



# Characterisation of ion transport in sulfonate based ionomer systems containing lithium and quaternary ammonium cations



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## ABSTRACT

Two sulfonated ionomers based on poly(triethylmethyl ammonium 2-acrylamido-2-methyl-1-propane sulfonic acid) (PAMPS) and containing mixtures of Li<sup>+</sup> and quaternary ammonium cations are characterised. The first system contains Li<sup>+</sup> and the methyltriethyl ammonium cation (N<sub>1222</sub>) in a 1:9 molar ratio, and the <sup>7</sup>Li NMR line widths showed that the Li<sup>+</sup> ions are mobile in this system below the glass transition temperature (105 °C) and are therefore decoupled from the polymer segmental motion. The conductivity in this system was measured as 10<sup>−5</sup> S cm<sup>−1</sup> at 130 °C. A second PAMPS system containing Li<sup>+</sup> and the dimethylbutylmethoxyethyl ammonium cation (N<sub>114(201)</sub>) in a 2:8 molar ratio showed much lower conductivities despite a significantly lower T<sub>g</sub> (60 °C), possibly due to associations between the Li<sup>+</sup> and the ether group on the ammonium cation, or between the latter cations and the sulfonate groups.

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## 1. Introduction

Due to the prevalence of lithium ion battery technologies and the increasing need for energy storage solutions, lithium-based solid polymer electrolyte materials are currently an active research field [1–5]. Solvent-free electrolyte systems, including linear chain polyethers such as PEO, with associated alkali metal salts such as lithium salts, have attracted much interest for use in electrochemical devices [6–11]. PEO-based systems support fast ion transport, and the polymeric chain of PEO is capable of wrapping around lithium cations, promoting dissolution and ionization of a lithium salt [11].

A serious limitation of PEO-alkali metal salt complexes is that both the cation and anion are mobile, which can lead to electrode polarisation [1,12]. In general, only one ionic species should be mobile, so this issue can be solved using single ion conductors in which the anion is chemically attached to the polymeric backbone or side chain [13] such that the cation is the sole charge carrier. These systems are referred to as polyelectrolytes, or ionomers. A number of these systems have been reported. For example, Feng et al. [14] have recently reported a single ion conducting polymer based on poly(4-styrenesulfonyl) (trifluoromethanesulfonyl)

imide anions. Unfortunately, such systems tend to exhibit low ionic conductivities ( $\leq 10^{-5}$  S cm<sup>−1</sup>) due to the strong interaction between the cation and the covalently bound anionic group. Hence ionomeric single ion conductors generally require a low glass transition temperature (T<sub>g</sub>), as the ion motion is coupled to the segmental motion of the polymer [15–17].

Recently, Colby and co-workers have shown that T<sub>g</sub> can be reduced by the incorporation of bulky organic cations such as quaternary ammonium cations [18]. This is primarily attributed to weaker electrostatic interactions between these bulky cations and the anions of the polymer backbone. The ammonium cations can be functionalised, and can also act as non-volatile plasticisers, to enhance the stability and improve the mechanical durability of the sample. Due to their bulky nature it may be assumed that only the counter ions such as Li<sup>+</sup> or Na<sup>+</sup> are able to move large distances rapidly, resulting in high transport numbers for the target cations. For example, Colby et al. [19] studied polyester-based ionomers and sulfonated polystyrene, substituting the inorganic cations Na<sup>+</sup>, Li<sup>+</sup> and Cs<sup>+</sup> with organic species including quaternary ammonium cations. They observed decreases in T<sub>g</sub> and increases in ionic conductivity by up to four orders of magnitude. The effects of incorporating tetraalkylammonium cations on T<sub>g</sub> and other dynamic relaxation modes in Nafion have also been extensively studied [20–22].

In the systems studied by Colby and co-workers, the ionic conductivities are correlated with the polymer glass transition

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temperature  $T_g$  [19]. However, some studies have suggested that the ion conductivity can be decoupled from the polymer dynamics, making the polymer segmental motion less of a restriction for ionic conductivity. Indeed, Wang and co-workers [23] have shown that even when the conductivity is coupled to the  $T_g$  of the system, there is still extensive decoupling of ion transport from local segmental polymer motions as measured by dielectric spectroscopy, especially in more rigid polymers where increased free volume provides a pathway for ion transport.

Very recently, our group has reported decoupled  $\text{Na}^+$  cation dynamics in ionomer systems based on poly(triethylmethyl ammonium 2-acrylamido-2-methyl-1-propane sulfonic acid) (PAMPS), as well as its co-polymer with poly vinyl sulfonate [24,25]. In these systems, a fraction of the  $\text{Na}^+$  cations was replaced with bulky quaternary ammonium cations such as methyltriethyl ammonium cation ( $\text{N}_{1222}$ , where the subscript numbers indicate the number of carbon atoms in each alkyl group). For the co-polymer system  $[\text{PAMPS}-\text{N}_{1222}]_x[\text{PVS}-\text{Na}]_{(1-x)}$ , as the ratio of the sodium to quaternary ammonium cation decreased, the conductivity was observed to increase, with a maximum value observed for 10 mol%  $\text{Na}^+$ . However, the  $T_g$  of these systems remained close to 100 °C for all compositions [24]. Evidence for the decoupling of the  $\text{Na}^+$  motion was also observed in the homopolymer PAMPS  $[\text{N}_{1222}]_x[\text{Na}]_{(1-x)}$ , and once again the 10 mol% sodium composition showed the highest overall conductivity [25]. However, quantitative characterisation of the sodium cation dynamics in these systems by  $^{23}\text{Na}$  solid-state NMR was hindered by a lack of variation in the observed spectral line widths with temperature. The study of lithium cations by  $^7\text{Li}$  NMR is generally more straightforward due to the smaller quadrupole moment of this isotope, and should provide insight into the decoupling behaviour in analogous systems containing  $\text{Li}^+$ . Moreover, due to the prevalence of lithium ion technologies, it is clearly of interest to determine whether  $\text{Li}^+$  ions can also be decoupled from the polymer dynamics in these PAMPS ionomer systems.

We have therefore prepared two mixed-cation PAMPS-based homopolymer ionomers containing both  $\text{Li}^+$  and quaternary ammonium cations. The molecular structures of the samples studied are shown in Fig. 1. The first sample contains  $\text{Li}^+$  with the

methyltriethyl ammonium cation ( $\text{N}_{1222}$ ) in a 1:9 molar ratio. This sample will hereafter be referred to as  $(\text{N}_{1222})_{0.9}\text{Li}^+_{0.1}$ . The composition of this sample was chosen based on our group's previous studies of the  $(\text{N}_{1222})_x\text{Na}^+_{(1-x)}$  PAMPS homopolymer system, for which the highest overall conductivity was observed for  $x=0.9$  as mentioned above [25]. The second PAMPS ionomer studied contains a combination of  $\text{Li}^+$  and the dimethylbutylmethoxyethyl ammonium cation ( $\text{N}_{114(201)}$ ) in a 2:8 molar ratio. This sample will be referred to as  $(\text{N}_{114(201)})_{0.8}\text{Li}^+_{0.2}$ . In this case, the presence of the ether group on the quaternary ammonium cation provides a localised negative charge that could potentially solvate the  $\text{Li}^+$ , thereby promoting the dissociation of this cation from the sulfonate anionic groups and helping to decouple it from the polymer dynamics. Since the  $\text{N}_{1222}$  cation is too small to incorporate an ether oxygen, a larger ammonium cation was necessary, and  $\text{N}_{114(201)}$  was chosen based on availability. Due to the combination of the larger size of the ammonium cation and the anticipated improvement in the level of  $\text{Li}^+$  decoupling due to the ether group, a higher  $\text{Li}^+$  content was also chosen compared to the first sample.

The cation mobility in these two systems has been characterised using a combination of  $^7\text{Li}$  solid-state NMR and electrochemical impedance spectroscopy. These measurements allowed various parameters to be quantified, including the activation energy and correlation time for the translational dynamics of the  $\text{Li}^+$  cation, and the bulk ionic conductivity. These quantities are discussed in relation to the glass transition temperature of each sample as measured using differential scanning calorimetry.

## 2. Experimental

### 2.1. Material synthesis

The materials were synthesised following previously published methods [24,25] and were stored, handled and packed for experimental characterisation in a dry, inert atmosphere.

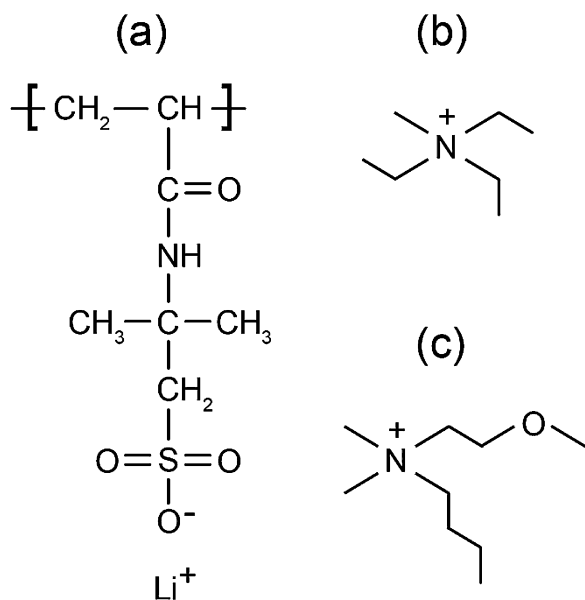
### 2.2. Differential scanning calorimetry (DSC)

DSC measurements were carried out using a DSC Q100 series instrument (TA Instruments), and the data were evaluated with Universal Analysis 2000 software. Approximately 8 to 10 mg of the ionomer samples were tested over a temperature range of 0 to 210 °C at a scanning rate of 10 °C min<sup>-1</sup>. The glass transition temperature ( $T_g$ ) was determined from the rise in heat capacity during the heating ramp. Both the onset and mid-point temperatures of these broad transitions are reported in Section 3.1, while subsequent discussions refer only to the onset temperatures.

### 2.3. Solid-state nuclear magnetic resonance (NMR) spectroscopy

Solid-state NMR experiments were carried out with a Bruker Avance III 300 MHz wide-bore spectrometer with a Larmor frequency of 116.6 MHz for  $^7\text{Li}$ . All  $^7\text{Li}$  spectra were referenced to 1 M LiCl (aq) at 0 ppm. A 5 mm static variable-temperature NMR probe was used to record the spectra from these solid materials. Spectra were acquired with a single pulse experiment using a 90° pulse length of 8.5  $\mu\text{s}$  and recycle delay of 15 s. The sample temperatures were calibrated using the  $^{207}\text{Pb}$  signal from lead nitrate [26]. Reported line widths correspond to the full width at half of maximum intensity (FWHM) of the spectral peak and were measured as a function of temperature from 20 °C to 170 °C, allowing approximately 15 min for the sample temperature to equilibrate at each temperature.

The temperature variation of the  $^7\text{Li}$  spin lattice relaxation times ( $T_1$ ) were also measured over the same temperature range



**Fig. 1.** The molecular structures of the materials under study. (a) The sulfonate-based PAMPS monomer unit with  $\text{Li}^+$ , (b) the quaternary ammonium cation methyltriethyl ammonium (referred to as  $\text{N}_{1222}$ ), and (c) the dimethylbutylmethoxyethyl ammonium cation ( $\text{N}_{114(201)}$ ).

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