“Acid-in-chain” versus “base-in-chain” anionic polymer electrolytes for electrochemical devices

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Abstract

We extend an earlier study of high conducting polyanionic (single ion conducting) electrolytes, obtained by Lewis acid plasticization of polyanions in which the in-chain anions are Lewis base in character, to the inverse case in which the Lewis acid is incorporated in the chain. The Lewis acid groups in the chain are spaced by polyethylene oxide segments of variable length. Such “Acid-in-chain” polymers are then turned into polyanions by reaction with a Lewis base anion, leaving the counter cation free to conduct. Depending on the Lewis base strength of the added anion, this type of system can range from strictly polyanionic to weakly anion trapping in nature. Conductivities in the range of $10^{-5}$ – $10^{-4}$ S/cm have been obtained. In the case of short interanionic spacers, high conductivities at $T_g$ have been observed, implying that the conducting modes are decoupled from the segmental modes and that the conductivity is therefore superionic glass-like in nature and presumably unicationic. Such polymers may serve alone as solid-state electrolytes, or as the polymer component for polymer-in-salt ionic rubber electrolytes. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Anionic polymer electrolytes; Electrochemical devices; Lewis base groups

1. Introduction

In a recent paper [1], we showed how highly decoupled, presumably single ion, conductivity could be generated in a polymeric material by synthesizing a chain polymer in which in-chain imide groups could be capped by Lewis base groups, thereby reducing the depth of the Coulomb traps on the chain and liberating the (lithium) cations to conduct freely. When the chain backbone was synthesized to be $-[\text{SO}^\text{N}^\text{C(O)}^\text{N}^\text{-SO}_2]^n$, the conductivity at the glass transition temperature was found to be $10^{-3.7}$ S/cm, the highest value yet reported for a single ion conducting chain polymer. Furthermore, the chain polymer could be plasticized with liquid LiAlCl$_4$ to yield even higher conductivities, without loss of single ion conducting character. The electrolyte was shown to support reversible lithium deposition and stripping and to have an electrochemical window of at least 4.5 V. While only the AlCl$_3$-complexed system was reported in detail, capping with BF$_3$ was also demonstrated [2] and presumably other Lewis acids could be used with comparable effects.

This is an example of what we will now call a “base-in-chain” polymer in which an old principle is applied to obtain high conductivity in a new material. It is the same principle used in the 1960s to produce low-melting, highly conducting, LiAlCl$_4$, from higher melting, lower-conducting (in solutions) LiCl, by complexing the Lewis base anion (Cl$^-$) with the Lewis acid AlCl$_3$ [3]. The manner in which the glass transition temperature of a basic halide is reduced, and the fluidity and conductivity accordingly increased, is best illustrated by the data shown in Fig. 1, reproduced from an obscure source [4]. Fig. 1 cautions that not all Lewis
acids will produce a favorable effect. A requirement is that the net charge on the anionic moiety remains small by avoiding multiple complexing. When the Lewis acid groups are separated sterically, as in the base-in-chain polymer, multiple complexing is not expected to be a problem. Still, it is unlikely that \( \text{CrCl}_3 \), or even \( \text{ZnCl}_2 \), would be effective adducts because they would be coordinatively unsatisfied at a single basic site. \( \text{SO}_3 \) and even \( \text{CrO}_3 \), on the other hand, may function well.

Adding to the favorable effect of the decreased glass transition temperature seen in Fig. 1 is the possibility of conductivity/viscosity (or conductivity/structure) decoupling. This may be realized in the case of small cations like \( \text{Li}^+ \) and \( \text{Na}^+ \), and may produce a liquid or glass in which the cationic motion becomes more or less independent of the larger anions. Depending on the decoupling index, \( R_t \), defined from the conductivity at \( T_g \), by the expression

\[
R_t = 3 \times 10^{-12} / \sigma_{T_g}
\]

and on the temperature dependence of \( R_t \), the system may then act as a single ion conductor at any temperature up to about 1.5\( T_g \).

The conductivity demonstrated for appropriate base-in-chain polymers and their salt-plasticized derivatives is very high, up to \( 10^{-3} \) S/cm [1]. However, the presence of Lewis acids, such as \( \text{AlCl}_3 \), in a system can have disadvantages. Because it is not completely immobilized by the imide nitrogen binding, it can exert its chemical activity on other components in a battery system, causing corrosion or other unwanted chemical processes. It is therefore of interest to explore the possibility of creating the inverse of the base-in-chain polymer, namely the "Acid-in-chain" polymer. This is a polymer in which one of the chain links is a Lewis acid, to which a charged Lewis base (an anion) can then be attached to form an anionic polymer. Since the Lewis acid is immobilized in the chain it is more under control than in the base-in-chain type polymer.

Polymers of this type were created as a by-product of our synthesis of a class of Lewis acid electrolyte additives called by us as BEGs — for borate esters of glycol — and used to trap anions and enhance cation conductivity in non-aqueous solutions [5]. The polymers were briefly investigated [6] but were not studied in detail. A related polymer has since been studied by Mehta et al. [7] who synthesized in-chain boroxine rings inserted at intervals along a polyethylene glycol chain. Boroxine rings contain three undercoordinated boron atoms per ring. Mehta et al. demonstrated that the transport number of lithium in lithium triflate was increased to 0.7 when it was dissolved in this polymer, demonstrating the existence of effective anion traps in this system. While this is a very interesting result our intention has

Fig. 1. The effect of Lewis acid additions on the glass transition temperature of the methylpyridinium chloride, in which the chloride is a strong Lewis base. Note that decreases in \( T_g \) and hence increases in fluidity, occur only when large singly charged anions are formed. These results help to explain the high conductivities of \( \text{AlCl}_3 \)-complexed base-in-chain polymers reported in Ref. [1] (after Angell and Zhang [2], by permission of the Electrochemical Society).
been rather to create permanently bound anion sites on the chain, such that the conductivity can be made purely cationic. The weakly trapped case is, however, also possible within our scheme, and will be considered further below.

2. Experimental section

2.1. Polymer synthesis

The acid-in-chain polymer used in this work for the preparation of anionic polymers with different levels of anion retention between permanent and weak trapping extreme is $-[\text{O-B}^-\text{(Ph)}_n\text{O-}[\text{CH}_2\text{O}]_n]\times$ where $n$ falls between 2 and 23. The base polymer containing undercoordinated, hence Lewis acid, boron moieties is prepared by reacting phenylboronic acid $\text{PhB(OH)}_2$ with PEG “spacer” units of variable molecular weights. The PEG used is chosen from diethylene glycol ($n = 2$), triethylene glycol, PEG200, PEG400, or PEG600 or PEG1000 ($n = 23$). The reaction is carried out in a refluxing toluene solution and the water produced in the condensation reaction is collected and measured to determine the extent of the reaction. When the reaction was complete, the product solution was filtered and the solvent was removed in a rotary evaporator. This yields a viscous liquid or rubbery product that is very reactive to Lewis bases.

Anionic polymers are generated when the acidic groups are brought into contact with Lewis bases which are also anions. The permanence of the anion attachment is proportional to the Lewis base strength, and is indicated by the amounts of heat evolved when the reaction is allowed to take place. In the synthetic procedures heat evolution was kept under control by the volume of solvent utilized and the rates of mixing. In the case of weak bases, e.g. lithium bis-perfluoromethane sulfonyl imide (LiTFSI), the electrolyte solution was stirred for another 4 h, and then the solution was filtered and the solvent was removed to yield a viscous liquid with a high conductivity.

3. Intermediate 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 undercoordinated boron links in the chain. The preparative procedure is the same in each case. One example that has been studied in some detail 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. Again this was performed by slowly adding polymer dissolved in THF to the slurry of NaCN or LiCN in THF at room temperature. After the addition, the solution was stirred for another 4 h, and then the solution was filtered and the solvent was removed to yield a viscous liquid with a high conductivity.

2.2. Physical and electrochemical characterization

To obtain the conductivity data displayed below, we used either film or liquid samples depending on the nature of the polymer or polymer + salt solution in hand. Conductivities were measured using equipment described in numerous previous papers [1,8]. Complex impedance plots were obtained using data in the frequency range of $5 \times 10^5$ Hz, obtained with a Hewlett-Packard model 4192 A frequency analyzer. The data plotted in Figs. 2–4 were obtained from the extrapolation of the complex impedance plots to $\rho'' = 0$, or directly from the plateau of the log $\sigma$ versus log $f$ plot. The latter is simpler for the majority case in which $\rho''$ in the complex impedance plot reaches zero at low frequency.

Glass transition temperatures, $T_g$, were obtained from a simple DTA apparatus using scans of approximately 10 K/min, and defining $T_g$ from the heat capacity jump onset. They therefore correspond to the temperatures at which the structural relaxation time is $\sim 100$ s, and the conductivity of a fully coupled con-
Fig. 2. Arrhenius plots of conductivities of: (1) Lower curve: the single ion (Li\(^+\)) conductor formed by reacting the phenyl anion from phenyllithium with the acidic boron group on the polymer chain. (2) Upper curves: solutions of lithium TFSI dissolved in the boron-in-chain polymer, with — (i) different length PEG spacers (400, 600, refer to molecular weights of PEO used in the synthesis, and (ii) different ratios B:Im of boron to TFSI (“imide”, Im) anions. Comparison is made with the conductivity of the LiTFSI-in-polyethylene oxide (from Ref. [12]).

ducting system (conductivity modes relaxing on the same time scale as segmental motion) would be \(10^{-15}\) S/cm.

Fig. 3. Arrhenius plots of conductivities of polyanionic polymers with nitrile side-groups made by reacting alkali cyanides with PEG-spaced boron-in-chain polymers. Filled and open circles compare Li\(^+\) with Na\(^+\) cases when the spacer is PEG400. Triangles and squares show results for larger and smaller spacers, respectively. Note that in the small spacer case the conductivity of the system (by short extrapolation) is about \(10^{-8}\) S/cm at its \(T_g\) (indicated by the arrow), showing that conductivity is highly decoupled from segmental motion, as in inorganic glasses.

Cyclic voltammograms to determine the electrochemical stability of the systems synthesized were obtained with a PAR potentiostat.

3. Results

We first present the results for the poorest conductor which, however, is the case in which it is clearest that an in-chain anion has been created. This is the case in which the basic anion added to the chain is the phenyl anion, giving a singly charged link in the chain which contains two indistinguishable (phenyl) side-groups. Since they are both very bulky, and bearing in mind the high glass transition temperature of polystyrene due to the phenyl side-groups, it is not surprising that the conductivity is not high. The conductivity for this polymer is shown in Fig. 2, lowest curve. The conductivity of the pure polymer would presumably be much higher in the case in which the boron is introduced using (much more expensive) methylboronic acid, and the charge is added using methyl lithium. This case will be considered in future work: the low conductivity of the
present product will not be further discussed here. Plasticization of this polymer could be carried out with a variety of solvents and would yield much more highly conducting electrolytes. These would, of course, also be single ion conductors. Plasticization studies will be performed after the optimum polyanionic structures have been determined.

In Fig. 2 we also show results for the opposite case in which the boron sites only serve as weak traps that change the lithium transport number in a favorable direction. This is the case in which we dissolve the salt of a weakly basic anion in the acid-in-chain polymer. To permit comparisons with the most favorable previous cases we choose LiTFSI as the salt to be dissolved. Data are shown for cases of different PEG spacer lengths, obtained using PEG400 and 600 in the synthesis. We also show results for different imide-to-acid site ratios. We expect that TFSI trapping will be more effective when there is an excess of trap sites over TFSI ratios. We expect that TFSI trapping will be more effective when there is an excess of trap sites over TFSI ratios. We expect that TFSI trapping will be more effective when there is an excess of trap sites over TFSI ratios.

Finally, we show data for the intermediate cases in which the added charged species is a strong Lewis base but one different from the side-group already present on the boron. The case illustrated in Fig. 3 is that of the base CN\(^{-}\), which is compensated by a lithium cation in one case and by a sodium cation in the other. The latter is simpler to investigate since it is commercially available. The LiCN we used was obtained by exchange on a resin column, and may have suffered some hydrolysis in the process [9]. Other cases of interest would be F\(^{-}\), SCN\(^{-}\) and S\(^{2-}\). We have briefly reported the latter two, and will report some data on SCN\(^{-}\) adducts below. Li\(_2\)S was found to dissolve slowly in the hot polymer, encouraging us to believe that some solubility of LiF may also be observable in future studies. These are the cases closest to the pseudo-polychloroaluminates (and polyfluoroborates) which yielded high conductivities in the case of base-in-chain polymeric systems reported in Ref. [1]. The CN\(^{-}\) anion binds strongly to boron, as witnessed by Pellet et al. [10], and we expect to find a transport number of unity for this electrolyte.

It is an interesting case, not only because of the high conductivities which may be obtained but also because of the manner in which decoupling of the conductivity from the segmental motion develops for shorter PEG spacer units (see Section 4). In Fig. 3 we compare the conductivities of the polyanions formed by dissolution of LiCN and NaCN, respectively (filled and open circles), for the case in which the spacer unit is PEG400, which means about 8–9 (CH\(_2\))\(_3\)O-units separate the anions. Fig. 3 also contains data showing the effect, for NaCN additions, of changing the spacer length to higher and lower values.

It is seen that the conductivity is higher when the cation is Na\(^+\) except at the lowest temperatures, and that the temperature dependence of the conductivity of the Li\(^+\) case is peculiar. We suspect that, in the case of Li\(^+\), ion pairing becomes prevalent at high temperature. This should be susceptible to confirmation by IR spectroscopy using the high frequency signal provided by the ~2100 cm\(^{-1}\) stretching mode of the CN\(^{-}\) anion. This sharp band has been observed to vary between 2089 and 2213 cm\(^{-1}\) depending on the environment of the anion.

4. Discussion

For the first case of a polyanionic system formed by application of the acid-in-chain principle, we consider the results seen in Figs. 2 and 3 to be quite promising. Even with the bulky phenyl group attached to the anionic moiety we have been able to obtain conductivities in excess of 10\(^{-5}\) S/cm in systems whose conductivity should be unicationic. While this is well below the conductivity of the AlCl\(_3\)-complexed base-in-chain polymers of Ref. [1], the polymers are now less chemically corrosive, water-sensitive, etc. and are more compatible with existing cathode and anode systems. Furthermore, improvements should be possible. For instance, replacement of the phenyl group with a smaller unit is only one of the many variables that remain to be explored on the way to fully exploiting the present polyanion formation principle.

Diffusivity data, to be reported separately [11], will confirm that the conductivity in the case of the strong base polyamions is unicationic, and that the relative mobility of the Li\(^+\) in the imide solution, where only weak trapping is expected, has indeed been enhanced with a small sacrifice of conductivity. The small conductivity gap seen in Fig. 2 between the simple LiTFSI-in-PEO system of Armand and co-workers [12], and our imide-in-boron-polymer solution (compare top two curves) will probably be removed by replacement of the phenyl group in our polymer with a smaller group.

Perhaps the most interesting result is the observation of strong cation decoupling in the case of the polyanion formed by the addition of NaCN to the short spacer (PEG200) boron-in-chain polymer, which we now describe.

The value of \(T_S\) for the case of this polyanion is \(-7.5^\circ\)C (Table 1). The conductivity plot for this polymer in Fig. 3 has been extrapolated to the temperature of \(-7.5^\circ\)C and it is noticed that the conductivity at \(T_S\) is unexpectedly high. Rather than being 10\(^{-15}\) S/cm as expected for a coupled system (or 10\(^{-17}\) S/cm for a supercoupled system such as LiClO\(_4\) in PPO was found to be in Ref. [13]), the conductivity is 10\(^{-8}\) S/cm, i.e. seven orders of magnitude higher. This means that the conductivity is highly decoupled from the segmental motions of the polymer chain. Indeed the decoupling
Table 1
The glass transition temperatures ($T_g$), ambient conductivities and physical appearance of different boron-containing polyethers + salt complexes

<table>
<thead>
<tr>
<th>Compositions</th>
<th>$T_g$ (°C)</th>
<th>$\log \sigma$ (S/cm)</th>
<th>Appearance at 25°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBTREG:LiCN(B:CN = 4)</td>
<td>–40</td>
<td></td>
<td>Viscous liquid</td>
</tr>
<tr>
<td>PBTREG:LiCN(B:CN = 1)</td>
<td>–23.4</td>
<td>–5.60</td>
<td>Viscous liquid</td>
</tr>
<tr>
<td>PB200EG:NaCN (B:CN = 2)</td>
<td>–14.5</td>
<td>–5.20</td>
<td>Viscous liquid</td>
</tr>
<tr>
<td>PB200EG:NaCN (B:CN = 1)</td>
<td>–7.5</td>
<td>–5.37</td>
<td>Viscous liquid</td>
</tr>
<tr>
<td>PB400EG:NaCN(B:CN = 2)</td>
<td>–59.5</td>
<td>–4.98</td>
<td>Viscous liquid</td>
</tr>
<tr>
<td>PB400EG:NaCN(B:CN = 1)</td>
<td>–58</td>
<td>–4.56</td>
<td>Viscous liquid</td>
</tr>
<tr>
<td>PB400EG:LiIm(B:Im = 2)</td>
<td>–44</td>
<td>–4.75</td>
<td>Viscous liquid</td>
</tr>
<tr>
<td>PB400EG:LiIm(B:Im = 1)</td>
<td>–37.8</td>
<td>–5.20</td>
<td>Viscous liquid</td>
</tr>
<tr>
<td>PB400EG:LiCN(B:CN = 1)</td>
<td>–50</td>
<td>–4.87</td>
<td>Viscous liquid</td>
</tr>
<tr>
<td>PB600EG:NaCN(B:CN = 2)</td>
<td>–57.3</td>
<td>–4.86</td>
<td>Viscous liquid</td>
</tr>
<tr>
<td>PB600EG:NaCN(B:CN = 1)</td>
<td>–46.5</td>
<td>–5.09</td>
<td>Viscous liquid</td>
</tr>
<tr>
<td>PB600EG:LiIm(B:Im = 2)</td>
<td>–56</td>
<td>–4.54</td>
<td>Viscous liquid</td>
</tr>
<tr>
<td>PB600EG:LiIm(B:Im = 1)</td>
<td>–47</td>
<td>–4.70</td>
<td>Viscous liquid</td>
</tr>
<tr>
<td>PB1000EG:NaCN(B:CN = 2)</td>
<td>–62.5</td>
<td>–6.00</td>
<td>Crystalline</td>
</tr>
<tr>
<td>PB1000EG:NaCN(B:CN = 1)</td>
<td>–61</td>
<td>–5.76</td>
<td>Crystalline</td>
</tr>
</tbody>
</table>

index for this case (from Eq. (1)) is comparable with those for the base-in-chain polymers of the previous publication [1]. 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 $T_g$. We note that, in this case (NaCN addition to the PEG200-spaced boron-in-chain polymer) the 100°C conductivity is almost as high as for the best “salt-in-polymer” electrolytes. For instance it is as high as that of LiTFSI in PEO [12], see Fig. 2.

The effect of replacing the phenyl ring on the boron will be more important for short spacer compositions, so we expect to be able to improve the conductivity at both low and high temperatures very substantially by substitution of smaller groups. Completely unexplored to date, also, are the effects of replacing the CN$^-$ anion with other strongly basic anions like methoxide and formate.

In view of the salt-like nature of the conductivity seen for the short spacer polymers it should also be possible to plasticize these anionic polymer systems with non-inflammable salts (as opposed to molecular liquids) of low melting point. Perhaps LiSCN and LiTFSI would be suitable. Perhaps, also, recently synthesized salts like the orthorhombates (e.g. Li bisoxalato-orthorhombate, LiBOB [14] (in which the anion seems to be similar in many properties to the perchlorate anion, while being non-hazardous), may serve well in this role.

The study of this case will also be extended to smaller spacer units, and to “spacer-creating” spacer units, in an effort to reproduce the higher decoupling ratios encountered in the new salt-in-glassy-polymer electrolytes currently being reported by MacFarlane and co-workers [15] and by Shriver and colleagues [16]. However, the performance of the more concentrated ionic polymers obtained using shorter spacer units with LiCN additions, is not good, as is seen in Fig. 4. Fig. 4, and also raises questions about the performance of SCN$^-$ anions, which are more weakly basic than CN$^-$, in these systems. Overall, it is likely to take considerable further research to find the best anion choice for achieving unicationic conduction at acceptably high values of the conductivity in these systems.

5. Concluding remarks

While we have described a simple approach to generating anionic polymers with a wide variety of properties, it is not clear that in situ creation of polyanions will be the best way to optimize the polyanionic type of polymer electrolyte. We will separately be making comparisons of the performance of the best cases in the present series with polyanionic systems in which large low charge density anions are linked into polyanionic form without invoking any simple base-to-acid complexing process as in Ref. [1] and the present paper. Only time and experience will tell whether the polyanionic systems will prove to have superior performance over the well-studied salt-in-polymer electrolytes.

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References