Free volume and conductivity of plasticized polyether-urethane solid polymer electrolytes

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Abstract. The effects of salt (LiClO$_4$) concentration and plasticizer (tetraglyme) concentration on the room-temperature conductivity and free volume of a polyether-urethane solid polymer electrolyte are studied. The free volume is probed by the positron annihilation lifetime spectroscopy (PALS) technique which uses the oPs pick-off lifetime, τ_3, as an indication of the local electron density and the mean free volume cavity radius. The oPs pick-off intensity, I_3, reflects the probability of oPs formation and the relative concentration of free volume cavities in the material. The mean size (τ_3) and relative number (I_3) of free volume cavities decrease with an increase in salt concentration in the host polymer due to the Li$^+$ coordination (effective cross-linking) with the oxygens of the host polymer. The addition of 25 wt% tetraglyme plasticizer to the 1 molal LiClO$_4$/host polymer complex is shown to counter the effective cross-linking resulting in a T_g decreased to a value equal to that of the pure host polymer, increased conductivity, and average free volume cavity size (τ_3) increased to a value equal to that of the pure host polymer. However, the relative number of free volume cavities (I_3) in the plasticized host polymer/salt complex remains fewer than that of the pure host polymer over the concentration range of plasticizer studied, and in a similar manner the density remains greater than that of the pure host polymer. The room-temperature conductivity, free volume, and density behaviour in conjunction with the T_g results suggest that the plasticizer addition leads to Li$^+$ coordination with the oxygens of the plasticizer chains as well as increased mobility of the host polymer chains. The increase in free volume of the host polymer/salt complex caused by the addition of plasticizer is shown to dominate the conductivity behaviour in this system.

1. Introduction

Solid polymer electrolytes (SPEs) have conductivities which are controlled to a great extent by the mobility of the host polymer chains in the polymer/salt complex. Other factors affecting conductivity include salt concentration, degree of ion aggregation, and the dielectric constant of the host polymer. The mobility of the host polymer chains, and hence the conductivity of the SPE, can be increased by the addition of plasticizers [1]. The increase in conductivity is not a simple function of the plasticizer effect on host polymer mobility because other factors such as the plasticizer dielectric constant, the host polymer/plasticizer interaction, and the ion/plasticizer coordination also affect conductivity. The complexities of the host polymer/salt/plasticizer system present an interesting challenge to the development of an understanding on the molecular level of the role of the plasticizer in increasing conductivity [1, 2].

In order to explore a molecular understanding of transport properties in SPEs, the following discussion introduces relationships developed to model transport in polymers. The applicability of these relationships to SPEs has been questioned due to the additional interactions present in salt containing systems [3]. Models of ion transport and polymer chain mobility have been developed which have a temperature dependence as described by the Vogel–Tamman–Fulcher (VTF) relationship:

$$M = M_0 \exp[-B/(T - T_0)] \tag{1}$$

where M represents the variable of interest such as diffusivity, conductivity, viscosity, etc, M_0 is proportional to $T^{1/2}$ or $T^{-1/2}$ dependent on the variable of interest, T_0 is a reference temperature, and B is a positive or negative constant dependent on the variable of interest and the material system. These models are empirical in nature; however, not all polymer systems and certainly not all SPE systems display VTF behaviour [3]. Nonetheless, VTF behaviour is characteristic of numerous polymer systems and hence the molecular mechanisms responsible for transport properties are thought to be similar. One unifying molecular mechanism which has been proposed to link transport properties is free volume. The Doolittle [4] and Cohen–Turnbull [5] models, which relate viscosity, η, and diffusivity, D, respectively to free volume, have been successfully used to predict transport properties of glassy and rubbery polymers. The Doolittle relationship for viscosity can be written

$$\eta = A \exp(bv_o/v_f) \tag{2}$$

where A and b are constants, v_o is the occupied volume per molecule at the measurement temperature, and v_f is the average free volume per molecule. In a similar form the Cohen–Turnbull relationship for diffusivity can be written

$$D = C \exp(-\gamma v^*/v_f) \tag{3}$$

where C and γ are constants, v^* is the critical free volume cavity size necessary for diffusive displacements, and v_f is the average free volume per molecule at the measurement temperature. In both equations (2) and (3), the constants A and C are dependent on $T^{-1/2}$ and $T^{1/2}$ respectively and contain parameters which are related to the polymer and, in the case of diffusivity, the diffusing substance.

Using the Nernst–Einstein relationship between conductivity, σ, and diffusivity, D,

$$\sigma = (nq^2/kT)D \tag{4}$$

where n is the carrier concentration and q is the carrier charge, gives an equation of the form

$$\sigma = (Cnq^2/kT) \exp(-\gamma v^*/v_f). \tag{5}$$

Hence, in the Cohen–Turnbull framework, conductivity can be related to free volume.

Of course complicating factors arise which separate measurement and theory. Some of these factors are crystallinity, dissolution of the diffusing molecule or salt, and interaction of the diffusing molecule or salt with the host polymer, and these factors are not accounted for in the single-parameter, hard-sphere models of polymer free volume available for transport. Nonetheless, correlations between transport properties and free volume (calculated based on specific volume measurements) are numerous [6–10], and free volume theory is used to

model diluent diffusion [11], polymer/polymer interaction on blending [12], plasticization [13], and other related phenomena [14, 15].
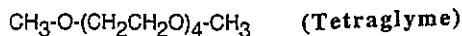
A simple direct measure of free volume in polymers is not available. The problem of free volume measurement arises from probes which are either larger than the intrinsic free volume cavities of the polymer or from probes which in some way interact with the polymer system affecting the results. Free-volume probes include electrochromic, photochromic, and fluorescent probes as well as xenon nuclear magnetic resonance (NMR), small-angle x-ray scattering, density measurements, and positron annihilation lifetime spectroscopy (PALS). Each method of free volume measurement has its strengths and limitations. The PALS technique has emerged in the past few years as a valuable non-destructive probe of free volume in polymers due to the localization of the positron species orthoPositronium (oPs) in free volume cavities which typically range in size from 100 to 400 Å^3. There is some discrepancy as to whether the cavities are pre-existing free volume cavities or holes formed by the oPs probe [7]. In either case, the cavity volumes compare well to non-bonded interatomic volumes in polymers and molecular or ionic volumes of diffusing substances. The oPs probe annihilates by an electron pick-off process and is sensitive to local electron density. Thus PALS would seem a useful probe for solid polymer electrolytes in which host polymer chain mobility as well as charge carrier density are important to conductivity. Indeed several recent publications have reported the use of PALS to study polypropylene glycol [16] and polyether-urethane [17, 18] SPEs as well as polypyrrole [19] and polyaniline [20] conducting polymers. The recent PALS studies of polyether-urethane SPEs were performed at constant salt concentration using variable temperature to effect change in free volume and conductivity [17, 18]. In the present work, the free volume variation in SPEs as a function of salt concentration as well as plasticizer concentration is measured in order to help build an understanding of the role of free volume in conductivity.

The present authors previously have used PALS to study the effect of various plasticizers on the room-temperature free volume and local electron density of a polyether-urethane [2]. The spin–lattice relaxation time, T_1, measured by ^{13}C NMR, and the glass transition temperature, T_g, measured by differential scanning calorimetry (DSC), were used as indications of host polymer chain mobility. It was postulated that the plasticizers occupied the free volume of the host polymer interrupting polymer/polymer bonding in favour of polymer/plasticizer bonding. It was further postulated that the free volume occupied by the plasticizer was dynamic free volume (at room temperature, over 80 °C above T_g) available for ion transport [2]. The present study explores (1) the effect of salt concentration on T_g and the room temperature conductivity, density, and free volume of a polyether-urethane, (2) the effect of plasticizer concentration on the T_g and room-temperature density and free volume of the polyether-urethane, and (3) the effect of plasticizer concentration on the T_g and room temperature conductivity, density, and free volume of the polyether-urethane/salt complex. This systematic study should contribute to an understanding of the differences in behaviour of the host polymer and the host polymer/salt complex.

2. Experimental details

A trihydroxypoly(ethylene oxide copropylene oxide) copolymer (molecular weight 5000 g mol^{-1}) (abbreviated as 3PEG) was mixed with variable concentration of tetraglyme (vacuum distilled over sodium) before cross-linking with hexamethylene diisocyanate (HDI) using a Thorcat 535 catalyst. Cross-linking was completed at 40 °C. Figure 1 displays the chemical structures of 3PEG, HDI, and tetraglyme. A second series of samples was prepared

by dissolving between 0.5 molal and 1.5 molal LiClO$_4$ (Aldrich) in 3PEG (stirring at 80 °C for 2 h) followed by cross-linking with HDI. A series of 1 molal LiClO$_4$/3PEG polymer electrolytes with variable concentration of tetraglyme also was prepared. Salt concentrations are expressed using the molal unit (M), i.e. moles of salt per kg of polymer plus plasticizer.

$$CH_3\text{-}O\text{-}(CH_2CH_2O)_4\text{-}CH_3 \qquad \textbf{(Tetraglyme)}$$

(3PEG)

$$H_2C\text{ - }O[(CH_2CH_2O)x\text{ - }(\overset{\overset{\textstyle CH_3}{|}}{CH}CH_2\text{ - }O)y]\text{-}_{\frac{x}{2}}CH_2CH_2\text{ - }OH$$

$$HC\text{ - }O[(CH_2CH_2O)x\text{ - }(\overset{\overset{\textstyle CH_3}{|}}{CH}CH_2\text{ - }O)y]\text{-}_{\frac{x}{2}}CH_2CH_2\text{ - }OH$$

$$H_2C\text{ - }O[(CH_2CH_2O)x\text{ - }(\overset{\overset{\textstyle CH_3}{|}}{CH}CH_2\text{ - }O)y]\text{-}_{\frac{x}{2}}CH_2CH_2\text{ - }OH$$

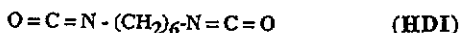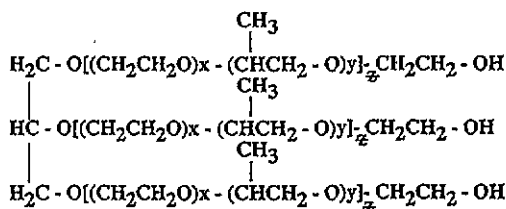$$O = C = N \text{ - } (CH_2)_6\text{-}N = C = O \qquad \textbf{(HDI)}$$

Figure 1. Chemical structures of 3PEG, HDI, and tetraglyme.

Samples were sealed in aluminium DSC pans, quenched in liquid nitrogen and then transferred to a Perkin Elmer DSC7 cold head. The liquid nitrogen quench ensured the necessary cooling rate consistency. Glass transition temperatures were measured at a heating rate of 10 °C min^{-1} and were recorded to an accuracy of ± 1 °C. The DSC was calibrated using cyclohexane with a crystal transition at -87.06 °C and a melting transition at 6.54 °C. The T_g values are quoted as the extrapolated onset T_g: the intersection of the baseline trace and the departure from baseline upon heating as the specific heat begins the transition from the glassy to the fluid state. Thermal lag due to varying sample mass did not affect the glass transition, within the range of sample mass used (7 to 15 mg) and the error of the experiment. Temperature-dependent conductivity measurements were performed using a Wayne–Kerr bridge operating at 1592 Hz. Density measurements were performed at 15 °C, using the Archimedean method with propane-2-ol (density $= 0.7869$ g cm^{-3}). Results are the mean value of three measurements with an accuracy of ± 0.009 g cm^{-3}.

PALS measurements were made using an automated EG&G Ortec fast/fast coincidence system with a ^{22}Na resolution of 250 picoseconds. The equipment and samples were thermally stabilized at 22 ± 0.5 °C. The ^{22}NaCl source was a 2 mm diameter spot source of 25 μCi sandwiched between two 2.54 μm titanium foil sheets. Data were collected at 22 °C on 2 mm thick cast polymer sheets and analysed using the PFPOSFIT program [21]. The shortest lifetime was fixed at 125 ps, characteristic of pPs self-annihilation. Five spectra of 30 000 peak counts were collected for each sample, and error bars are population standard deviations of these results. The PALS parameters (lifetimes and intensities) for these polymers did not change as a function of contact time with the source. The source

gave a two-lifetime (166 ps, 98.2%, and 450 ps, 1.8%) best fit to 99.99% pure annealed and chemically polished aluminium samples. No source correction was used in the analysis.

3. Results and discussion

3.1. Effect of salt concentration on the host polymer

Figure 2 displays the effect of lithium perchlorate (LiClO$_4$) salt addition on the T_g of 3PEG. It is postulated that the free ions (Li$^+$) coordinate the oxygens of the 3PEG resulting in an effective cross-linking and reduced mobility of the polymer chains. This reduced chain mobility is reflected in an increased T_g. The increase in T_g is linear with salt concentration. The addition of salt also affects the room temperature conductivity of 3PEG as shown in figure 3. Initially the conductivity increases due to the increase in charge carriers from the addition and dissociation of the salt. The population of charge carriers increases with increasing salt concentration, but charge carrier mobility must decrease as indicated by the decrease in conductivity after the addition of approximately 0.6 M salt. It is postulated that the charge carrier mobility decreases in part because the 3PEG becomes more coordinated by the salt which restricts polymer chain mobility [22]. Hence polymer chain mobility at room temperature (80 °C above T_g) is important to conductivity.
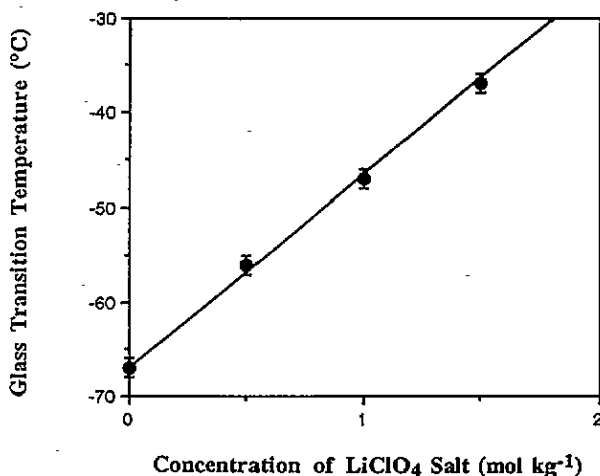

Figure 2. Glass transition temperature as a function of salt concentration in 3PEG. Line of best fits has a linear regression coefficient of 0.999.

The effect of salt on the room-temperature free volume and electron density characteristics were measured by PALS. The PALS analysis typically gives three lifetime components in polymers: τ_1 attributed to paraPositronium self-annihilation, τ_2 attributed to free positron and positron/molecular species annihilation, and τ_3 attributed to orthoPositronium pick-off annihilation. Each lifetime τ_i has a corresponding intensity I_i indicative of the relative number of annihilations taking place with a particular lifetime. It is the third component (τ_3, I_3) that is of interest in the present work due to its dependence on free volume. Figures 4 and 5 examine the dependence of τ_3 and I_3 on LiClO$_4$ concentration in pure 3PEG. The mean free volume cavity radius (as indicated by τ_3) and relative free
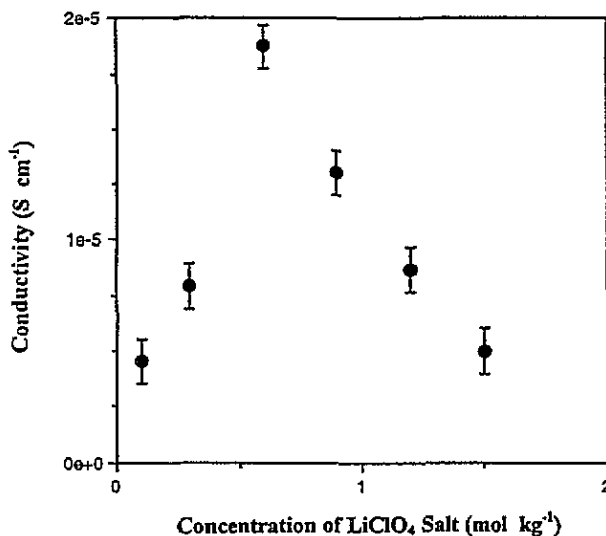
Figure 3. Conductivity as a function of salt concentration in 3PEG.

volume concentration (I_3) decrease with increasing salt concentration indicating a significant decrease in overall free volume in 3PEG as salt is incorporated. As mentioned in the introduction, τ_3 gives an indication of the local electron density at the oPs annihilation sites. These sites are free volume cavities located inter- and intrachain. As these free volume sites become smaller, the local electron density seen by the oPs increases and the oPs lifetime τ_3 shortens. Alternatively, the size of the cavity may remain constant, but the oPs lifetime can be quenched by various oxidizers including paramagnetic ions and chlorides [23]; however, as illustrated in the following discussion and as shown in the plasticized system in this work, ClO_4^- does not act as an oPs quenchant in these polyethers.
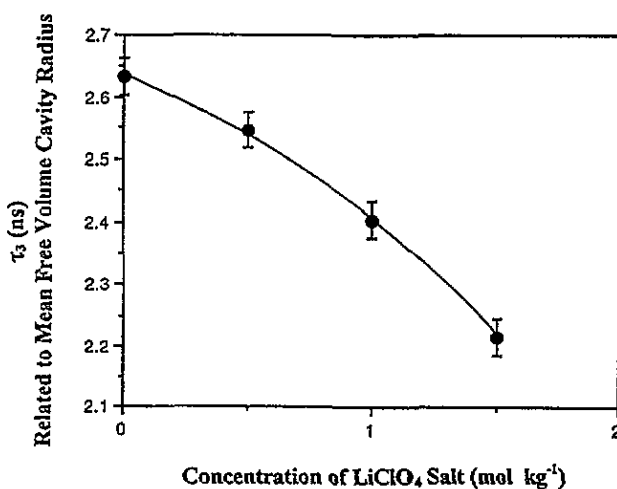

Figure 4. oPs pick-off lifetime, τ_3, as a function of salt concentration in 3PEG. Curve drawn to indicate trend.
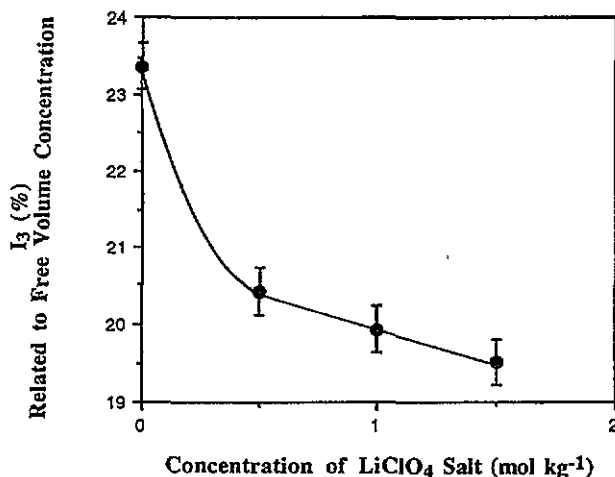
Figure 5. oPs pick-off intensity, I_3, as a function of salt concentration in 3PEG. Curve drawn to indicate trend.

Most of the work on chemical quenching of oPs has been performed in liquids. In some cases, the reduction of oPs lifetime on the addition of salts could be attributed to increasing density of the solution and the corresponding increase in the rate of oPs pick-off annihilation (i.e. the free volume model) [23]. The addition of $LiClO_4$ to a low-molecular-weight polyether analogue has been shown to have no effect on the value of τ_3 measured at room temperature. Thus this salt is an unlikely species for oPs quenching in polyether polymers. This point is discussed further in the final section of the results and discussion. It is postulated that the decrease in τ_3 shown in figure 4 is indicative of the contraction of inter- and intrachain free volume cavities due to Li^+ coordination with the oxygens of the host polymer chains.

Peng *et al* [17, 18] have shown that as the measurement temperature, T_M, is increased above T_g in a 1.14 m $LiClO_4$ polyether-urethane SPE, the value of τ_3 increases linearly with T_M for temperatures up to $T'_g + 100$ °C. In their work, Peng *et al* [17, 18] used the value T'_g measured by PALS which is typically 5 to 15 °C lower than that found by DSC due to the sensitivity of τ_3 to local segmental motions which are precursors to T_g. Hence the linear region of τ_3 increase with temperature can be estimated as from T_g to $T_g + 85$ °C in the polyether-urethane SPE studied by Peng *et al* [17, 18]. Similarly, Stevens *et al* [16] have shown that τ_3 is a linear function of $T_M - T_g$ for temperatures from T_g up to $T_g + 80$ °C in polypropylene glycol SPEs of varying salt concentration. The value of τ_3 becomes independent of temperature at T_e ($\sim T_g + 85$ °C). The occurrence of T_e was first reported in glass forming liquids by Brandt and Spirn [24] and indicates the temperature at which the motional correlation times in the liquid become similar to the oPs pick-off lifetime [16, 24, 25]. The value of T_e has been measured in numerous cross-linked polymers as approximately $T_g + 85$ °C [16–18, 25]. At measurement temperatures above T_e, the oPs pick-off lifetime τ_3 ceases to reflect the characteristics of the polymer packing and, as reported by Stevens *et al* [16], becomes insensitive to the effects of salt on polymer structure. For the present study, in which all PALS measurements are made at room temperature ($T_M = 22$ °C), it can be postulated that a variable such as salt concentration which raises T_g, and hence lowers $T_M - T_g$, will concomitantly lower τ_3 in the measurement regime $T_g < T_M < T_e$. The data of figure 2 indicate that T_M is less than $T_g + 85$ °C for this

SPE series, and as seen in figure 4, the τ_3 behaviour reflects the decreasing free volume cavity size at 22 °C with the addition of salt. It can be noted at this point in the discussion that a variable such as plasticizer addition, which lowers T_g and hence raises $T_M - T_g$, should concomitantly increase τ_3 in the measurement regime $T_g < T_M < T_e$.

In molecular solids, a decrease in the oPs pick-off component intensity, I_3, can be due either to a decrease in the number of oPs annihilation sites (decrease in relative free volume concentration) or to a decrease in the probability of Ps formation. An example of a decrease in I_3 due to changes in free volume is observed when pressure is applied to polymers squeezing out the number of inter- and intrachain sites [26]. The decrease is approximately linear with applied pressure [26]. An example of a decrease in I_3 due to oPs inhibition (introduction of a competing mechanism to Ps formation) is observed due to the addition of salts which can cause increasing dipole character of the polymer molecules and increasing localization of negative charge [23]. It is thought that the formation of oPs is chemically inhibited in favour of positron capture caused by the presence of anions [23]. The decrease in I_3 due to chemical inhibition is approximately exponential with anion concentration approaching some saturation value. In the present work, it is possible that the Li^+ or ClO_4^- ions provide a competing mechanism to Ps formation. Pure $LiClO_4$ was measured and gave no evidence of oPs formation. If Ps inhibition were occurring, a concomitant decrease in the intensity I_1 of the paraPositronium (pPs) component would be expected. In this work, I_1 is approximately constant ($15 \pm 0.6\%$) with salt concentration. Hence it is argued that in the present work the decrease in I_3 with increasing salt concentration is due to a reduction in the number of inter- and intrachain free volume cavities. This reduction may be due to the coordinating effects of Li^+ and the filling of cavities by the ions.
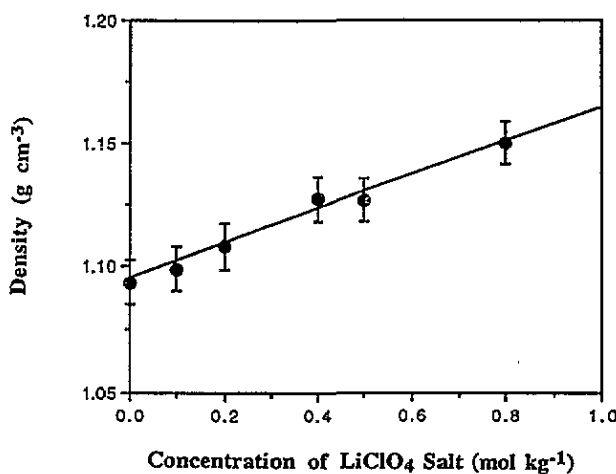

Figure 6. Density as a function of salt concentration in 3PEG. Line of best fit has a linear regression coefficient of 0.984.

Density measurements have been performed on this system in order to evaluate the postulated reduction in free volume as opposed to chemical quenching or inhibition of oPs. The density data shown in figure 6 reflect an additive increase with salt concentration. The density of $LiClO_4$ salt is 2.428 g cm^{-3}, and this additive behaviour does not give an indication of a change in packing of the polymer chains. This simple additive response can be contrasted with the non-linear trends of the PALS free volume parameters. The

PALS data, indicative of radius (τ_3) and concentration (I_3) of free volume sites, give information on the free volume distribution, unlike density measurements. For comparison with the density data, the PALS data can be converted to a quantity proportional to fractional free volume ($\tau_3^3 I_3$), and this quantity decreases linearly with increasing salt concentration. Hence although the density data show additivity and give no information on the polymer/salt interaction, the PALS results show a decrease in the fractional free volume of the polymer/salt complex with increasing salt concentration indicative of changes in the atomic scale free volume and polymer packing.

The PALS results support the postulated effect of $LiClO_4$ on the polymer structure: a coordination causing conformational changes and increased segmental interaction via the cations resulting in an increased T_g. The competition between charge carrier population and charge carrier mobility (as shown by the maximum in figure 3) also supports the suggestion that the Li cation strongly coordinates the 3PEG. Hence the free volume, conductivity, and T_g results provide a coherent picture of the effect of salt on the host polymer chain mobility. It is interesting to note that the effective cross-linking (due to Li^+ coordination) reduces even the room-temperature free volume measured 80 °C above T_g. PALS sensitivity to cross-linking effects on free volume measured above T_g has been reported by Jean *et al* [25] in epoxy polymers. Similar to the present study, increasing the cross-link density decreased the value of τ_3 in the epoxies even at temperatures 80 °C above T_g. In addition, a recent study by Stevens *et al* [16] has reported a decrease in τ_3 and I_3 attributed to increasing cross-link density with increasing $NaCF_3SO_3$ concentration in polypropylene glycol measured over a similar temperature range above T_g as that used in the present study. Thus for the measurement temperature $T_M < T_e$, the values of τ_3 and I_3 appear to reflect the decreasing free volume size and concentration caused by the Li^+ ion coordination of the polymer chains.

3.2. Effect of plasticizer concentration on the host polymer

Tetraglyme was chosen from a number of plasticizers known to enhance the mobility and conductivity of 3PEG and its salt complexes [1, 2]. Tetraglyme has a compositional and structural similarity to 3PEG which reduces the number of variables with possible effects on the T_g, conductivity, density, and free volume behaviour of the plasticized host polymer and polymer/salt complex. Figure 7 shows the effect of plasticizer concentration on the glass transition temperature of the host polymer, pure 3PEG (open circles in figure 7). The decrease in T_g of pure 3PEG with increasing tetraglyme concentration is linear (correlation coefficient of 0.993) indicating an interruption of polymer/polymer bonding and an increase in host polymer chain mobility over the concentration range studied. This increase in host polymer chain mobility inferred from the T_g data has been verified by ^{13}C NMR [1,2]. The T_g of pure tetraglyme can be estimated as -123 °C by extrapolating the data in figure 7 (open circles) to 100% tetraglyme.

A few PALS studies of plasticization and antiplasticization have been reported in the literature, and these studies have noted either a decrease or no change in the amount of free volume below T_g due to the addition of plasticizer [27, 28]. Free-volume models of plasticizer behaviour in polymers postulate that the addition of the low-molecular-weight plasticizer increases the total free volume of the system resulting in the achievement of the cooperative chain mobility required at the glass transition at lower thermal energies (hence reducing T_g). In some polymer systems, antiplasticization is known to occur at low concentrations of plasticizer leading to reduced mobility of the amorphous chains. Antiplasticization is thought to be due to the reduction in mixture free volume as well
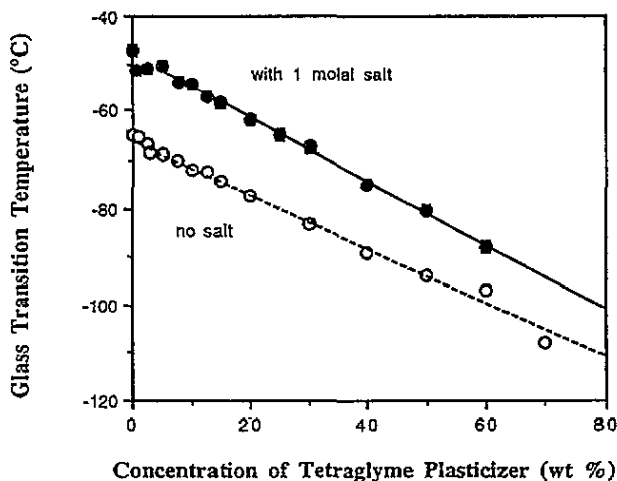
Figure 7. Glass transition temperature as a function of plasticizer concentration in 3PEG (O) and in the host polymer/salt complex (●). Lines drawn to indicate trends.

as contributions from the absolute free volume of the plasticizer which effectively reduce mobility [29].

The free volume sites probed by PALS are both static and dynamic free volume. Static or interstitial free volume sites can be pictured as the holes defined by Eyring [30] which are necessary for the flow of polymer chains. Dynamic free volume is the time-dependent fraction of the total free volume. The ratio of static to dynamic free volume is thought to be greater than one and is dependent on temperature [31]. In terms of transport properties, it is thought that the dynamic free volume plays the major role in diffusion whilst static free volume plays the major role in sorption [31]. The detection of dynamic free volume by PALS is dependent on the frequency of molecular motion. As noted by Kobayashi *et al* [32], the measurement of free volume in rubbery polymers and molecular liquids is most often discussed in terms of the bubble model [33] such that the oPs is localized in a cavity called a bubble. Kobayashi *et al* [32] show that the oPs pick-off lifetime, τ_3, is correlated with the free volume (calculated by the Bondi group contribution method [34]) for glassy polymers as well as rubbery polymers and molecular liquids. Thus the oPs lifetime, τ_3, appears to be sensitive to changes in free volume whether dominated by changes in static (pre-existing free volume cavities) or dynamic (hole energy or cohesive energy) forces.

Figure 8 shows that the addition of various concentrations of plasticizer to the pure 3PEG does not change τ_3 (open circles in figure 8). As 3PEG and tetraglyme are polyether analogues, it is not surprising that the oPs lifetime, τ_3, which is a function of local electron density (and according to the bubble model reflects molecular cohesion of polymer liquids) is similar for the two polyethers at a temperature more than 85 °C above their respective T_g values. As discussed previously, above T_e which is approximately $T_g + 85$ °C, the oPs lifetime τ_3 becomes insensitive to the polymer packing [16]. At the measurement temperature (22 °C), 3PEG is at $T_g + 89$ °C; therefore, the lowering of T_g caused by the plasticizer has moved the polymer/plasticizer system into the regime in which τ_3 no longer reflects polymer packing. In studies where the measurement temperature is raised in order to reach T_e, the value of τ_3 remains approximately constant once T_e is exceeded [16–18, 25]. In the present study, plasticizer concentration is used to lower T_g and hence
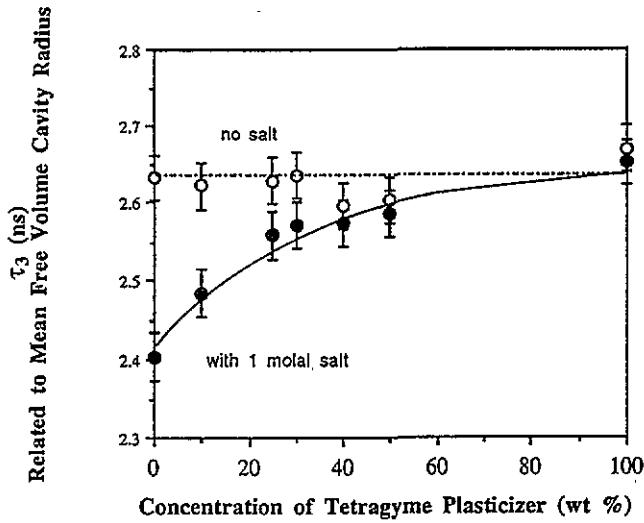
Figure 8. oPs pick-off lifetime, τ_3, as a function of plasticizer concentration in 3PEG (O) and in the host polymer/salt complex (●). Lines drawn to indicate trends.
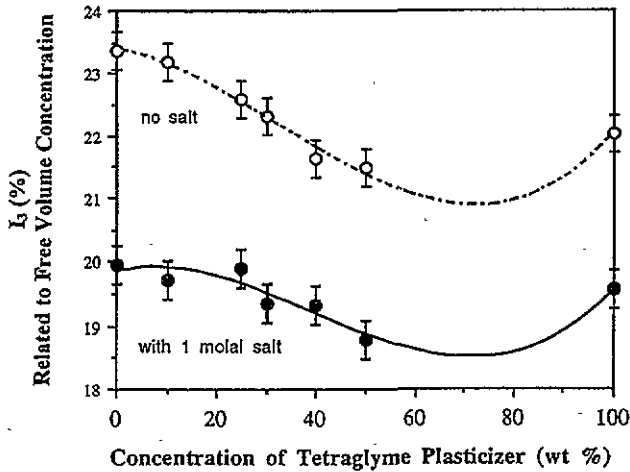

Figure 9. oPs pick-off intensity, I_3, as a function of plasticizer concentration in 3PEG (O) and in the host polymer/salt complex (●). Curves drawn to indicate trends.

raise the measurement temperature above T_e. The result is the same for either case in that τ_3 is constant and no longer reflects the polymer characteristics once T_e is reached.

Comparison of the I_3 values for the host polymer and pure tetraglyme (figure 9) indicates that there are fewer oPs annihilation sites in the low-molecular-weight polyether analogue (open circles in figure 9). The lower I_3 is due to the higher number of dynamic free volume sites (in the total free volume fraction) in the plasticizer; the oPs 'sees' these sites as occupied if the frequency of molecular motion through the sites is faster than the annihilation rate. The I_3 behaviour shown in figure 9 (open circles) also indicates a decreasing number of free

volume cavities with the addition of tetraglyme. It can be postulated that the tetraglyme in the pure 3PEG is filling free volume cavities and hence decreasing the relative number of cavities. The decrease in I_3 suggests either a conformational change in the host polymer which leads to better packing or a filling of the free volume sites by the plasticizer. The action of the plasticizer linearly decreases T_g over the concentration range studied. This weighted average response of the chain mobility to the addition of plasticizer indicates no significant antiplasticization in this system. Thus the decreased T_g may be a result of greater polymer configurational freedom whilst the decreased relative free volume concentration (I_3) may be a result of space filling and increased polymer/plasticizer interactions, which increase packing efficiency. The filling of free volume sites might be expected to increase T_g; however, if those sites represent dynamic free volume, then they can appear full to the oPs but still be available for molecular and ionic motion [2]. These results illustrate that flexible plasticized polymers can have free volume occupied by the plasticizer which is still available for polymer chain mobility due to the high frequency of the plasticizer motion. This point is discussed in more detail in the following section.
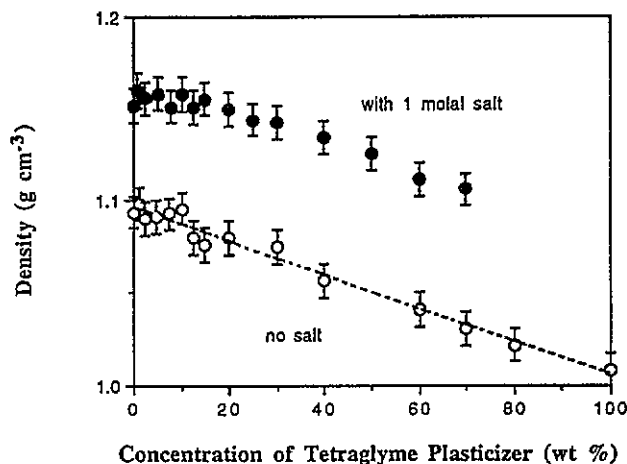

Figure 10. Density as a function of plasticizer concentration in 3PEG (O) and in the host polymer/salt complex (●). Line drawn to indicate trend.

Figure 10 displays the density at 15 °C as a function of tetraglyme concentration (open circles in figure 10). The density decreases with plasticizer addition following simple mixing behaviour. Previously it was illustrated that the PALS parameters can give details on the distribution of free volume which are unavailable from the density data. The PALS I_3 response (figure 9) shows no decrease in relative free volume concentration with the first 10 wt% addition of tetraglyme to the pure 3PEG. It is possible that the constant relative free volume concentration for low plasticizer additions is due to antiplasticization. The T_g behaviour is that of simple mixing, however, NMR relaxation times for ^{13}C have indicated an antiplasticization effect in this system on initial addition of plasticizer.

Comments on the relationship between chain mobility, as indicated by T_g, and room-temperature free volume are speculative at best due to the large temperature differential (the free volume is probed over 80 °C above T_g). Work by Elwell and Pethrick [27] has shown that the PALS free volume parameters far above T_g in antiplasticized and plasticized systems are not systematic functions of T_g because the temperature dependence of the free

volume parameters measured by PALS changes with the addition of plasticizer. A more meaningful discussion of free volume and mobility can arise from the comparison of room temperature conductivity (which is a function of solvent mobility) and the room-temperature PALS parameters in the polymer/salt complex.

3.3. Effect of plasticizer concentration on the polymer/salt complex

As mentioned in the introduction, the behaviour of polymers and of SPEs is not always similar due mainly to the interactive effects between the salt and the host polymer. As has been illustrated thus far, the presence of salt in the host polymer/salt complex can alter the conformations and glass transition of the polymer. The effects of plasticizer addition to 3PEG both without salt and with 1 M LiCO₄ present are shown in figures 7–11. Figure 7 compares the linearly decreasing T_g of pure 3PEG on addition of plasticizer with the two-stage T_g behaviour in the polymer/salt complex. An addition of 25 wt% tetraglyme to the polymer/salt complex results in a polymer chain mobility (as indicated by T_g) similar to pure 3PEG. In other words, the chain mobility restriction due to coordination of the 3PEG polymer by LiClO₄ can be offset by the effect of approximately 25 wt% plasticizer which competes with the polymer for coordination with the salt in addition to interrupting polymer/polymer interactions. The coordination of the tetraglyme by the Li cation can be inferred from the increase in T_g of the tetraglyme due to the addition of 1 M LiClO₄. The increase in T_g can be estimated as approximately 11 °C (from −123 °C to −144 °C) by extrapolation of the data in figure 7. This increase compares to the 20 °C (from −67 °C to −47 °C) increase observed in the host polymer indicating that the Li⁺ coordination of the low-molecular-weight tetraglyme chains has less effect on mobility than the Li⁺ coordination of the 3PEG chains. This difference is due to chain end contributions to mobility and free volume and also due to differences in extent of cation coordination.
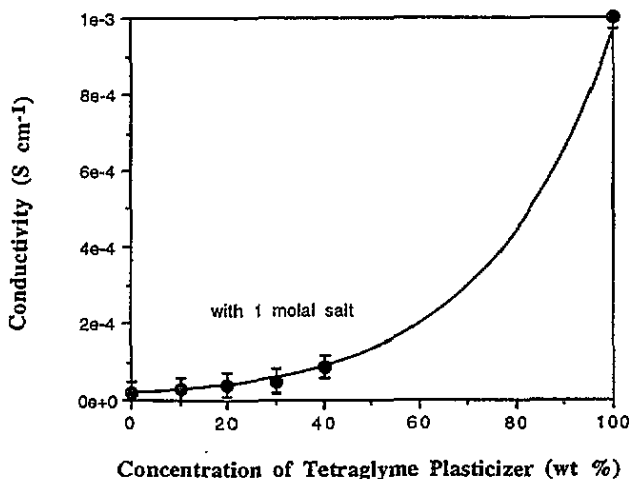

Figure 11. Conductivity as a function of plasticizer concentration in the host polymer/salt complex. Exponential fit has a correlation coefficient of 0.997.

The effect of plasticizer on the room temperature conductivity of the polymer/salt complex is shown in figure 11. The dielectric constants of tetraglyme and 3PEG are the same [1, 2] so this does not contribute to changes in conductivity. The increase in

conductivity could be partly due to an increase in the number of mobile charge carriers if the low-molecular-weight tetraglyme helps cause salt dissociation; however, recent Fourier transform infrared (FTIR) studies suggest that this is not the case [35]. The exponential increase in conductivity with increasing plasticizer concentration suggests, according to equation (1), that plasticizer concentration is proportional to the quantity $(T - T_0)$. If the reference temperature T_0 is set to the glass transition temperature, and T is the measurement temperature (room temperature), the increasing plasticizer concentration is equivalent to decreasing the glass transition temperature (as shown in figure 7). This correlation has been qualitatively supported in previous work [36]. A semilogarithmic plot of the data in figure 11 (log(σ) versus wt% tetraglyme), not shown, reveals that a steady increase in conductivity occurs over the entire concentration range of plasticizer including the initial additions of tetraglyme. The glass transition temperature, however, is almost independent of *plasticizer concentration for the first few per cent. Thus the room temperature conductivity* behaviour is not completely explained by the decreasing T_g with plasticizer addition as would be expected by equation (1). The PALS results can shed some light on this question.

Figures 8 and 9 show the effect of plasticizer concentration on pure 3PEG and the polymer/salt complex (closed circles). The oPs pick-off lifetime τ_3 is insensitive to any effect of salt in pure tetraglyme as indicated by the overlapping points at 100% plasticizer in figure 8. In contrast, the addition of 1 M LiClO$_4$ to tetraglyme causes a decrease in I_3 similar to but smaller in magnitude than that which occurs in the host polymer. The decrease in I_3 of the host polymer on the addition of 1 M LiClO$_4$ is 3.4% (absolute %) whilst in pure tetraglyme the decrease is 2.5% (absolute %). This result supports the inference drawn from the T_g data that the Li cations coordinate the tetraglyme in a similar manner to the host polymer but with less effect. The PALS technique probes an approximately 1 mm^3 volume of material. The number of chain ends per unit volume probed is greater in the plasticizer than in the polymer. Hence the contribution of chain end mobility and free volume to the total mobility and free volume is greater in the plasticizer. Thus the reduction in inter- and intrachain mobility and free volume due to Li$^+$ coordination will be proportionately smaller in the plasticizer. The lack of change in the τ_3 of tetraglyme with the addition of 1 M salt *is because the measurement temperature is higher than T_e in these tetraglyme samples.*

The τ_3 behaviour of the polymer/salt complex with increasing plasticizer concentration is shown in figure 8 (closed circles). It is interesting to observe that τ_3 (the free volume cavity size) for the polymer/salt complex increases rapidly during the first 20wt% addition of tetraglyme and then is effectively constant at the value for the pure host polymer. This result is consistent with the T_g data which show that the addition of 25 wt% plasticizer lowers the T_g to that of the pure host polymer. The τ_3 data as a function of plasticizer concentration can be used to estimate the value of T_e in the 1 M LiClO$_4$/3PEG sample as $T_g + 90$ °C. The addition of 10 wt% plasticizer to the polymer salt complex does not appreciably lower T_g; however, this addition does appreciably increase τ_3. Hence the initial increase in τ_3 is not due to an increase in $T_M - T_g$. Therefore, an interaction between Li$^+$ ions and tetraglyme is suggested, which can reduce the number of polymer segment/polymer segment cross-links and hence increase the interchain spacing. This interaction in turn would allow higher *conductivity at room temperature through increased mobility.*

The I_3 behaviour with plasticizer concentration observed for the polymer/salt complex shows an initial plateau region and then parallels that of the pure 3PEG (figure 9). The initial plateau region also can be observed in the T_g data for the polymer/salt complex. This plateau indicates that the initial addition of plasticizer contributes more toward plasticizer/salt interaction than toward plasticizer/host polymer interaction.

The density data are shown in figure 10. The density of the host polymer/salt complex

remains greater than that of the pure 3PEG with increasing plasticizer concentration over the range studied. The density results agree with the I_3 data of figure 9 which suggest that the relative number of free volume cavities remains decreased in the host polymer/salt complex with the addition of plasticizer.

A model of this system in which the plasticized host polymer/salt complex is heterogeneous on a nanoscale and composed of Li^+ coordinated regions where the mobility of the plasticizer and host polymer are restricted, and non-coordinated regions where the plasticizer acts to increase the main chain mobility, is consistent with the experimental results discussed thus far.

The PALS technique is sensitive to the interactions among the plasticizer, salt, and polymer as well as the solvent (plasticizer and polymer) mobility through the effects of these interactions on the free volume of the system. These effects also influence conductivity. However, although the T_g and free volume data of the polymer/salt complex indicate two stages of plasticizer interaction, the conductivity data show a steady increase over the entire concentration range. This discrepancy suggests a more complex conductivity mechanism at low plasticizer concentrations.

Equation (4) shows that $\log(\sigma)$ should be linear with $1/v_f$ if temperature, carrier concentration, carrier charge, salt solubility, and salt/polymer interaction are constant. It has been speculated thus far that changes in the number of mobile charge carriers and the salt/polymer interaction are dominant for plasticizer additions up to 10 wt%, beyond which the increase in free volume and polymer chain mobility caused by further plasticizer additions begin to dominate conductivity behaviour. The PALS parameters τ_3 and I_3 can be used to calculate v_f for tetraglyme concentrations up to 25 wt% (above 25 wt% T_M is greater than T_e). The quantity τ_3^3 is related to the average free volume cavity volume and has been illustrated to be proportional to v_f in glassy and rubbery polymers [37–39] as has the quantity $\tau_3^3 I_3$ which is related to the fractional free volume, f, if τ_3 represents mean free volume cavity radius and I_3 represents free volume concentration [38, 39]. A plot of $\log(\sigma)$ versus $1/\tau_3^3$ is linear with a correlation coefficient of 0.998 whilst a plot of $\log(\sigma)$ versus $1/\tau_3^3 I_3$ is linear with a correlation coefficient of 1.0 (plots are not shown). This results agrees with that of Peng *et al* [17, 18] who measured the conductivity and PALS free volume of a polyether-urethane/$LiClO_4$ SPE as functions of temperature and demonstrated that $\log(\sigma)$ is proportional to $1/f$ (where f is basically proportional to $\tau_3^3 I_3$). The result of the present work also suggests that whether the plasticizer increases the free volume by competing with the host polymer for Li^+ interaction or by increasing the host polymer chain mobility, the net result is an increase in conductivity. The effect of the tetraglyme on the number of mobile charge carriers appears to be of secondary importance.

4. Conclusions

It has been shown that increasing the segmental mobility of salt-coordinated 3PEG by the addition of tetraglyme plasticizer increases room temperature conductivity, increases the mean free volume cavity size and relative number of dynamic free volume cavities, and decreases T_g. The effect of the plasticizer on the conformations and mobility of the host polymer (3PEG) is different than on the host polymer/salt complex at low concentrations of plasticizer as indicated by the T_g and PALS data. It was postulated that the initial addition of plasticizer contributes more toward plasticizer/salt interaction than plasticizer/polymer interaction. This plasticizer/salt interaction increases the mobility of the ions causing an increase in conductivity. Further increases in plasticizer concentration

affect the polymer/salt complex similarly to the pure host polymer and cause an increase in host polymer chain mobility which also increases conductivity. The effect of tetraglyme on chain mobility in pure 3PEG and the 3PEG/LiClO$_4$ system will be measured by ^{13}C NMR and published separately [40]. Forsyth *et al* [41] have recently shown by ^{13}C NMR that at low concentrations some plasticizers can increase the salt coordination to the host polymer and hence lower chain mobility. Thus as illustrated by the present study and others [2, 41] the action of plasticizer on the polymer/salt complex can be very different from the action of the plasticizer on the pure host polymer.

The decrease in the relative number of oPs annihilations (I_3) with the addition of plasticizer indicates a filling of the free volume by plasticizer but not a decrease in chain mobility or conductivity. The concept of dynamic free volume was invoked to explain the effect of the plasticizer on the pure host polymer and the polymer/salt complex. The *important of static and dynamic free volume to transport properties in polymers has been* discussed by many authors [3, 5, 8–10, 13, 30, 37]. In addition, the effect of crystallinity on transport properties of polymers and SPEs is well known and has highlighted the need for a sensitive probe of the amorphous component of semicrystalline systems. PALS provides such a sensitive probe as illustrated by this work and recent work on the amorphous properties of semicrystalline polymer blends [42]. The relationship between the free volume probed by PALS and transport properties in polymer systems is the subject of ongoing work [39].

Acknowledgments

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