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The role of ionic salts in determining T_g and ionic conductivity in concentrated PEG electrolyte solutions

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The glass transition temperature, T_g, and ionic conductivity, σ, have been measured for mixtures of low molecular weight poly(ethylene glycol)s with $LiCF_3SO_3$, $LiClO_4$, $NaClO_4$, $LiBF_4$ and $NaBF_4$. The variation of σ with temperature T has been fitted to the Vogel–Tammann–Fulcher (VTF) equation, $\sigma = AT^{-1/2}\exp[-B/(T-T_0)]$ (where A is a pre-exponential factor, B is an apparent activation energy and T_0 is the ideal glass transition temperature). It is found that both T_g and B are dependent on the anion but not the cation, that B varies linearly with T_g and that T_0 is independent of salt concentration. These observations are interpreted in terms of the effect of salt on the flexibility of the oxyethylene chain helix.

(Keywords: poly(ethylene oxide); salt complexes; ionic conductivity)

Introduction

Polymer electrolytes consisting of solutions of various salts in poly(ethylene oxide) (PEO) have been studied intensively for several years[1–5], and investigations into the way in which salt affects the structure and dynamics of these complexes is of fundamental interest and importance for the development of polymer battery electrolytes and other devices. At ambient temperatures, however, PEO salt complexes are semicrystalline and it is perceived that ionic conduction takes place predominantly in the amorphous region. The use of low molecular weight polymers obviates problems associated with crystallinity, and simplifies the preparation of reproducible samples. In this study, we report measurements of the glass transition temperature, T_g, and ionic conductivity, σ, for mixtures of low molecular weight poly(ethylene glycol)s with $LiCF_3SO_3$, $LiClO_4$, $NaClO_4$, $LiBF_4$ and $NaBF_4$. The properties of these simpler melt systems, which are dependent on molecular structure and dynamics, shed light on processes occurring in the amorphous regions of high molecular weight analogues.

Experimental

The glass transition temperatures were measured using a Perkin–Elmer DSC 7 differential scanning calorimeter operating with a scanning rate of 10°C min^{-1}. T_g was identified with the onset temperature of the glass transition, as it proved to be a more consistent figure, generally being reproducible to within ±0.3°C. A.c. conductivity measurements were performed using a Philips conductivity cell, connected to a Schlumberger SI 1260 Impedance/Gain-Phase Analyser. Temperature control was provided by a Eurotherm 815S Temperature Controller. Conductivity was measured over the range −10 to 80°C at intervals of 2°C and was controlled to within ±0.2°C.

Poly(ethylene glycol) of molecular weight 300 (PEG300, Aldrich) was dried under vacuum at around 75°C for 2–3 days. At the same time, the salt to be used ($LiCF_3SO_3$, $NaClO_4$, $LiBF_4$ and $NaBF_4$, Aldrich; $LiClO_4$, BDH) was dried separately at a temperature of around 135°C. Carefully weighed quantities of polymer and salt were mixed, and dried under vacuum at around 75°C to remove any moisture absorbed during the mixing procedure and to ensure complete dissolution of the salt. Samples were stored in a desiccator when not being used. Samples of end-esterified PEG300 (PEG300E) were prepared by adding an excess of acetic anhydride to the polymer sample and refluxing for 3 h at 140°C under a stream of dry nitrogen; the acetic acid and excess acetic anhydride were removed by rotary evaporation[6]; salt complexes were prepared as for PEG300.

Results and discussion

The T_g measurements are presented in *Figure 1*. The increase in T_g with salt concentration is approximately linear to concentrations approaching 15 : 1 ether oxygens to alkali metal cations (1.4 mol kg^{-1}), as has been noted by previous workers[7–9]. At the higher salt concentrations the rate of increase begins to level off, in agreement with other studies[8–10] which show a saturation or a decelerated rise of T_g with increasing salt concentration. The crucial detail to be observed from *Figure 1* is the effect of changing the cation and/or the anion. Substitution of lithium for sodium has no significant effect on the initial linear concentration dependence of T_g of the perchlorates or the tetrafluoroborates. In contrast, a change of anion from triflate to tetrafluoroborate to perchlorate has a marked effect. The fact that the anion, and not the cation, is the factor which influences the concentration dependence shows that the anion is strongly influencing the oxyethylene chain mobility. This is consistent with the notion that the anion can act as a bridge between solvated cations[6,11].

Measurements of the conductivity σ as a function of

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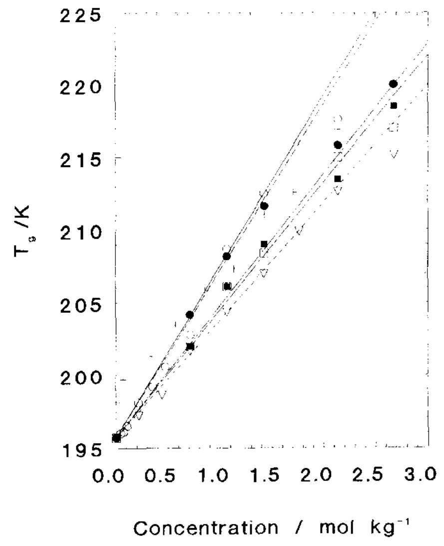

Figure 1 Plots of the d.s.c. glass transition temperature T_g as a function of salt concentration; the lines show the slopes for molalities less than 2 mol kg^{-1}: □, ---, PEG300 with LiBF$_4$; ■, ----, NaBF$_4$; ○, ——, LiClO$_4$; ●, ——, NaClO$_4$; ▽, ---, LiCF$_3$SO$_3$; +, ······, PEG300E with LiCF$_3$SO$_3$

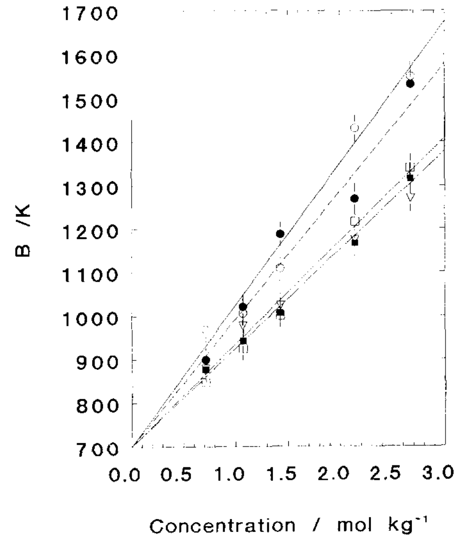

Figure 2 Plots of the variation of the VTF parameter B as a function of the concentration of salt: □, ---, PEG300 with LiBF$_4$; ■, ----, NaBF$_4$; ○, ——, LiClO$_4$; ●, ——, NaClO$_4$; ▽, LiCF$_3$SO$_3$

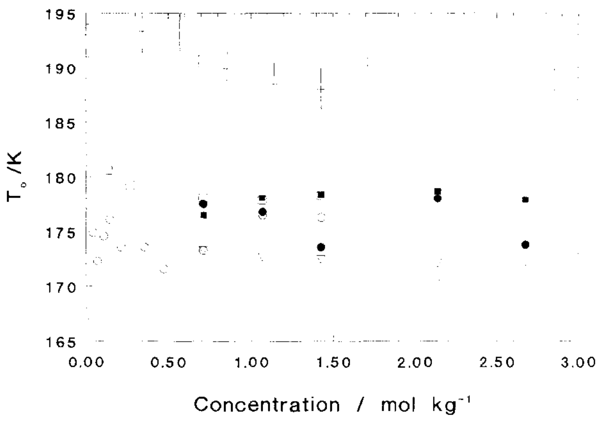

Figure 3 Plots of the VTF parameter T_0 as a function of salt concentration for various salts: □, PEG300 with LiBF$_4$; ■, NaBF$_4$; ○, LiClO$_4$; ●, NaClO$_4$; ▽, LiCF$_3$SO$_3$; +, PEG300E with LiCF$_3$SO$_3$ showing error bars

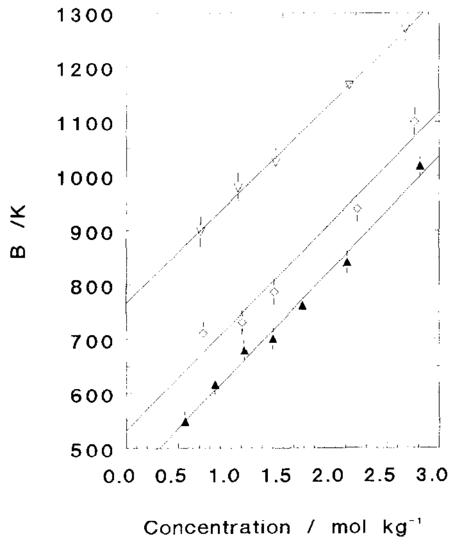

Figure 4 Plots of the variation of the VTF parameter B as a function of the concentration of salt for PEG300 (▽), PEG300E (▼) and PEG600 (◇) with LiCF$_3$SO$_3$

temperature can be fitted to a Vogel–Tammann–Fulcher (VTF) equation[12–14] given significance through Gibbs and DiMarzio's configurational entropy model[15,16] for glass-forming polymers:

$$\sigma = AT^{-1/2}\exp[-B/(T - T_0)] \qquad (1)$$

where T is the absolute temperature and T_0 the ideal glass transition temperature, i.e. the temperature at which the configurational entropy vanishes, B is an apparent activation energy, dependent on the free energy barrier opposing configurational rearrangements, and A is a pre-exponential factor related to the number of carriers. The results of such fitting, over the same temperature range and allowing all three parameters to vary, show that B increases linearly with the concentration of added salt (*Figure 2*) and, surprisingly, that T_0 is independent of salt concentration (*Figure 3*). Comparison of *Figures 1* and *2* clearly shows the similarity in the behaviour of both T_g and B. Once again, we see that a change in cation has little effect, whilst a change in anion produces the same trend in gradient with salt type as seen in *Figure 1*.

To ensure that the observed effect is not due to the OH end-groups, comparison has also been made with the end-esterified PEG3000E doped with lithium triflate. *Figure 1* shows that there is a small increase in T_g for all salt concentrations corresponding to a slight increase in the unsalted value, but that the slope is the same as for PEG300 complexes with LiCF$_3$SO$_3$. *Figure 4*, which shows the concentration dependence of B for PEG300, the end-esterified PEG300E and PEG600 complexes with LiCF$_3$SO$_3$, does show a large increase in B for PEG300 with the OH end-groups. However, the slopes of these three curves remain unchanged. Similarly, T_0 values for PEG300E shown in *Figure 3*, although slightly higher than for PEG300, are again independent of salt concentration. The presence of the OH end-groups clearly does not affect the major observations of these studies on salt complexes of PEG300, namely, that the anion is crucial in the salt dependence of B and T_g, that B varies linearly with T_g, and that T_0 is salt independent.

The relation between T_g and B may be understood if we assume that a relaxation time τ governing the glass transition mechanism is described by VTF-type dynamics[17], i.e. $\tau = \tau_0 \exp[B/(T - T_0)]$, where τ_0 is a pre-exponential constant. We can then define T_g as the temperature at which τ reaches some value, τ', whereupon no structural relaxations take place on the timescale of the experiment. Therefore at T_g, $\tau' = \tau_0 \exp[B/(T_g - T_0)]$ and $T_g = T_0 + k'B$, where $k' = 1/\ln(\tau'/\tau_0)$ is constant. Thus, since the VTF fitting shows T_0 as a constant for these materials, it follows that T_g is linearly related to B. Moreover, we find that the constant of proportionality, $k' \approx 0.03$, is a property of the polymer and not of the salt. In this particular case, B is directly related to T_g because T_0 is independent of salt concentration, which is not true in all polymer electrolyte systems[10,18], emphasizing that T_g and T_0 are not always related in a simple manner. Now B must be associated with T_g in some way through the ability of the polymer to ionize the salt and thereby change the activation energy for chain rearrangement. But T_g and B are dynamic quantities relating to chain stiffness, and the interchain steric properties of the anions and the change in T_g and B with salt cannot be understood simply on the basis of salt solvation, ion dissociation and pairing[19].

We can give these observations a molecular interpretation in terms of the recently established structure[20,21] of the crystalline complex $PEO_3 : LiCF_3SO_3$. The PEO chain is seen to adopt a helical conformation with the cations being coordinated by three intrachain ether oxygens and two anionic oxygens, and the anion forming ionic bridges between adjacent cations within the same helix. Now it is quite reasonable to assume that the local structure in the melt is very similar to that in the crystalline solid except that now the helix is undergoing large angular deformations. The flexibility of the chain is expected to decrease as the amount of salt in the helix increases and this accounts for the observation that both T_g and B are related to the concentration of the salt. The fact that the observed behaviour is more closely related to the nature of the anion than the cation stems from the much greater size and complexity of the anion. In contrast, the fact that T_0 is not apparently affected by the presence of the salt suggests that the properties of the configurational ground state of the fluid are predominantly determined by the packing properties of the polyoxyethylene helices, which will be relatively less sensitive to the nature and concentration of the salt which is intrahelically bound.

We are currently investigating whether these results are applicable to other polymer electrolytes.

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