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Polymer Materials for Charge Transfer in Energy Devices.

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Abstract

Charge transfer through the bulk and across the electrode interfaces is of fundamental importance for use of polymers in energy devices. Protons or lithium ions are transported by means of a solvent or solvating groups incorporated in the polymer, without which no charge can be passed. Typically the solvent groups for protons are water and carbonates or ethylene oxide units for lithium ions. The choice of a good solvent for transport through the bulk membrane may not be the best for charge transfer at the interfaces. This chapter describes efforts to develop alternative solvation methods particularly for proton transfer in fuel cells where the reduction of dependence on external humidification is a major goal. The design, synthesis and characterization of proton conducting polymers containing heterocylic

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bases and phosphonic acids will be described. The roles of the solvating groups, molecular architecture and morphology of the polymers is discussed.

INTRODUCTION

Polymer electrolyte membrane (PEM) fuel cells and lithium ion batteries are of considerable interest as power sources for transportation and stationary applications. These devices have several properties in common which are responsible for inadequate performance and ultimate failure. They include bulk transport of ions across a separator, mass transport resistance to the electrode surfaces for ions and substrates and most importantly the impedance to charge transport across the interfaces which is often the process that leads to poor performance and failure. For example, the poor kinetics of the electrochemical reactions of lithium ions at the electrodes leads to large impedances, the generation of heat and inefficient side reactions and ultimately the failure of the battery. Similarly, the sluggish oxygen reduction reaction in PEM fuel cells results in the generation of heat instead of electrical current and which is difficult to reject at temperatures below 100°C. Presently used membrane materials such as perfluorinated sulfonic acids (e.g. Nafion®) require the presence of liquid water to provide adequate conductivity and hence complex heat and water management systems are required. This is but one example of where better kinetics of charge transfer at the electrode would solve many of the issues that impede the introduction of fuel cells.

For fuel cells an alternative approach involves membrane materials that contain no or little free solvent but are conductive at low temperatures as well as high temperatures under dry conditions. The use of alternative solvent molecules such as imidazole, triazole and phosphonic acids have been considered as the proton conducting

medium instead of water in PEM fuel cells[1,2]. The need to operate fuel cells at higher temperatures (120°C) to facilitate heat rejection has moved the operating conditions to a range where the remarkable properties of the perfluorosulfonic acids [PFSAs] no longer satisfy the requirements. A proton conducting system with practical proton conductivities for fuel cell separator membranes has been a challenge to realize. In the past decade, several studies have been conducted by different groups that have successfully achieved proton conductivities on the order of 10^{-3} S/cm at 200°C[3]. This paper outlines some syntheses, characterization and properties of homopolymers and copolymers with tethered imidazole groups which may be of interest for high temperature PEM fuel cells operating under dry conditions.

Figure 1 shows the general design of a material that shows a phase separated polymer backbone with covalently tethered imidazole groups and acid groups so that the solvating molecules are not washed out of the membrane by the product water. The acid groups provide the excess protons and the imidazoles provide the solvation for the proton to allow the proton to hop from one solvent site to the next without the need for the solvent molecule to move with it. This mechanism, commonly called the Grotthuss mechanism[4], is a low energy pathway and is different from ionic conduction assisted by the segmental motion of the polymer. The two types of ionic motion can be distinguished by the dependence of conductivity upon temperature with the Grotthuss motion having a low dependence while the segmental motion exhibits a typical WLF dependence that increases as the temperature decreases. The Grotthuss mechanism is therefore favored by phase separation of the backbone from the acid and solvating heterocyclic bases so that the proton hopping mechanism is not impeded by the polymer side chains. Thus self-organization of the polymer is important and this dictates the length of the tethers for the solvent and acid moieties. Ideally the organization should provide sufficient connectivity across the whole membrane to provide high conductivity and the design and synthesis of

such well controlled materials represents a major challenge. This paper describes the effects of the backbone identity, side chain length and concentration of the acid groups on the proton conduction both under dry conditions and humidified states. The backbones studied are polystyrene, polysulphone, polyether, polysiloxane and PTFE.

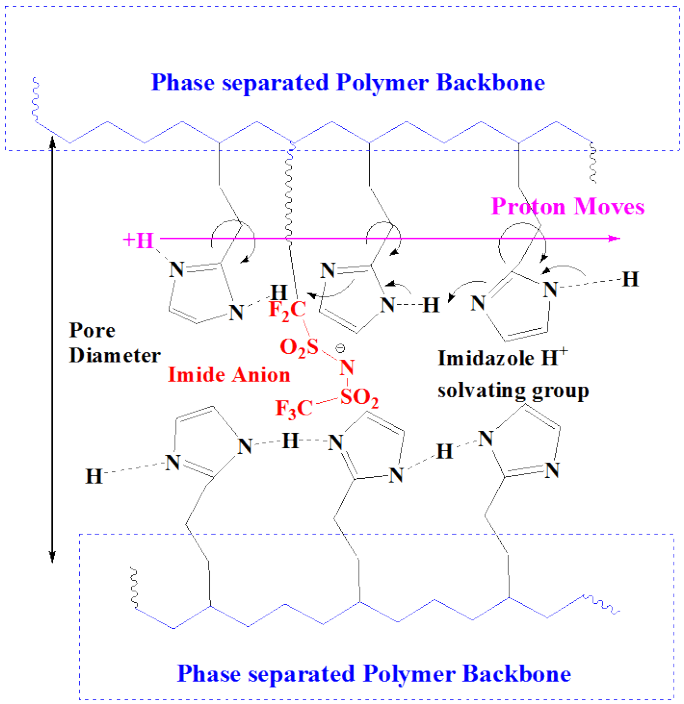


Figure 1. Ideal design of water-free proton conducting polymer

RESULTS AND DISCUSSION

Covalent tethering of the imidazole to the polymer backbones is not easy as it is complicated by the need for protecting groups for the

imidazole. Benzyl, Tosyl and Trityl groups are among the groups that have been examined. Figure 2 shows the general

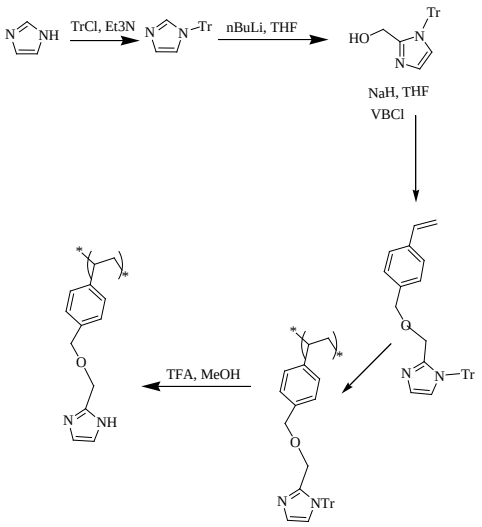


Figure 2*. Synthetic route to obtain tethered imidazole polystyrene polymers (IMVBCl)*

synthetic route followed to prepare an imidazole tethered to a polystyrene backbone. In order for the imidazole to support Grotthuss transport the tether must be accomplished via the 2-position rather than the 1-position and this introduces much synthetic difficulty. In order to reduce the synthetic complications this polymer was blended with Nafion 1100 to give films that have measurable conductivities. The conductivities of the dry and humidified blended polymers are shown in Figure 3.

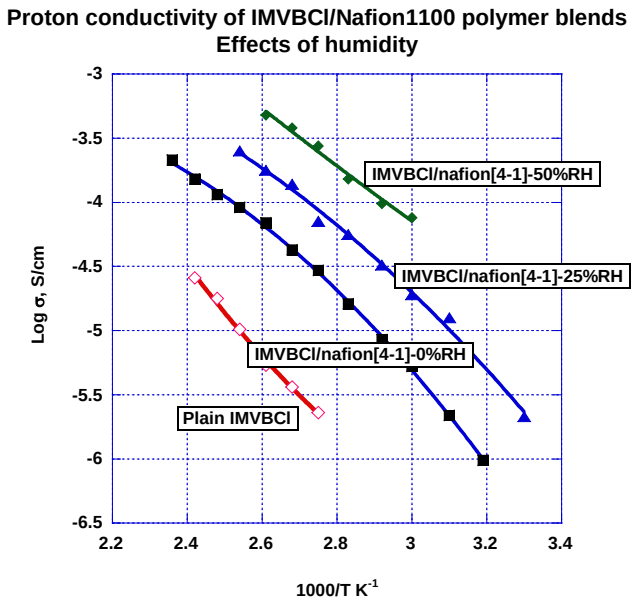


Figure 3. Conductivity as a function of temperature of imidazole tethered polystyrene polymers blended with Nafion under dry and humidified conditions.

The neat polymer is conductive due to the self-ionization of the imidazole but conductivity is enhanced due to the addition of the PFSA polymer. Humidification of the polymer results in increases in the conductivity as shown in Figure 3. However, the conductivity is somewhat lower than that of Nafion alone under these conditions because the presence of the imidazole suppresses the uptake of water and the effective equivalent weight of the acid is over 2000 resulting in a low concentration of charge carriers. The use of blends leads to this problem since there is a greater preponderance of backbone in the

medium than would be the case if the bases and acids were attached to the same chain.

It can be seen from Figure 3 that the dependence of conductivity upon temperature is very similar to typical WLF dependences which indicates that the mechanism is dominated by segmental motion of the polymer. This conclusion is also supported by the DMA behavior which is shown in Figure 4.

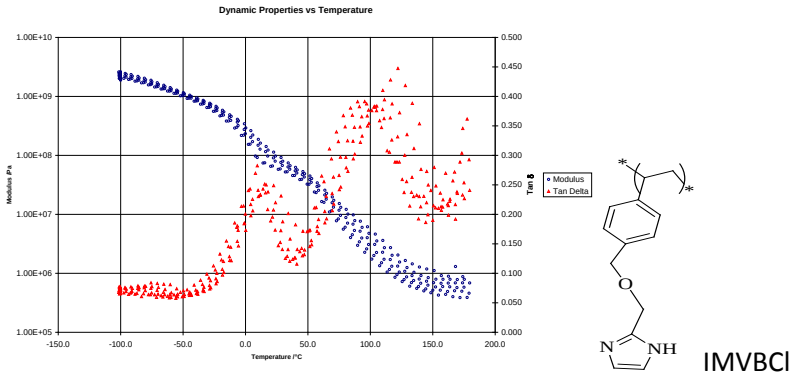


Figure 4. *DMA of IMVBCl short side chain polymer blend with Nafion in the ratio 4:1.*

The DMA shows considerable plasticization of the backbone by the imidaziole and SAXS measurements also indicate a lack of pahse separation.

Figure 5 shows methods of attaching imidazoles and acids to polysulfones and Figure 6 shows the conductivity of the proton and lithium ion conducting acid polymer under dry conditions and in the presence of water. The dry polymers exhibit Arrhenius behaviour as is expected due to the lack of solvent but upon addition of solvent water the conductivity increases markedly and the temperature dependence is consistent with Grotthuss transport. This appears to support the

notion of the importance of phase separation in order to facilitate Grotthuss transport of protons. The DMA measurement shown in Figure 6b shows a single transition with no sign of mobility in the backbone again indicating a very stiif material with strong phase separation.

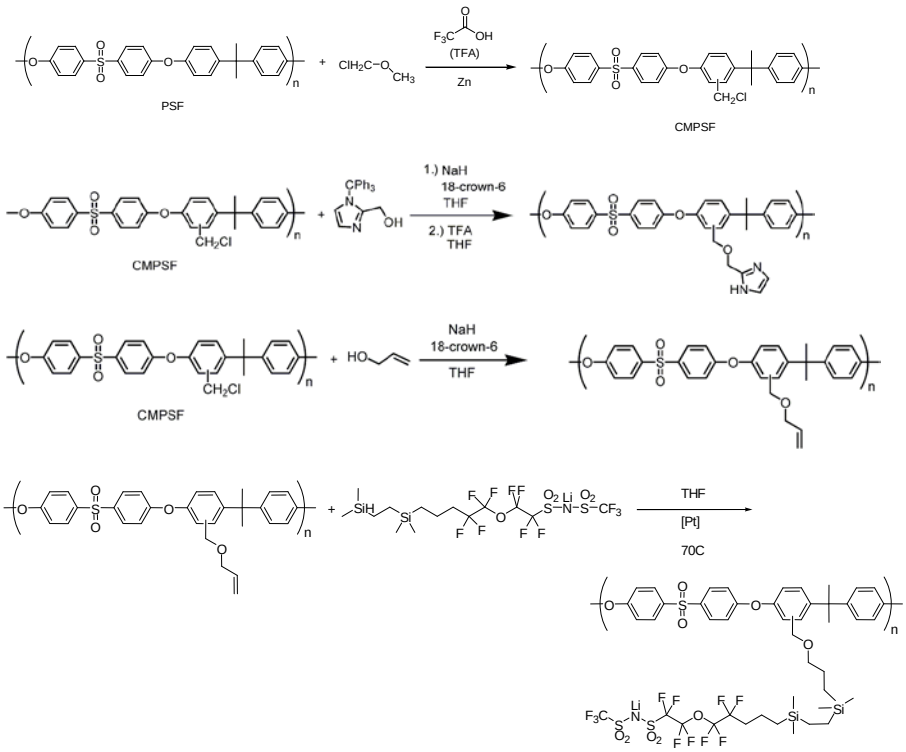
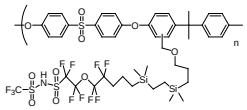
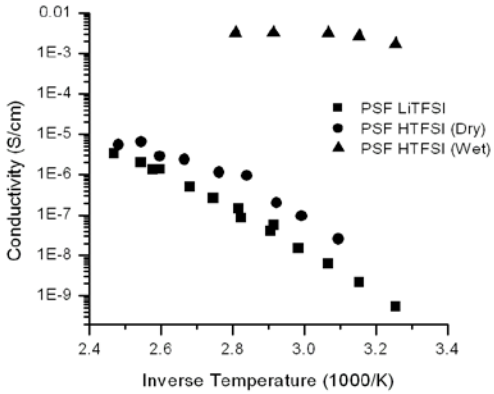
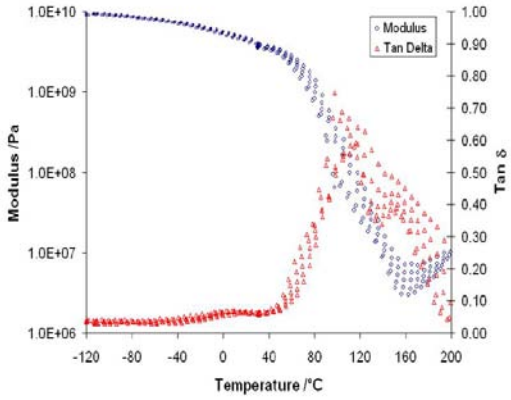


Figure 5. Synthetic routes to attach imidazoles and acid groups to polysulfones.





a)



b)

Figure 6. Conductivity and mechanical properties of Polyetherpolysulfone modified with a fluoroalkylimide side chain; a) conductivities of dry(Li^+ and H^+ forms) and wet(H^+)polymers; b) DMA of H^+ form

Moving on to an alternative protogenic group which can act as the proton donating species as well as the solvating species[2], Figure 7 shows the synthetic scheme for attaching phosphonic acid groups to the polysulfone backbone. The initial functionalization reaction gives mopno-functionalization after one day and bi-functionalization after 7 days. Increase of the functionalization density leads to a much more satisfactory concentration of the active functions. The conductivity of the bi-functional phophonic acid polymer (DPPSU) is shown in Figure 8 as a function of relative humidity and temperature. The remarkable lack of effect of humidity of the conductivity is striking as is the low dependence of conductivity on the temperature. These results are quite consistent with the Grotthuss mechanism of proton transport that is promoted by the strong phase separation. Water uptake measurements made on this polymer show only an uptake of 15% by weight even at 100% RH at 25 ^{o}C indicating that thewater is not critical to the conduyction mechanism. These membranes appear to have considerable promise for high temperature operation under dry conditions.

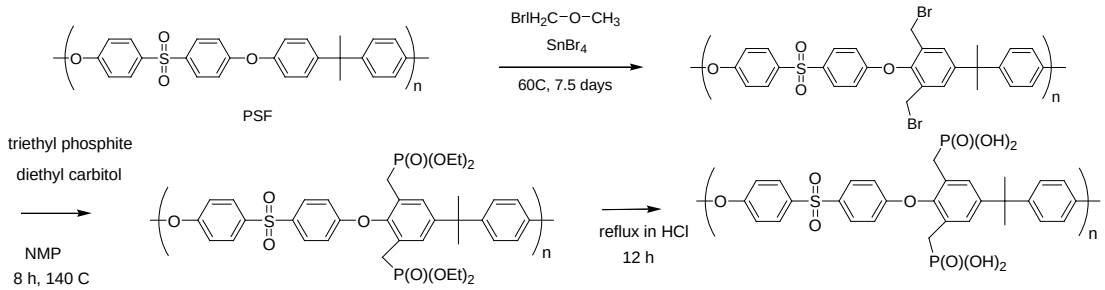


Figure 7. Synthesis route to Phosphonic acid functionalized polysulfone(DPPSU).

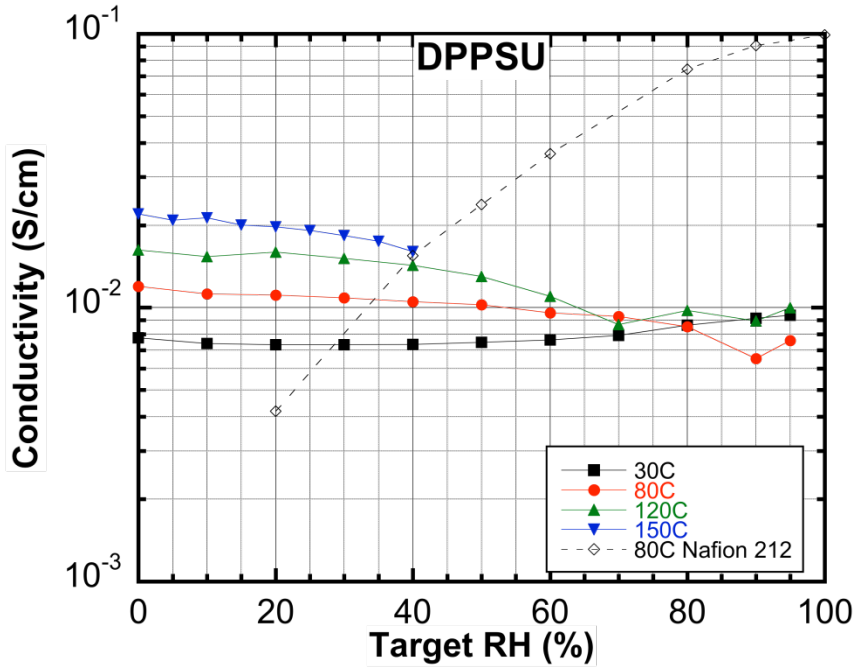


Figure 8. Conductivity of Polysulfone phosphonates(DPPSU) as a function of temperatyre and humidity (Nafion 212 included for comparison)

To investigate the role of morphology in the promortion of proton hopping or Grotthuss-type transport a number of systems have been investigated using block copolymers to try to control the morphology. Some of these systems have used proton conducting ionic liquids based on imidazolium bis(trifluoromethylsullfonyly)imide as the conducting medium[5,6]. Recent measurements using pulsed field gradient nmr has shown large enhancements of the proton diffusion rates over the diffusion of the supporting ionic liquid when the liquid is confined in the nanochannels of the block copolymer[7]. Similar effects have been observed with water in block copolymers[8] where enhanced proton transport has been observed with nano-separated polymers. However, it has been observed that these effects are often greatly reduced upon

cycling the humidity and/or temperature which indicates that the morphology is not stable to the change in conditions. The provision of the correct morphology and its stabilization throughout the conditions that the membrane may see during operation is a severe challenge for polymer scientists.

The importance of providing and maintaining the appropriate connectivity through the membrane is illustrated by Figure 9 which shows the effect of discontinuities of the connectivity across the membrane. The conductivity of the entire membrane is estimated according to the equation whereby the effective conductivity K_{eff} divided by the Grotthuss conductivity, K_{Grott}, is plotted against the proportion of vehicular (or segmental) motion, $K_{Vehicle}$. The different curves assess the effect for different ratios of the K_{Grott} to the $K_{Vehicle}$. The modeling shows that for a ratio of 100 the effect of a small loss of connectivity is very significant. For a comparison ofwith segnmental motion this ratio is more like 10,000 so the effect is likely to be even worse for a polymer m embrane with no mobile solvent in it. This model is a worst case scenario since it only considers a single one-dimensional motion and this is greatly alleviated by 2-d and 3-d pathways that provide alternative pathwatys around a bottleneck. However it very clearly shows the need for great control of the membrane morphology and this represents a major chjallnge for the synthetic chemicts as well as the polymer physics community.

$$\frac{\kappa_{\text{eff}}}{\kappa_{\text{Grot}}} = \frac{1}{1-\left(1+\frac{\kappa_{\text{Vehicle}}}{\kappa_{\text{Grot}}}\right)\frac{\delta_{\text{Vehicle}}}{\delta_{\text{Membrane}}}}$$

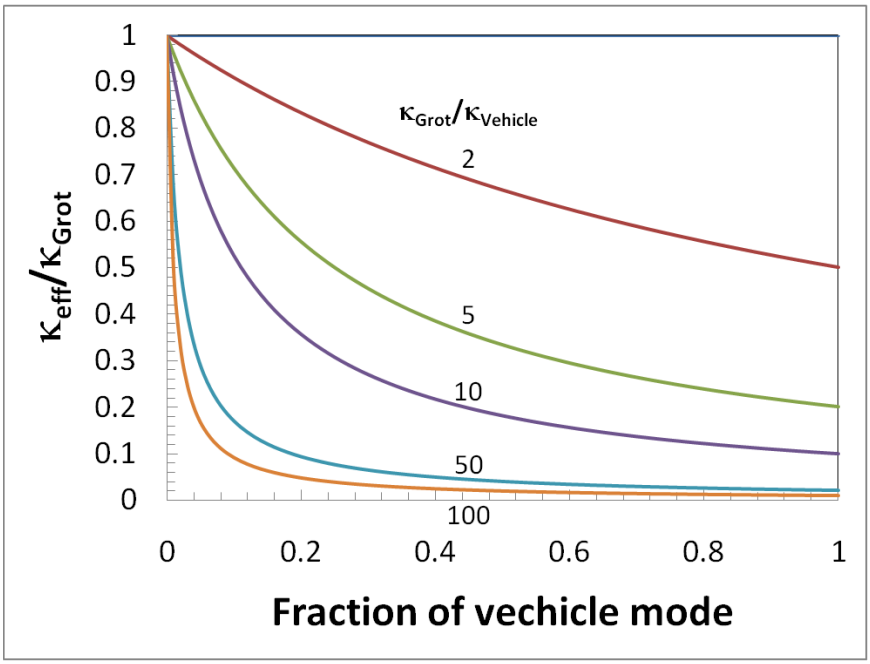


Figure 9. Effect of loss of connectivity on the overall conductivity, $K_{eff,}$ for different ratios of Grotthus conductivity , K_{Grott}. and vehicular or segmental conductivity, $K_{Vehicle}$.

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