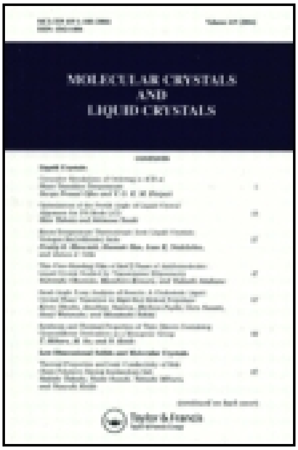

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Bridging the Gap between Polymer Electrolytes and Inorganic Glasses: Side Group Liquid Crystal Polymer Electrolytes

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Bridging the Gap between Polymer Electrolytes and Inorganic Glasses: Side Group Liquid Crystal Polymer Electrolytes

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We review the evidence indicating that ion transport can be decoupled from structural relaxations of the host material in polymer electrolytes. Particular emphasis is given to side group liquid crystal polymer electrolytes consisting of poly(ethylene oxide)-based backbones and pendent mesogenic groups. In salt complexes of these materials appreciable ionic conductivities are observed below the glass transition temperature. Thus, truly solid polymer electrolytes have been obtained. Structural similarities are discussed between these materials and rigid polymers containing powerful ion solvating groups which also appear to exhibit a decoupled conductivity mechanism. The conductivity mechanism in solid polymer electrolytes is compared to that proposed for inorganic glasses.

Keywords: side group liquid crystal polymers; polymer electrolytes; ionic conductivity; decoupled transport mechanisms

INTRODUCTION

Polymer electrolytes have considerable application potential in a wide range of all-solid-state electrochemical devices for many reasons, including their ease of processability and inherent viscoelasticity [1].

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This potential, however, has still to be fully realised because of the modest ambient ionic conductivities reported to date in unplasticized materials. To understand the root of this problem we must consider the mechanism of ion transport in these systems.

A polymer electrolyte is an ionically conducting solid or elastomeric phase comprising salt dissolved in a polymeric solvent [2]. Typically these are solutions of lithium salts in a polyether such as poly(ethylene oxide). In such a system, the backbone is said to form helical arrangements within which the cations are solvated [1-3]. The ions may move through these helices but to achieve conduction, *i.e.* long range transport of ions, an interchain hopping mechanism must also be invoked. The motion of the ions, therefore, is intrinsically linked to the motions of the polymer segments. This coupling of the ionic motions to the local viscosity of the polymer means that ionic conductivity dramatically decreases as the glass transition is approached [4]. The formation of ion pairs and their effect in reducing the conductivity must also be taken into account [4].

To achieve high ionic conductivities at ambient temperatures, the molecular design strategies have focussed in the past on *(i)* reducing the glass transition temperature so speeding up the motions of the polymer segments and *(ii)* incorporating additional ion solvating groups to minimise the formation of ion pairs [2,4,5]. It should be noted that when the glass transition temperature is reduced to below ambient temperatures, the mechanical stability is much reduced and indeed, many polymer electrolytes investigated are in fact liquids. This design approach mitigates against producing a solid but processable electrolyte. In any case, after two decades of intensive research these design strategies have not resulted in the discovery of solvent free polymer electrolytes exhibiting high ambient temperature ionic conductivities.

If we now turn our attention to inorganic "polymers", such as phosphates and borates, quite different behaviour is seen. Specifically, ionic conduction is widespread in the glassy state, and in some superionic glasses containing appropriate dopants reaches values of 10^{-2} S cm^{-1} at ambient temperature [6-8]. In these systems ionic conductivity can be explained using a model in which ion motion is a thermally activated process involving hopping between empty cation sites whose presence is essential to cation transport. Thus, in inorganic systems, motions of the ions become (or appear to become) decoupled from relaxations of the host matrix.

These coupled and decoupled conductivity mechanisms may be distinguished using Angell's decoupling index, R_τ [6,9], which is defined at the glass transition temperature, T_g, as:

$$R_\tau = \tau_s/\tau_\sigma \qquad (1)$$

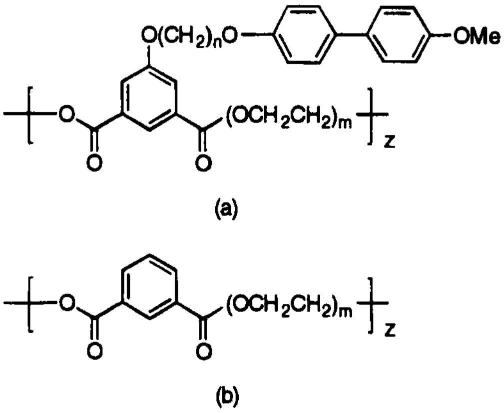
where τ_s and τ_σ are the shear and conductivity relaxation times, respectively. τ_S may be thought of as the time taken for a polymer segment to move from one minimum energy conformation to another, while τ_σ represents the time spent by an ion in a given co-ordination site. Typically, for inorganic glasses R_τ is *ca.* 10^{11} and can reach 10^{13} - 10^{14} for superionic glasses (such as those doped with silver iodide or the aluminosilicate glases). Values of R_τ *less than* one are often reported for polyether-based polymer electrolytes [10]. Values less than one reflect the problem of ion pairing which reduces average ion mobilities. (Strictly speaking, the mobilities of the "free" ions are not reduced.) We note, however, that these estimates of R_τ for polymer electrolytes necessarily involve the extrapolation of conductivity data over a wide temperature range, which may place considerable uncertainty over their absolute values.

Within Angell's framework, the decoupling index spans 17 orders of magnitude from *ca* 10^{-3} for a strongly coupled system (with ion pairing) to 10^{14} for a fully decoupled superionic glass. We argue now that such a large variation in R_τ exaggerates the differences in behaviour; indeed log R_τ could be used as a better measure of the degree of coupling. Even so, is it possible to find a way of bridging this gap?

Returning to the question of obtaining high ionic conductivities in solid polymer electrolytes, it is clear that we may need to achieve a decoupling of ion motions from the segmental motions of the polymer matrix [4]. As we have seen this notion runs contrary to current models for ion transport in polymers [1,2]. Nevertheless it is possible to identify several instances where such a positive outcome has been realised. We will use these examples to comment on the structural factors likely to lead to decoupled conductivity in polymer electrolytes.

SIDE GROUP LIQUID CRYSTAL POLYMER ELECTROLYTES

We have ourselves reported recently on the thermal and ionic conductivity behaviours of a series of side group liquid crystal polymer electrolytes (SGLCPEs), see Figure 1*(a)*[11-13]. In these polymers, mesogenic groups (4-methoxybiphenyl) are attached *via* alkyl spacers to a predominantly poly(ethylene oxide) backbone containing isophthalate linking groups. The number of methylene units in the spacer and the number of ethylene oxide units in the backbone have been varied in a systematic fashion but here we restrict ourselves to a discussion of the polymer containing 6 methylene units in the spacer and 6 ethylene oxide units in the backbone. The acronym MeOC6G6 refers to this polymer. We note that Wright and his co-workers have described similar materials containing pendent alkyl chains [14-17], but crystallisation in his samples almost certainly prevented the observation of the behaviour we describe here.



(a)

(b)

FIGURE 1 Molecular structures of *(a)* side group liquid crystal polymer electrolytes and *(b)* the corresponding polymers without mesogenic side groups.

MeOC6G6 exhibits a glass transition at 278 K and a smectic-isotropic transition at 317 K. The side groups are arranged in a bilayer arrangement within the smectic phase. The addition of lithium perchlorate to give a 10:1 (AO:Li) stoichiometry, where active oxygen

(AO) includes all oxygen atoms along the backbone with the exception of carbonyl oxygens, increases T_g to 293K and the clearing temperature to 325K, although the molecular arrangement within the smectic phase appears to remain unchanged. The rise in T_g on the addition of salt reflects the loss of segmental mobility arising from the co-ordination of lithium ions by ether oxygens. The concurrent increase in the clearing temperature is presumably a result of the preferential dissolution of the ions in the backbone which serves to reinforce the microphase separation between EO chainlets and mesogenic side groups which apparently drives the smectic phase formation. The shear modulus of the polymer-salt complex shows a sudden decrease not at T_g but at the clearing temperature, which is consistent with observations made on conventional side group liquid crystal polymers [18,19]. The ionic conductivity of the polymer salt-complex lies in the range 2×10^{-7} to 10^{-4} S cm^{-1} over the temperature range 299 to 381 K; these values are unremarkable for amorphous poly(ethylene oxide)-based materials.

The atypical behaviour of this polymer-salt complex is revealed, however, when the thermal, mechanical and conductivity data are overlayed, see Figure 2. It is clear that the conductivity does not "freeze out" as T_g is approached, but instead varies in an Arrhenius fashion over a temperature range inclusive of T_g. Furthermore, appreciable conductivities are observed at temperatures for which the shear modulus is entirely solid-like, *i.e.* $\log G' \approx 8$. These data strongly suggest that ionic motions have been decoupled from segmental motions of the backbone. Indeed $\log R_\tau \approx 5.7$, a value intermediate between those observed for conventional polymer electrolytes and for inorganic glasses.

We may also consider the behaviour of analogous polymers without mesogenic side groups, see Figure 1*(b)*. The acronym for this polymer is 0G6. 0G6 exhibited a T_g at 237 K which increased to 262 K on the addition of lithium perchlorate (AO:Li = 10:1). Both the polymer and the corresponding polymer-salt complex are amorphous materials. The thermal, mechanical and conductivity behaviours for the polymer-salt complex are overlaid in Figure 3. Compared with MeOC6G6 ionic conductivity does decrease more rapidly as T_g is approached, but the conductivities in the relaxation regime ($\log G' \approx 6$) are still greater than is normally observed for conventional poly(ethylene oxide)-based materials. It appears, therefore, that some degree of decoupling has been achieved even in the absence of liquid crystallinity.

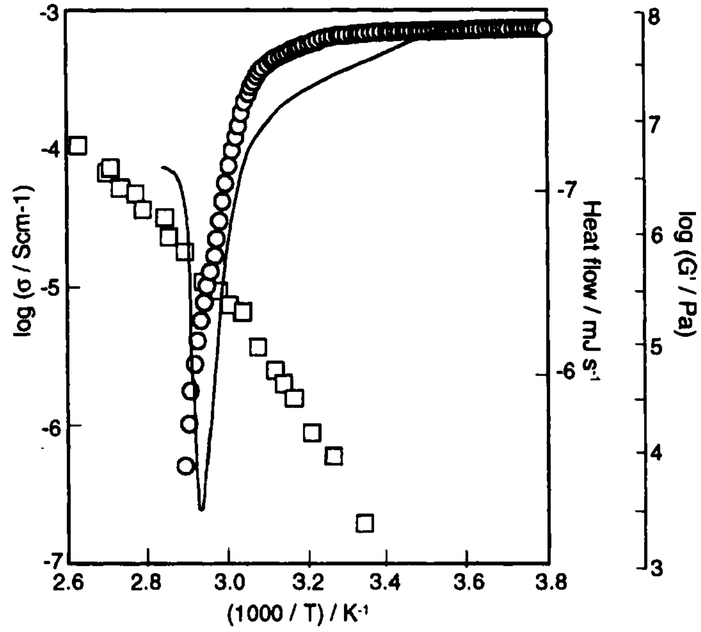


FIGURE 2 Dependence of the log (ionic conductivity) (□), log (real component of the shear modulus) (○), and heat flow in DSC experiments (solid line) on reciprocal temperature for the 10:1 AO:Li MeOC6G6 complex. (Taken from [13]).

One explanation for the behaviour seen in Figure 2 invokes a phase separated morphology in which the poly(ethylene oxide) backbones constitute one domain and the mesogenic side groups the other. At the observed glass transition it might then may be argued that, in such an arrangement, the side groups could vitrify while the backbones remain rubbery. Thus, a conventionally coupled conductivity mechanism would operate below the glass transition temperature. Indeed, such an explanation has been used to account for the conductivities of Li salt complexes of the so-called hairy rod

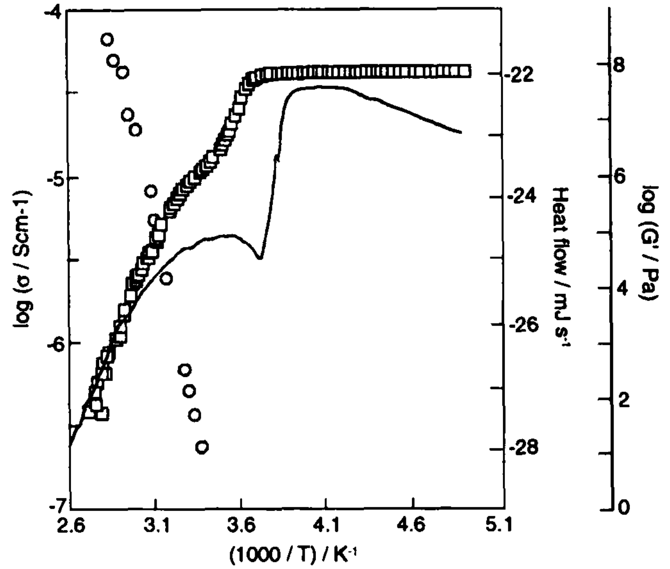


FIGURE 3 Dependence of the log (ionic conductivity) (○), log (real component of the shear modulus) (□), and heat flow in DSC experiments (solid line) on reciprocal temperature for the 10:1 AO:Li OG6 complex. (Taken from [13]).

polymers, see Figure 4 [5]. These polymers consist of rigid poly(p-phenylene)-based backbones to which are attached oligo(ethylene oxide) side chains. The polymer exhibits a smectic B phase in which the rigid backbones are arranged in layers separated by ethylene oxide regions which exhibit a glass transition decoupled from structural relaxations of the backbones. Thus the ethylene oxide segments would behave in a liquid-like fashion within an essentially solid-like smectic B matrix. Hence appreciable ionic conductivities would be observed at ambient temperatures. This class of materials has been termed "molecularly reinforced solid polymer electrolytes" [5].

It is tempting to apply a similar interpretation to the behaviour seen in Figure 2. However, we have already noted that for MeOC6G6, appreciable conductivities are observed at values of the shear modulus of *ca.* 10^8 Pa, *i.e.*, for an entirely solid-like material. By comparison,

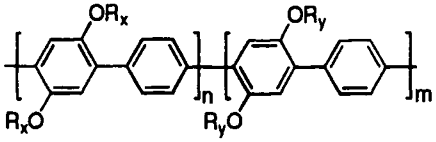


FIGURE 4 Molecular structure of a "molecularly reinforced solid polymer electrolyte", after W.H. Meyer [5].

in the molecularly reinforced polymer electrolytes, the shear modulus is typically 10^6 - 10^7 Pa, which is a value comparable to that of a hard rubber. In addition, the softness of the ethylene oxide regions is associated with a lower shear modulus. Such an effect is absent for MeOC6G6, for which only one glass transition is observed. A phase separated morphology cannot plausibly be invoked, therefore, to account for the conductivity behaviour seen in Figure 2.

Instead we have proposed elsewhere [12,13] that the decoupling of ion transport from the segmental motions of the polymer matrix stems from the suppression of helix formation involving the poly(ethylene oxide) backbones. We suggest that it is within such helical conformations that the ions become trapped below T_g. By inhibiting the formation of helices, a more open ethylene oxide structure is obtained in which the lithium ions are more free to move. Empty sites exist for the ions to hop into, leading to a mechanism analogous to that found in inorganic glasses [20]. A much weaker effect is observed for the unsubstituted polymer, 0G6, and here the isophthalate units needed to attach pendent mesogens in MeOC6G6 will disrupt helical formation. The effect is more pronounced for the liquid crystalline material because the structuring of ethylene oxide helices is further inhibited by the existence of ultrastructure imposed by interactions between mesogens.

RIGID ROD POLYMER ELECTROLYTES

Yamamoto and his colleagues adopted a quite different design strategy to achieve a decoupled conductivity mechanism in polymer electrolytes [20]. This was based on polymers which are structural analogues of propylene carbonate, which itself is an excellent solvent for alkali metal salts. The first example of such a polymer was poly(parabanic acid), PPA, see Figure *5(a)*, in which the five membered 1,3-imidazolidine-

2,4,5-trione unit is the propylene carbonate analogue [20]. PPA has a T_g of 350 °C which is reduced on the addition of lithium salts as is the melting temperature, T_m. The PPA-salt complexes have appreciable ambient conductivities, *ca.* 10^{-6} S cm^{-1}, even though the glass transition temperatures are above 150 °C.

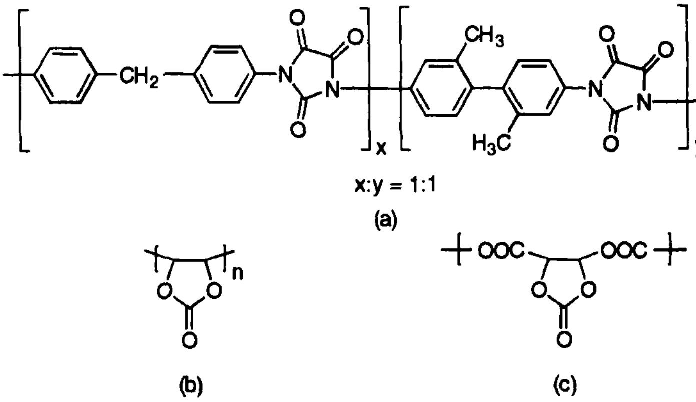


FIGURE 5 Rigid rod polymer electrolytes, *(a)* PPA; *(b)* PVIC; *(c)* PVICOX (after [21] and [22]).

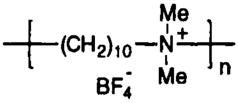
Wei and Shriver adopted this design approach and incorporated propylene carbonate itself into polymeric structures to obtain poly(vinyl carbonate), PVIC, and poly(1,3-dioxolan-2-one-4,5-diyl oxalate), PVICOX, see Figures 5*(b* and *c)*, respectively [21]. Addition of lithium triflate to both these polymers reduces both T_m and T_g. The maximum conductivity for these complexes is found for higher salt concentrations than for conventional poly(ethylene oxide)-based electrolytes and this is also found for MeOC6G6. In addition, for PVIC and PVICOX the crystalline phases appear to be ionically conducting in stark contrast to the insulating behaviour of crystalline poly(ethylene oxide) complexes. These observations strongly suggest a decoupled conductivity mechanism. This view is supported by the observation that the complexes of PVICOX exhibit higher conductivities than the corresponding complexes of PVIC because greater structural complexity may lead to less efficient packing in the solid state.

POLY(VINYL ALCOHOL)

Appreciable sub-T_g ionic conductivities have also been reported for poly(vinyl alcohol) (PVA)-lithium salt complexes [20,22,23]. For example, PVA-lithium triflate complexes exhibit conductivities in the range 10^{-8} - 10^{-4} S cm^{-1} at temperatures below the glass transition temperature [22]. MacFarlane and his co-workers attribute this behaviour to a decoupled conductivity mechanism but do not exclude the possibility that protonic transport may have an influence on the behaviour observed. This ambiguity must be resolved before the structural significance of this result can be discussed further.

IONENE POLYMERS

The final class of polymeric materials for which some degree of decoupling appears to occur are ionene polymers [24]. For example, I-10-Me-BF_4, see Figure 6, exhibits an ionic conductivity of 10^{-5} S cm^{-1} at T_g. Unlike the rigid rod polymer electrolytes, however, the crystal phases of the ionene polymers appear to be poor ionic conductors. To our knowledge, this surprising behaviour of ionene polymers has been largely overlooked. A conductivity mechanism has yet to be established.



$$\left[(CH_2)_{10}-\overset{\text{Me}}{\underset{\text{Me}}{\text{N}^{+}}} \right]_n \quad BF_4^-$$

FIGURE 6 Molecular struture of the ionene polymer I-10-Me-BF_4 (after [25]).

OVERVIEW

There is evidence that decoupled conductivity has been found in at least two (and possibly four) different classes of polymer electrolytes, especially the side group liquid crystal polymer electrolytes [11-13] and the rigid rod polymers containing powerful ion solvating groups [21,22]. In all cases, however, the key structural issue is probably the same, namely that the ions are not entrapped in strongly co-ordinating sites below T_g. Such entrapment occurs in conventional polymer electrolytes as a result of the helical conformations adopted by poly(ethylene oxide). Thus, a central aim in the design of novel materials is the elimination of such "ion cages". In the rigid rod polymers this has been achieved by increasing the rigidity of the backbone, while in the SGLCPEs a combination of enhanced backbone rigidity and interactions between the side groups prevents the backbone adopting such specific (trapping) conformations. In all systems, therefore, we must have an open structure in which ions are free to move, and there are empty sites for ions to move into. In the SGLCPEs, moreover, there is the exciting possibility of being able to control and tailor this structure by tuning interactions between mesogenic groups. This may give rise to new liquid crystal phases and presumably new conductivity and rheological behaviours. It should be possible, in time, to tailor the properties of the polymer electrolyte to a range of electrochemical and other applications.

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