, setting the lithium cations free as mentioned earlier. Alternative to AlCl₃, BF₃ can be used as the Lewis base additive, and it results in lower glass transition temperatures than in the case of AlCl₃. The conductivities of the BF₃-complexed polymers have yet to be determined.

2.1.2. Acid-in-chain polymers, and their conversion to polyanions. To obtain the acid-in-chain molecular polymer that is used as a precursor to the formation of the polyanion, phenylboronic acid PhB(OH)₂ is reacted with PEG. This produces a chain in which the repeat unit is



Here the phenyl group remains attached to the boron. The boron is only three coordinated, hence is strongly acidic in character. In order to vary the spacing of the Lewis acid centres along the chain, the PEG used is chosen from diethylene glycol, triethylene glycol, PEG200, PEG400, PEG 600, or PEG1000. This yields polymers with the above repeat unit in which *n* varies from 2 to 23. The reaction is carried out in a boiling toluene solution and the water produced in the condensation reaction is collected and measured to determine the extent of the reaction. When the reaction is complete the solution is filtered and the solvent is removed on a rotary evaporator. The product is then further dried by overnight evacuation at 100 °C in a vacuum oven. This yields a viscous liquid or rubbery product. Because of the Lewis acidity of the undercoordinated boron, the polymer is very reactive to Lewis bases. This can then be used to synthesize the following three types of solid polymer electrolyte.

(i) *A purely anionic polymer.* The repeat unit is



in which there are now two phenyl groups attached to the boron, and the boron moiety carries a negative charge.

To create the above-illustrated anionic polymer, the molecular polymer obtained in the first step described above is reacted with phenyllithium in which the phenyl anion is a very strong base. The choice of the Ph^- anion as the base to combine with the Lewis acid boron on the initial chain guarantees the anionic character of the chain link because the two non-oxygen ligands on the boron are indistinguishable.

This polymer has only been made using poly(ethylene glycol) (PEG) with molecular weight of 600, and it is not known yet which PEG chain length will optimize the conductivity. For this choice of polyether segment, the polymer is a fluffy rubber that has a glass transition temperature of 219 K. The conductivity is low, $10^{-8} \text{ S cm}^{-1}$ at 25 °C, though it should rise quickly when plasticized, e.g. by 1,2-dimethoxyethane (DME). Both in neat and plasticized forms the conductivity must be purely cationic since the covalent bond formed in the acid–base reaction that binds the anionic phenyl moiety to the chain, has a bond energy far above any thermal energy at which the polymer will be tested. This leaves Li^+ as the only possible mobile species. Since it will be shown below how really high conductivity can be obtained in a purely anionic polymer, the case of Ph^- addition to the acid-in-chain polymer will not be discussed further. It is used here only to exemplify an extreme case (strongly bound, or fully incorporated, anionic reactant) of the present polymer class.

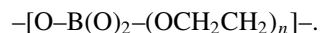
(ii) *A weakly anion-trapping molecular chain polymer.* At the other extreme, the same chain polymer described in the above synthesis is used simply as a solvent for a commonly used, and favourable, salt: lithium imide. The imide anion, intrinsically weakly coordinating, does not become incorporated in the polymer as in the previous case, but it is attracted to the acid site and is weakly trapped. This leads to a salt-in-polymer electrolyte with a high conductivity but also enhanced cationic transport, as described elsewhere [15].

We should note here that the trapping of the imide without binding, that occurs in this case, provides a contrast with the previous experience of molten salts [6] and of ‘base-in-chain’ polymers [13, 14]. There the imide group was in the chain and was reacted with the free Lewis acids AlCl_3 or BF_3 , which bonded strongly. The reason for the different strength of binding is that boron joined to three (unpolarizable) fluorine atoms is a much stronger Lewis acid than is boron joined to two oxygen atoms and a phenyl ring. This is because, in the latter case, the boron is able to draw charge from the oxygens and the phenyl ring to compensate for its formal deficiency in electrons. The result is that it binds less strongly to Lewis bases in the environment, e.g., imide anions. However, it is enough to provide a trapping effect on the anion and thereby to impede its motion. In so doing it enhances the cation transport number.

(iii) *An intermediate case in which there may be some anion mobility but it will be small.* Intermediates between these two cases are a number of possible variants on the same theme in which anions of intermediate basicity are used to provide the fourth ligand to the under-coordinated boron links in the chain. The preparative procedure is the same in each case. One example that has been studied in some depth is the case of the CN^- ligand which becomes the nitrile group in cases of sufficiently strong covalent linkage. In the present case, this ligand presumably retains considerable freedom particularly when the counter-cation is Li^+ with its greater field intensity. We prepared materials using both NaCN and LiCN in order to compare the effects of the different counter cation acidities (see figure 2 in section 3).

2.1.3. Polyanionic chains by direct synthesis. We have also made a polyanion [16] with a weakly charged anionic group, by means of a procedure that is quite different from any of the above—a simple two-step process that is described below. This polymer has a very promising conductivity, as will be seen. In order to relate this polymer to the conceptual scheme discussed in sections 2.1.1 and 2.1.2, the new polymer can be thought of as being formed by the following two-stage sequence.

- (i) The creation of polyethyleneglycolato orthoborate polyanion with the following repeat unit



In this chain, the B(O)_2 part of the in-chain orthoborate group carries three negative charges, hence is very basic (a base-in-chain polyanion) and would strongly trap lithium counter cations. This is avoided by the second step, which is:

- (ii) the capping of the two out-of-chain basic oxides of the orthoborate link with a doubly positive (Lewis acid) oxalato group $[\text{C(O)-C(O)}]^{2+}$. This yields a singly charged oxalato-borate anionic moiety in the chain. The single charge is distributed over four oxygens and two carbonyl groups to give a very weakly coordinating anionic link in the chain. As already stated, this description is not meant to represent the reaction mechanism but only to illustrate the conceptual relation to the polymers described in section 2.1.1.

In practice the polyanion is obtained by first creating the oxalato-capped orthoboric acid and then reacting it with PEG. Equal molar quantities of lithium hydroxide monohydrate, oxalic acid dihydrate and boric acid were reacted by boiling and all the water then removed. The solid acid residue was then refluxed with PEG in benzene in a distillation flask equipped with a water separator, and the reaction continued until no more water was released. The solvent in the polymer solution was evaporated on a rotary evaporator under reduced pressure to obtain a rubbery residue. This mass was refluxed with anhydrous chloroform followed by filtration of undissolved precipitates. The filtrate was evaporated down and the polymer was dried in a vacuum oven at 90°C for 48 h.

The charge density in the polymer is controlled to the optimum value by the choice of the parameter n , the number of the ethyleneoxy repeating unit in the PEG anion-spacer chain. We find an optimum performance for the value $n = 14$ which yields a single ion conductor with ambient temperature conductivity of $10^{-5.0} \text{ S cm}^{-1}$, as will be shown below. The belief that the polymer is a single ion conductor is, at this time, a chemical one. For a pure product of the formula described it is impossible to see how current can be carried by anything but the Li^+ species. It remains to be established that the polymer is in practice produced in a state of purity where its unicationic character can be manifested. Impurities such as unpolymerized LiBOB salt [21], can lead to some anionic conductivity, and its absence must be ensured by solvent extraction, and established by measurement. Determination of the lithium ion diffusivity, hence Li^+ contribution to conductivity, will be important for this purpose.

2.2. Physical and electrochemical characterization

To obtain the conductivity data displayed in figures 1–3, we used either film or liquid samples depending on the nature of the polymer or polymer–salt solution in hand. Conductivities were measured using an automated Hewlett Packard model frequency analyzer and Eurotherm temperature controller, as described in numerous previous papers [19, 20]. Electrochemical stabilities were determined on Pt using a PAR potentiostat at sweep rates of 1 mV s^{-1} and a three electrode cell, with metallic Li as counter and reference electrodes.

3. Results and discussion

The data from the original base-in-chain and acid-in-chain polyanionic materials that have been described in detail elsewhere [13, 14], were presented in figure 1. For the acid-in-chain type of polyanionic material of section 2.1.2, results for the case in which CN^- in the base added to

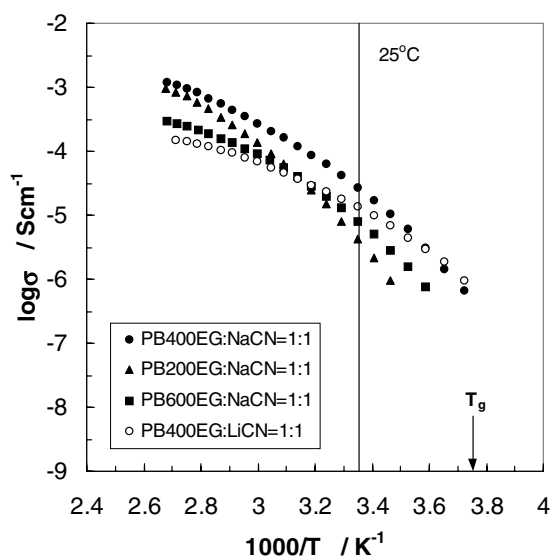


Figure 2. Arrhenius plots of conductivities of polyanionic polymers with nitrile side-groups made by reacting alkali cyanides with PEG-spaced boron-in-chain polymers. Open and filled circles compare Li^+ with Na^+ cases when the spacer is PEG 400. Triangles and squares show results for smaller and larger spacers, respectively. Note that in the small spacer case (filled triangles) the conductivity of the system (by short extrapolation) is about $10^{-8} \text{ S cm}^{-1}$ at its T_g (indicated by the arrow), showing that the conductivity is highly decoupled from the segmental motion, as in inorganic glasses (from [15], by permission).

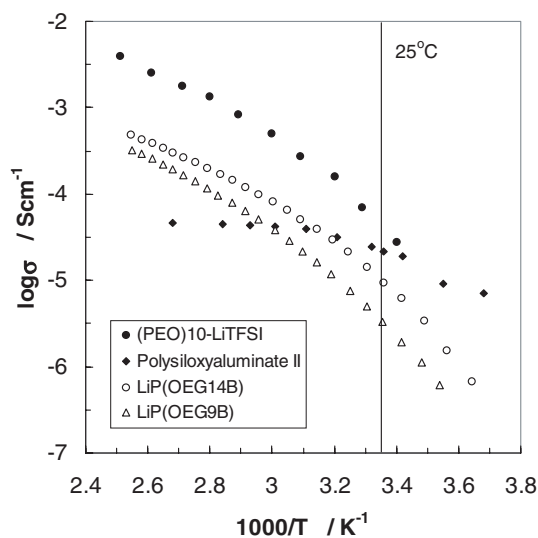


Figure 3. Comparison of the PEG-spaced oxalato borate anion polymer (open symbols for 9 and 14 ethyleneoxy unit spacers) with the siloxyaluminate anionic polymer of [22] and LiTFSI in PEO salt-in-polymer electrolyte of [2].

the chain (to become nitrile) are shown in figure 2. The conductivities of these systems, which are presumed to be unicationic, are not as high as those of the polytetrahaloaluminate polymers

of figure 1, but are comparable to those of the best salt-in-polymer electrolytes (introductory paragraph, and figure 3) in which at least 70% of the current is carried by anions.

The plot for the polyanion formed by addition of NaCN to the short spacer (PEG 200) boron-in-chain polymer, is of special interest. Figure 2 shows that while this polymer does not have a very high ambient temperature conductivity, its high temperature conductivity is comparable to that of the best salt-in-polymer systems [2]. Most interesting, however, is the conductivity at lower temperatures, since a short extrapolation shows that it remains unexpectedly high at its T_g (the arrow in figure 2). Rather than being 10^{-15} S cm $^{-1}$ as expected for a coupled system (10^{-17} S cm $^{-1}$ for a supercoupled system as LiClO $_4$ in PPO was found to be [14]), the conductivity is 10^{-8} S cm $^{-1}$, i.e. seven orders of magnitude higher. This means that the conductivity is highly decoupled from the segmental motions of the polymer chain, an occurrence which has not been seen previously in polyether type polymers. Indeed the decoupling index, R_t^* , for this case (from $\log R_t^* = 14.3 + \log \sigma_{T_g}$, equation 1 of [13]) is comparable with those for the base-in-chain polymers of figure 1 [13]. Even in a non-polymeric salt system this would imply that the conductivity would be unicationic at T_g and would remain unicationic to temperatures far above T_g .

The conductivity of the latter type of polymer should become much higher when the phenyl ring on the boron is replaced with a methyl group (methylboronic acid is available but is much more expensive than phenylboronic acid). The pendant phenyl ring has a major effect on the glass transition temperature of chain polymers (compare polystyrene with polypropylene) and its effect will be more important for short spacer compositions. Thus we may expect to be able to improve the conductivity of these systems very substantially.

For the third type of polyanionic polymer, which we have presented in section 2.1.3 as a novel version of the base-in-chain approach, the data are shown in figure 3. They are compared there with results from [2] for the best salt-in-polymer case, and with results for the most conducting of the single ion conducting polyanionic electrolytes previously reported [22]. Considering that only the Li $^+$ ion is conducting, the superiority of the present material is clear. The electrochemical stability of the polymer is comparable with that of solutions of the unpolymerized oxalato borate salt, LiBOB [21], namely, in excess of 4.5 V versus Li $^+$ /Li.

We have not yet explored the effects of plasticization on the conductivities of these polymers, but it must lead to values of conductivity approaching those of liquid solutions, while remaining unicationic in nature. Conductivities of at least 10^{-3} S cm $^{-1}$ at room temperature must be attainable, as demonstrated in figure 1 for the case of (section 2.1.1) base-in-chain polymers plasticized with LiAlCl $_4$. Measurements to establish the numerical values are in progress.

4. Conclusions

When suitable means of reducing the strength of the coulomb traps in anionic polymers are employed, the conductivity of polymeric electrolytes can become rather high, while continuing to offer the advantage of unicationic transport. The strategy of connecting anions together by variable length polyether spacer chains offers control over the ion concentration, and simultaneously a remedy for the crystallization problems that plague the polymer-in-salt type of electrolyte. Development of this approach may well lead to superior electrolyte components for lithium batteries.

Acknowledgments

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