^{13}C NMR spin–lattice relaxation times as a probe of local polymer dynamics in plasticized polyethers

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^{13}C NMR spin–lattice relaxation times T_1 are used to investigate the effect of low molecular weight diluents, including *N*,*N*-dimethylformamide, *N*-methylformamide, propylene carbonate, γ-butyrolactone, triglyme and tetraglyme, on the local polymer segmental motion in polyether–urethane networks. In all cases, an increase in the local mobility is deduced from the increasing T_1 measurements consistent with a decreasing glass transition temperature. The extent of plasticization, however, is dependent on the nature of the small molecules. Those molecules which can either form strong polymer-diluent interactions (for example through dipolar interactions) or are themselves rigid, give the least enhancement of polymer mobility and the greatest deviation from the Fox equation for T_g. In the presence of alkali metal salts, *N*,*N*-dimethylformamide and propylene carbonate are shown to have opposite effects on the local polymer motion, as seen from the T_1 measurements. In both cases, addition of the plasticizers increases the ^{13}C T_1 relaxation times for the plasticizer. However, propylene carbonate decreases the polymer ^{13}C T_1 whilst *N*,*N*-dimethylformamide results in the expected increase in polymer ^{13}C T_1.

It has been well established that the dissolution of alkali metal salts in polyethers results in ionically conductive materials which have great potential as solid polymer electrolytes in all-solid battery and other electrochemical applications. The highest conductivity achieved in purely polyether-based solid electrolytes is less than 10^{-4} S cm^{-1},[1] which is at the lower end of the useful range of conductivities. However, the addition of low molecular weight liquids, or plasticizers, have been shown to significantly enhance the ionic conductivity while still maintaining useful material properties.[2–4]

In polymer language the term plasticizer refers to a species which will decrease the glass transition temperature of a polymer. It was shown at an early stage in the development of polymer electrolytes that lower glass transition temperatures resulted in higher conductivities since, it was believed, the mechanism of ionic conduction was strongly coupled to the segmental motion of the polymer backbone.[1,5] In recent years it has been shown that, at the salt concentration levels used, ionic aggregation also plays a major role in limiting conductivity by decreasing the available number of charge carriers.[6–8] This is a result of the low relative permittivity of the polyethers. Therefore, the addition of plasticizers with higher relative permittivities may have an additional effect on the ionic conductivity of polymer electrolytes. Previous work in our laboratories[2,9] has shown that the nature of the plasticizer is important in determining the level of conductivity enhancement in polyether-based polymer electrolytes. In addition, it has been shown that the level of ion association is dependent on the type of plasticizer, where solvents such as *N*,*N*-dimethylformamide, with a high relative permittivity as well as strong solvating ability, result in a greater fraction of free ions compared to tetraglyme.[10]

Nuclear magnetic resonance (NMR) is a useful tool for characterizing polymer electrolytes. Its nucleus specificity allows the separate investigation of the structure and dynamics of cations, anions and polymer by using chemical shifts and relaxation measurements for nuclei such as ^{23}Na, ^{19}F, ^{13}C and ^{1}H. Ionic structure and mobility have been investigated in a range of systems as a function of temperature and ion concentration using ^{23}Na and ^{7}Li.[11–13] ^{1}H NMR relaxation measurements have also been invaluable in determining the correlation between the amorphous nature of the polymer, as well as polymer mobility, and ionic conductivity.[14] Relatively fewer ^{13}C studies have been reported, although these have also given great insight into the polymer–salt interactions[15–18] and the effect of crosslink density in amorphous network polyethers.[19] For example, Spindler and Shriver[15] have shown that mid-chain polyether oxygens in a copolymer of polysiloxane and polyether are capable of strong interactions with cations which result in upfield ^{13}C chemical shift changes. Similar results have been found by Forsyth *et al.*[20] Spin–lattice relaxation times T_1 have also shown a strong interaction between the salt and the polymer as indicated by a decreasing T_1 which reflects a slowing down of the local polymer dynamics.[15,16,20]

Schantz *et al.*[16] investigated the effects of divalent cation addition to poly(ethylene oxide) (PEO) and found that the interactions between Ba^{2+} and PEO were stronger than the alkali metal–PEO interactions as indicated by the significant reduction of the segmental motion in the amorphous phase. The effect of siloxane crosslinking on polyether mobility has also been reported by Lestel *et al.*[19] These experiments have illustrated the fact that polyether segmental motion remains relatively unrestricted in the case of cyclosiloxane crosslinked polymers as determined by linewidth and ^{13}C T_1 measurements. ^{13}C NMR relaxation times have also been used to probe the molecular motion of glassy polymers after blending and on the addition of low molecular weight diluents.[21,22] In all of the above studies, the T_1 measurements can be related to molecular motion through the correlation time τ by assuming that the relaxation time is governed by the ^{13}C–^{1}H dipolar relaxation mechanism[16,23] [eqn. (1) and (2)],

$$1/T_1(\mathrm{C}) = N/10\ (\mu_o \gamma_C \gamma_H h/4\pi r^3)^2 \times [J(\omega_H - \omega_C) + 3J(\omega_C) + 6J(\omega_H + \omega_C)] \quad (1)$$

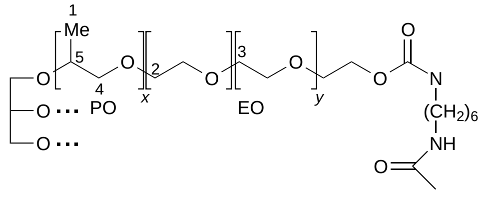
$$J(\omega) \sim f(\tau).\ \text{For simple cases}\ J(\omega) = \frac{\tau}{1+\omega^2\tau^2} \quad (2)$$

where N is the number of directly bonded protons, μ_o is the vacuum magnetic permeability, γ_C and γ_H are the magnetogyric ratios of the ^{13}C and ^{1}H nuclei respectively, r is the C–H internuclear distance, $J(\omega)$ is the spectral density of motions and ω_C and ω_H are the ^{13}C and ^{1}H Larmor frequencies respectively. Eqn. (2) has the additional assumption that the spectral density is governed by isotropic motion and hence a single correlation time τ. In polymer systems motion of the polymer chain has been shown to be distinctly anisotropic and therefore eqn. (2) is an oversimplification for the spectral density function. More complex functions based on the Havriliak–Nagami or Cole–Cole distribution of correlation times are perhaps more valid.[16] Nevertheless, in all cases, since the relaxation time is directly related to the spectral density function and since this is in turn related to the correlation time for segmental motion (or distribution of correlation times), it is clear that T_1 measurements provide an important means of probing molecular motion in polymer systems. Moreover, high resolution ^{13}C NMR techniques make it possible to study individual carbons and hence the relative effect of additives such as salt and plasticizers on the motions of different parts of a polymer chain.

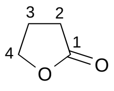
In a previous communication, we presented some preliminary results of the effects of different plasticizers on the motion of urethane crosslinked polyethers which are commonly used as host polymers for polymer electrolytes, using ^{13}C T_1 measurements.[9] This paper provides a more extensive discussion of this work with the intention of understanding the role of plasticizers in the conduction mechanisms of polyether-based solid polymer electrolytes.

Experimental

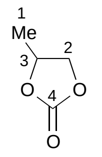
The polyether was a poly(oxyethylene-co-oxypropylene)triol of molecular weight *ca.* 5000 g mol^{-1} (3PEG), obtained from ICI Australia.



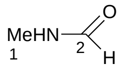
3PEG



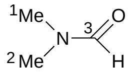
γ-butyrolactone



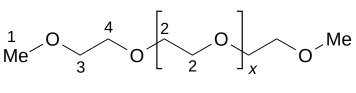
propylene carbonate



N-methylformamide



N,*N*-dimethylformamide



triglyme $x = 1$
tetraglyme $x = 2$

The ethylene oxide:propylene oxide ratio in this material is approximately 3 : 1 on a random basis. The liquid polyether was dried under vacuum for three days, resulting in a moisture content undetectable with Karl Fisher reagent (<0.1% m/m). The plasticizers [propylene carbonate (PC) and *N*,*N*-dimethylformamide (DMF)], the salts [lithium perchlorate and sodium trifluoromethanesulfonate (triflate)] and the cross linking agent [hexamethylene diisocyanate (HDI)] were obtained from Aldrich, and were of 99% purity. The salts were dried to constant weight in a vacuum oven at 80 °C. All samples were prepared in a dry box under a nitrogen atmosphere. The plasticized polymer blends were prepared on a mass percent basis from stock polymer and salt solution containing a stoichiometric amount of HDI and magnetically stirred for 30 min. The salt–3PEG 5000 solution was heated to 60 °C to dissolve the salt, and the lithium perchlorate–3PEG 5000 solution was further dried at 80 °C in the vacuum oven for three days. The salt-containing plasticized samples were prepared as above, except that, due to the viscosity of the salt stock solution, these samples required heating to attain a homogeneous mix. To the systems containing various concentrations of salt and the salt–plasticizer–polymer systems a stoichiometric amount of HDI was then added and samples stirred further. Finally, Thorcat 535 catalyst (nonadecanoate carboxylic ester, approximately 0.5%) was stirred in to promote the reaction of the diisocyanate with the 3PEG over any residual water in addition to catalysing the reaction between the diisocyanate and the 3PEG. The samples were pipetted into the NMR tubes and these, including the samples used for glass transition temperature measurements, were cured between 35–45 °C in an oven in the dry box.

The spin–lattice relaxation times T_1 of the ^{13}C in the polymer and plasticizer were measured at 22 °C on the 200 MHz Bruker AC-200 spectrometer operating at 50.32 MHz for carbon, by the inversion recovery method and analysed with a single-exponential curve fitting routine. The T_1 measurements for systems having both very long and very short T_1 times were carried out in two steps. The polymer T_1 times varied from >100 to 600 ms and the plasticizer T_1 times from 100 ms to 72 s (PC carbonyl group). Thus for systems containing zero or low mass percent of plasticizer, which exhibited broad, low intensity peaks for the polymer carbons and low T_1 times the number of scans used was increased from 32 to 128. The number of experiments, with the appropriate variable delay times, was also increased to minimize the error in the fitted curve. The chemical shifts of the spectra were obtained by external reference to chloroform (δ 77).

The glass transition temperatures T_g were measured by differential scanning calorimetry (DSC) on a Perkin Elmer DSC-7 at a heating rate of 10 °C min^{-1}, between −140 and 20 °C, on sample sizes varying from 5 to 15 mg. Reproducible traces to ±0.5 °C or better were obtained by quenching the samples, sealed in aluminium pans, in liquid nitrogen before placing them into the DSC head which had been pre-cooled to −140 °C.

Results

^{13}C spin–lattice relaxation times of plasticized 3PEG

A typical ^{13}C NMR spectrum for a plasticized crosslinked 3PEG sample is shown in Fig. 1. The ^{13}C resonances are slightly broadened as a result of restricted mobility due to crosslinking, however, the resolution and intensities are still adequate for measurement of relaxation times and chemical shifts. The addition of plasticizer usually enhanced the resolution, as a result of the decreased linewidth (increased local

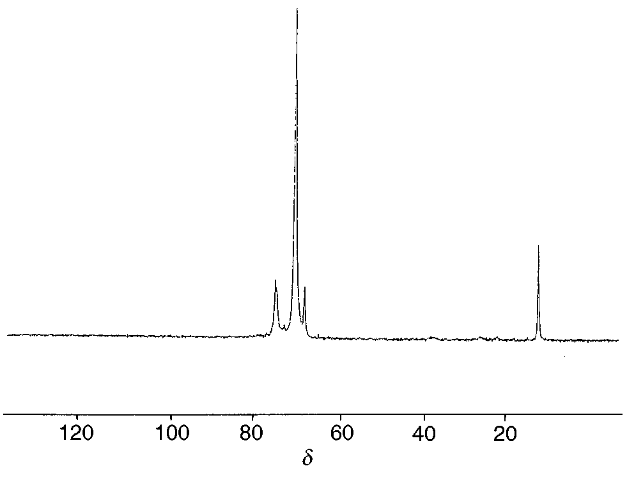


Fig. 1 Typical ^{13}C NMR spectra for 3PEG5000 (crosslinked) at 50.32 MHz

mobility). Table 1 presents the chemical shifts and assignments for the pure polymer and plasticizers.

The behaviour of the polymer ^{13}C T_1 times as a function of DMF, NMF, PC, γ-butyrolactone, tetraglyme and triglyme content are illustrated in Figs. 2(*a*)–7(*a*)respectively. Figs. 2(*b*)–7(*b*) show the same data for the plasticizer carbons. In all cases, the error in the measured T_1, as obtained from the curve fitting, is less than the size of the data symbol used.

Table 1 Structure and NMR assignments of ^{13}C resonances in crosslinked 3PEG 5000 polymer, triglyme, tetraglyme, γ-butyrolactone, propylene carbonate, *N*-methylformamide and *N*,*N*-dimethylformamide

carbon	δ/ppm
3PEG	
CH_3 = 3PEG C1	17.7
CH_2 = 3PEG C2	68.8
CH_2 = 3PEG C3	70.8
CH = 3PEG C4	75
CH_2 = 3PEG C5	75.3
γ-butyrolactone	
CH_2 = BUT 3	22.2
CH_2 = BUT 2	27.7
CH_2 = BUT 4	68.6
C=O = BUT 1	178
DMF	
CH_3 = DMF 1	31.1
CH_3 = DMF 2	36.2
C=O = DMF 3	162
propylene carbonate	
CH_3 = PC 1	19.1
CH_2 = PC 2	70.8
CH = PC 3	73.9
C=O = PC 4	155
tetraglyme	
CH_3 = TET 1	58.5
CH_2 = TET 2	70.6
CH_2 = TET 3	70.8
CH_2 = TET 4	72.2
triglyme	
CH_3 = TRI 1	58.4
CH_2 = TRI 2	70.6
CH_2 = TRI 3	70.8
CH_2 = TRI 4	72.2

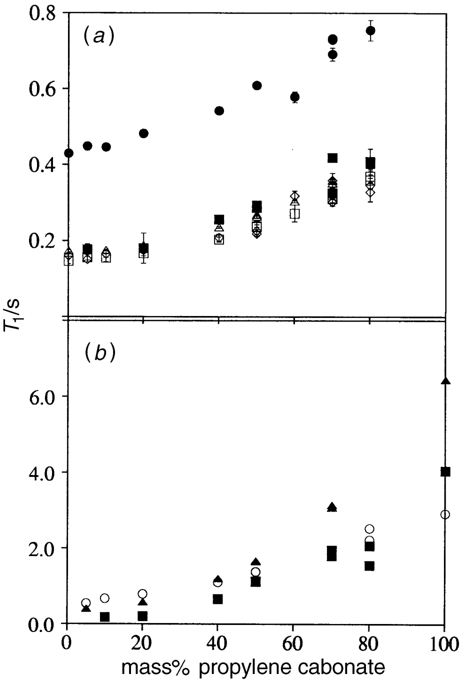


Fig. 2 T_1 *versus* propylene carbonate content for (*a*) each polymer carbon type [3PEG C1 (●), C2 (□), C3 (△), C4 (■), C5 (◇)] and (*b*) each plasticizer carbon type [PC C1 (○), C2 (■), C3 (▲)] (T=295 K)

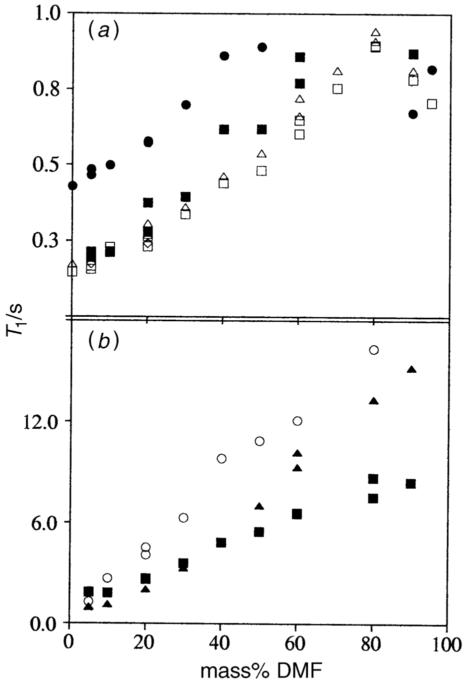


Fig. 3 T_1 *versus* DMF content for (*a*) each polymer carbon type [3PEG C1 (●), C2 (□), C3 (△), C4 (■), C5 (◇)] and (*b*) each plasticizer carbon type [DMF C1 (○), C2 (■), C3 (▲)] (T=295 K)

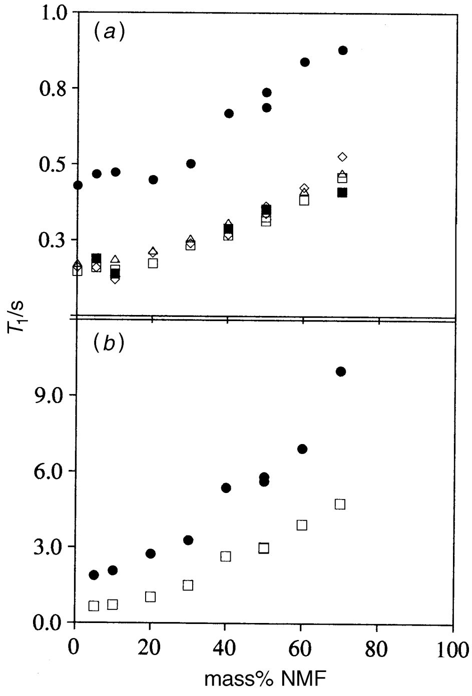


Fig. 4 T_1 *versus* NMF content for (*a*) each polymer carbon type [3PEG C1 (●), C2 (□), C3 (△), C4 (■), C5 (◇)] and (*b*) each plasticizer carbon type [NMF C1 (●), C2 (□)] (T=295 K)

The results show that as the low molecular weight plasticizer is incorporated into the crosslinked 3PEG, the relaxation times of all the polymer carbons increase. This is consistent with an increasing mobility of the polymer and the narrowing of the ^{13}C linewidths. The magnitude of the influence of plasticizer on the individual carbons appears to be independent of the nature of the carbons. When comparing the rate of change of T_1 with increasing plasticizer content for both the main chain polymer carbons (C2, C3) with that of the plasticizer carbons,

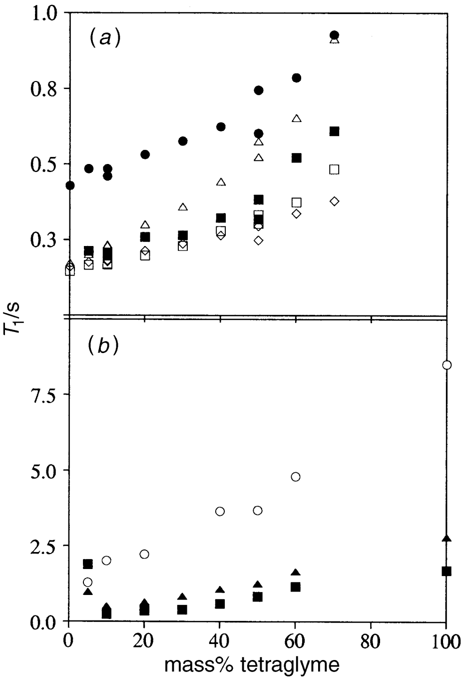


Fig. 5 T_1 *versus* tetraglyme content for (*a*) each polymer carbon type [3PEG C1 (●), C2 (□), C3 (△), C4 (■), C5 (◇)] and (*b*) each plasticizer carbon type [TETRA C1 (○), C2 (■), C3 (▲)] (T=295 K)

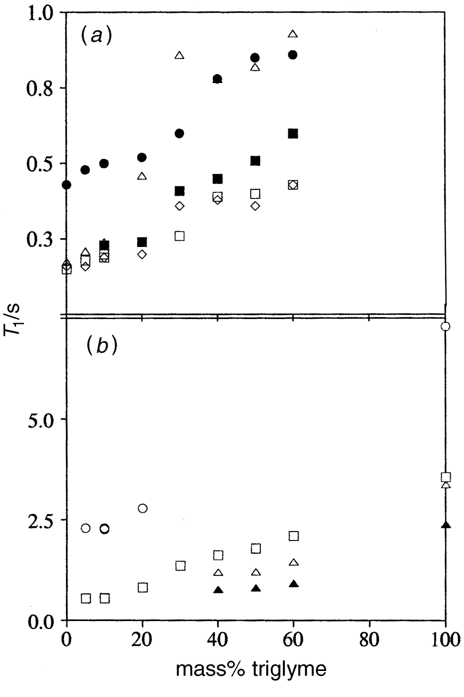


Fig. 6 T_1 *versus* triglyme content for (*a*) each polymer carbon type [3PEG C1 (●), C2 (□), C3 (△), C4 (■), C5 (◇)] and (*b*) each plasticizer carbon type [TRI C1 (○), C2 (△), C3 (▲), C4 (□)] (T=295 K)

it appears that a twofold increase in the polymer relaxation rate is accompanied by a comparable increase in the plasticizer carbon T_1 times.

In the case of tetraglyme and triglyme additions to 3PEG, the rate of increase of the spin–lattice relaxation time for the C3 carbon is considerably greater than with any of the other plasticizers. In addition, the relaxation time of the 3PEG C3 carbon appears to be influenced to a greater extent than the remaining polymer carbon relaxation times. This anomaly is most likely due to the fact that the methylene groups of triglyme and tetraglyme are coincident with the 3PEG C3 carbon. This is not unexpected since these plasticizers are low molecular weight analogues of the polymer itself. Only a single resonance can be resolved, at approximately δ 72, in these cases and therefore the T_1 measured will be a weighted average of the two different species. Similarly, an overlap was found between the 3PEG C2 carbon and the γ-butyrolactone resonance at δ 68.

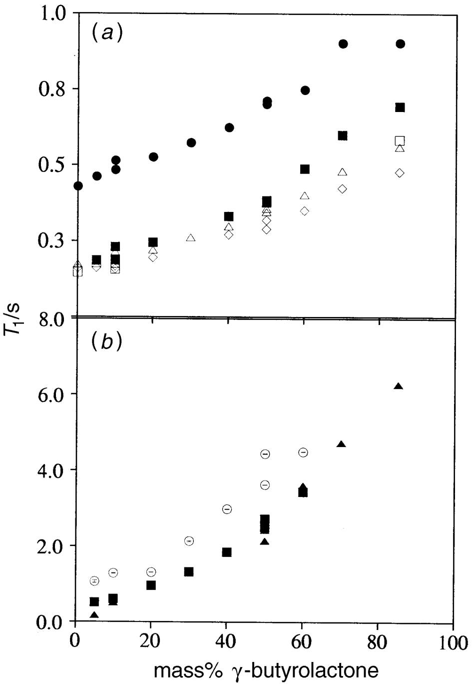


Fig. 7 T_1 *versus* γ-butyrolactone content for (*a*) each polymer carbon type [3PEG C1 (●), C2 (□), C3 (△), C4 (■), C5 (◇)] and (*b*) each plasticizer carbon type [BUT C1 (○), C2 (■), C3 (▲)] (T=295 K)

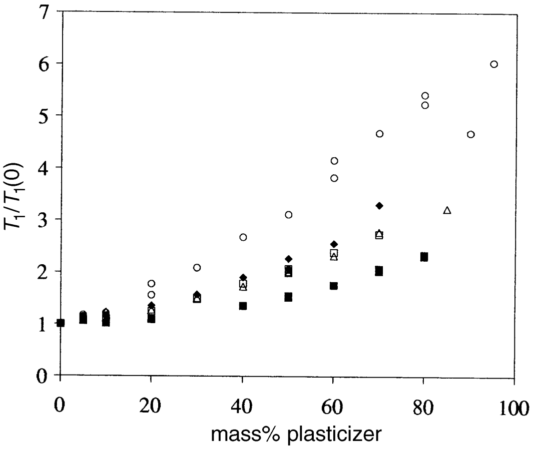


Fig. 8 Comparison of reduced T_1 times for the main chain methylene resonance (C3) with different plasticizers. [N,N-dimethylformamide (○), γ-butyrolactone (□), N-methylformamide (△), propylene carbonate (■), tetraglyme (◆)]. The C2 T_1 times are given in the case of tetraglyme.

In order to directly compare the effects of each of the plasticizers on the polymer ^{13}C T_1 times and hence on polymer mobility, the reduced relaxation times [$T_1/T_1(0)$] have been calculated, where $T_1(0)=T_1$ at 0% plasticizer content. These are plotted for the main methylene resonance (C3) of the polymer as a function of plasticizer concentration in Fig. 8. In the case of tetraglyme, the C2 resonance is shown. This diagram shows that DMF addition results in the greatest enhancement of polymer mobility whereas PC gives the least. All other plasticizers show similar relative increases in the C3 or C2 T_1 times. In particular, PC appears least capable of 'plasticizing'

Table 2 Comparison of fluidity of various plasticizers and their effect on polymer ^{13}C T_1 for C3 carbon in 50% plasticizer–50% 3PEG systems

plasticizer	fluidity/ 10^3 Pa^{-1} s^{-1}	$T_1(50)/T_1(0)$
N,*N*-dimethylformamide	1.266	3.1
N-methylformamide	0.606	2.1
γ-butyrolactone	0.571	2.1
propylene carbonate	0.394	1.4
tetraglyme	0.244	2.3

the motions of the polymer. This is evident both from the small slope of T_1 *versus* plasticizer concentration curve, and also from the fact that the polymer C3 T_1 remains unchanged up to almost 30 mass% PC, whereas all other curves are increasing with concentration. These differences cannot be totally explained by comparing the fluidity of the plasticizers (Table 2).

At DMF concentrations higher than 85 mass% the polymer ^{13}C T_1 is observed to decrease for 3PEG–DMF systems and two separate resonance are observed. This suggests two different polymer environments and the possibility of phase separation in the high DMF content samples. In all other cases, a single resonance with a perfectly exponential decay curve (and hence a single relaxation time) is obtained consistent with an intimately mixed, homogeneous system. Phase behaviour will be addressed further in the next section.

Thermal analysis measurements of plasticized 3PEG

The most common method for testing whether a multicomponent polymer system is miscible or immiscible is *via* measurement of its glass transition temperature T_g. The glass transition temperature is also a measure of flexibility in a polymer system and generally decreases as a low molecular weight diluent is added. Polymer electrolyte systems with lower glass transition temperatures have been shown to result in higher conductivities since the ionic motion is intimately linked to the motion of the polymer.[1,5] Fig. 9 shows a typical DSC trace for the pure 3PEG polymer crosslinked with HDI. A well defined T_g is observed at 209 K followed by a crystallization exotherm with onset temperature T_c at 234 K and a melting endotherm at 251 K. The relative sizes of the heat flows at T_g and T_m suggest that the majority of the sample remains amorphous below 251 K and is clearly 100% amorphous at room temperature. This pattern of T_g followed by crystallization and melting is observed in all of the plasticized systems, with the exception of those containing PC as plasticizer. The greater the difference between T_c and T_g, the greater is the stability of the amorphous phase relative to the crystalline phase. It is interesting to note that for samples containing tetraglyme and triglyme plasticizers, crystallization occurred almost immediately after passing through T_g. This indicates that these plasticizers readily crystallize and is consistent with the difficulty in quenching the pure plasticizers into a glassy state. In all mixtures investigated, with the exception of high concentrations of DMF, only a single T_g was observed, suggesting a homogeneous single phase system. This is consistent with a single T_1 observed for all carbons in the 3PEG–plasticizer systems. The two T_g values observed for higher DMF contents are also consistent with two ^{13}C T_1 times measured for the polymer and suggest a phase separated system.

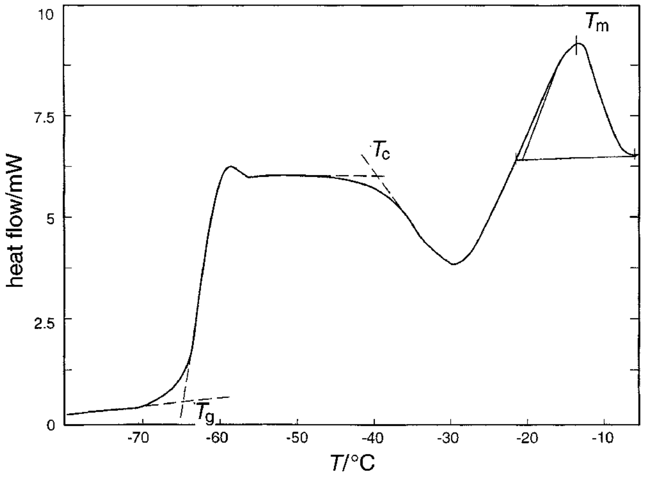


Fig. 9 Typical DSC trace for crosslinked 3PEG showing T_g, T_c and T_m

Fig. 10 shows the dependence of inverse T_g on plasticizer concentration for 3PEG–plasticizer blends. The straight lines in Fig. 10 are the theoretical lines expected for an intimately mixed system following Fox's equation, *i.e.* $1/T_g$ blend $= w_1/T_{g1} + w_2/T_{g2}$. This behaviour would be expected if the interaction energies between plasticizer and polymer segments were comparable to polymer–polymer and plasticizer–plasticizer interactions; in other words, ΔE for mixing was close to zero. In some cases, the Fox equation is obeyed and linearity is observed, however, in the cases of PC and γ-butyrolactone significant deviations are observed. These deviations suggest an interaction which results in 'antiplasticization' since the T_g of these systems is above that predicted by the Fox equation. Indeed in the case of PC, the lower than expected decrease in T_g, particularly at low concentrations, is consistent with the lack of dependence of the ^{13}C T_1 measurements for the polymer in the 3PEG–PC system when up to 30% PC is added. It is difficult to determine whether the 'antiplasticization' effect is a result of strong interactions between the plasticizer and polymer segments, which can restrict segmental motion of the polymer (*e.g.* *via* a bulky side group), or whether molecules such as PC and γ-butyrolactone, which are quite rigid, simply occupy free volume that was once available to the polymer and thereby hinder polymer segmental motion.[24] Recent positron annihilation lifetime spectroscopy (PALS) experiments[25,26] in these systems have in fact indicated that the overall free volume, as measured by PALS, is reduced when certain plasticizers are added.

The effect of the addition of salt to the 3PEG–plasticizer

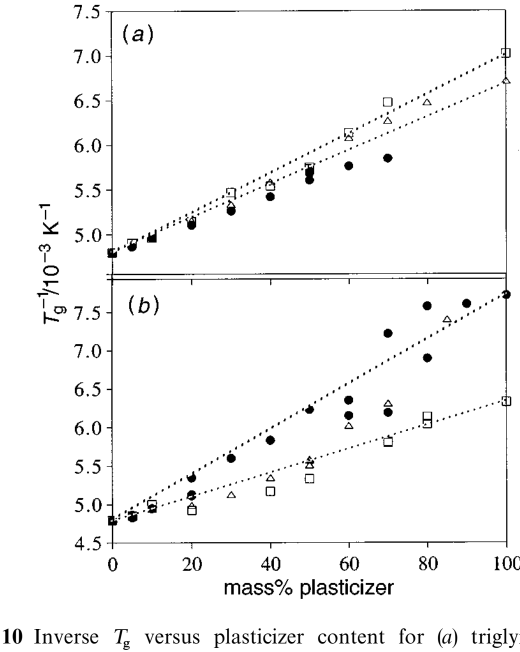


Fig. 10 Inverse T_g versus plasticizer content for (*a*) triglyme (△), tetraglyme (●) and NMF (□) and (*b*) γ-but (△), PC (□) and DMF (●). The straight dotted line is the behaviour predicted by the Fox equation.

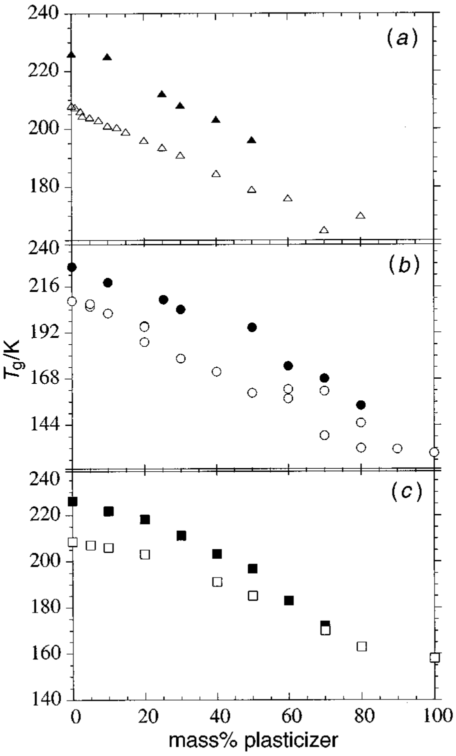


Fig. 11 Glass transition temperatures as a function of plasticizer content for systems with (filled symbols) and without (open symbols) 1 mol kg^{-1} LiClO$_4$; (*a*) tetraglyme, (*b*) DMF and (*c*) PC

systems has previously been reported[20,26] in the case of the 3PEG–LiClO$_4$ as a function of PC, DMF and tetraglyme concentration. A single glass transition temperature was observed in all cases. It is notable that PC and DMF produce similar reductions in glass transition temperatures of the salt-containing sample. It is of interest here to compare the effect of adding plasticizer to pure 3PEG and 3PEG–LiClO$_4$ (Fig. 11). In the case of DMF and tetraglyme additions, the rate of decrease of T_g with increasing DMF content is only slightly greater in the presence of the salt. PC displays more complex behaviour, almost sigmoidal in shape, and the T_g of both 3PEG–PC and salt-containing complexes approach the same value at high PC concentrations. These differences are likely to reflect differences in interactions between plasticizer and salt and are discussed further in the following sections.

^{13}C T_1 relaxation measurements in 3PEG–plasticizer–salt complexes

We have previously reported[9,20] that the addition of salt to both pure 3PEG and 3PEG–50 mass% plasticizer results in a decrease in the spin–lattice relaxation time which is interpreted as a decreased mobility (and increased T_g) of both the polymer backbone and the plasticizer. In Figs. 12 and 13 the effect of plasticizer concentration on the spin–lattice relaxation times of the C3 3PEG carbon and the plasticizer carbons respectively are given for 1 mol kg^{-1}LiClO$_4$ and 1 mol kg^{-1} NaCF$_3$SO$_3$ systems. With increasing PC or DMF concentration, the spin–lattice relaxation times of the ^{13}C resonances associated with the plasticizer increase; the rate of increase of T_1 is greatest at the higher plasticizer concentrations. The T_1 times for the carbonyl carbons of both plasticizers were also determined and displayed similar behaviour, however, due to extremely long relaxation times (more than 10 s in samples containing greater than 50% plasticizer) the absolute values are not reliable since often the delay time between experiments was less than 5 × T_1. The relaxation times of the polymer carbons show considerable deviation on PC addition from the behaviour observed in the salt-free systems and the DMF plasticized polymer (with and without salt). Whereas the addition of DMF increases the spin–lattice relaxation time of the polymer C3 carbon, consistent with decreasing T_g and increased segmental motion, the addition of PC to both LiClO$_4$ and NaCF$_3$SO$_3$ containing 3PEG results in a decreased polymer T_1. These measurements were reproduced several times and the uncertainty in the values is indicated in Fig. 12.

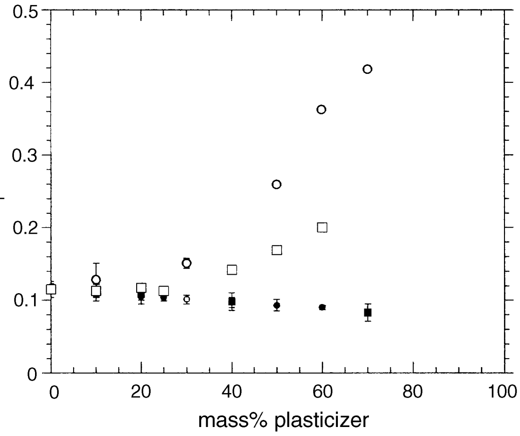


Fig. 12 T_1 of the polymer main chain CH$_2$ (C3 carbon) as a function of plasticizer content with 1 mol kg^{-1} salt [PC–LiClO$_4$ (●), PC–NaOSO$_2$CF$_3$ (■), DMF–LiClO$_4$ (○), DMF–NaOSO$_2$CF$_3$ (□)]

The nature of the salt also appears to affect the rate of increase of the polymer C3 T_1 upon addition of DMF with a 300% increase in the case of LiClO$_4$ when 60% DMF is added as compared with only 150% increase in the sodium salt. Similar trends in behaviour were observed in all the polymer ^{13}C resonances.

Discussion

The glass transition data indicate that the plasticized samples investigated in this work are single phase over most of the composition region ranging from pure polymer through to pure plasticizer both with and without salt present. There is thus no evidence of domains which are sufficiently extensive spatially to produce a separate T_g. This domain size needed to produce a distinct T_g is often taken to be of the order of 100 Å^3.[27] The conduction in these plasticized polyether samples where the plasticizer is not the major component (*e.g.* ≤50 mass%) is therefore distinctly different from gel electrolytes such as poly(methyl methacrylate)–PC[28] and poly(acrylonitrile)–PC[29] discussed by others. In the latter cases the low molecular weight solvent, which is by far the major component (*ca.* 80%), in all likelihood exists in channels which can conduct ions. As shown previously[4] in work from this laboratory involving mixtures of this type, the conduction process passes smoothly from a realm dominated by the polymer to one dominated by the low molecular weight solvent. No obvious percolation threshold is observed, as might be expected if enhanced conduction was an event controlled by connected solvent channels. Instead, we were able to show that the behaviour was as expected on the basis of the increased configurational entropy contributed to the system by the presence of the plasticizer.[4]

Furthermore, our previous NMR work[9,20] and the relaxation measurements presented in this work, have shown that there is significant interaction between the polymer and salt in the plasticized polymer electrolytes across the whole phase diagram. Hence the plasticizer does not become the predominant solvent species even at quite low polymer contents.

Having established that polymer–salt and polymer–plasticizer interactions exist in these systems, it is of interest to

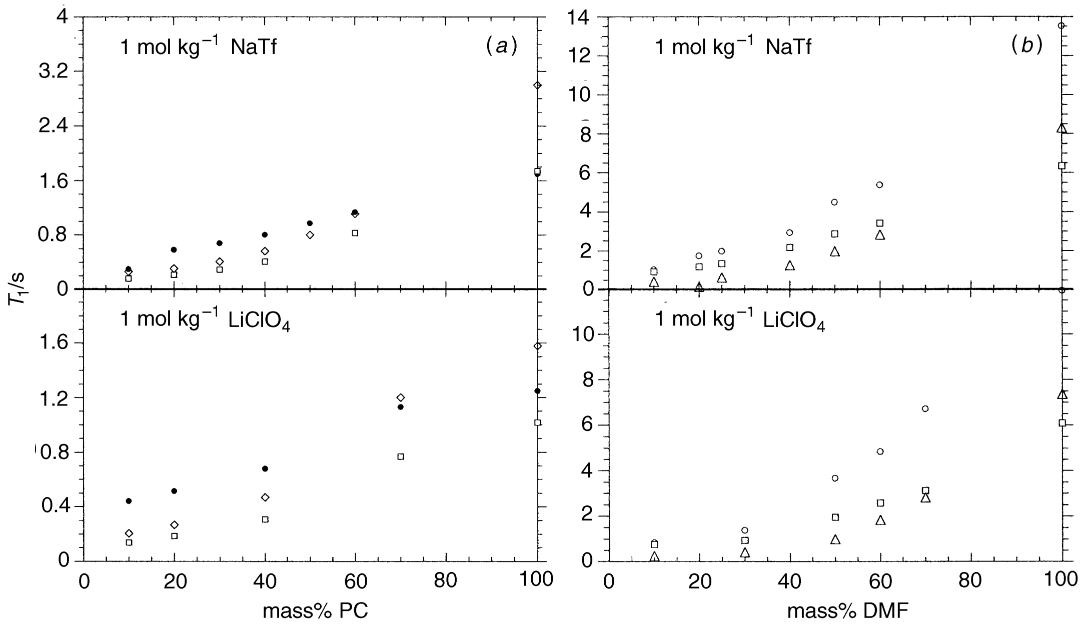


Fig. 13 T_1 of the plasticizer carbons as a function of plasticizer content with 1 mol kg^{-1} salt; (a) PC [● = PC 1 (δ 19.1), □ = PC 2 (δ 70.8), ◇ = PC 3 (δ 73.9)] and (b) DMF [○ = DMF 1 (δ 31), □ = DMF 2 (δ 35), △ = DMF (δ 162)]

understand what the actual role of the plasticizer is in the ionic conduction mechanism in these polymer electrolytes. If we consider that the low molecular weight component serves merely as a traditional plasticizer, *i.e.* it increases the free volume and/or the configurational entropy of the binary solvent such that the overall mobility of the system is enhanced (as indicated by lower T_g values), then the polymer segmental motion will increase, and the conductivity will therefore increase. Table 2 gives the relative increases in ^{13}C polymer T_1, which reflect the increase in polymer segmental motion at 50% plasticizer concentration in the absence of salt. Propylene carbonate has the least effect on the polymer segmental motion, and tetraglyme, γ-butyrolactone and NMF all have a similar effect, whereas DMF has a distinctly greater influence than any of the others. To a large extent, this is a result of the higher mobility of the pure DMF relative to the other pure plasticizers. However, this cannot be the only factor in enhancing polymer mobility since the T_1 ranking does not follow the plasticizer fluidity ranking. Hence a number of specific factors must be influencing the overall effect. Some of these are further discussed below.

In the presence of salt the addition of plasticizer in some cases, for example PC, restricts the mobility of the polymer relative to its unplasticized state. This observation was somewhat unexpected given that the glass transition temperature of these samples continues to decrease with addition of PC. Furthermore, the ^{13}C spin–lattice relaxation times of the PC itself still increases with increasing PC content. An explanation for this behaviour can be found when the chemical shift results are also considered.[20] Previous work discussing the behaviour of ^{13}C chemical shifts of polyethers suggested that when PC is added, in the presence of alkali metal ions, the ion–polymer interactions are enhanced for both Li and Na salts. In contrast, the addition of DMF diminishes the coordination of the cations by the ether oxygens. DMF, which is known to be good donor solvent, would appear to be able to displace the ether oxygen from the Li ion solvation sphere; PC on the other hand appears to be less effective in this sense but nonetheless can provide more effective anion–cation charge shielding than can the polyether alone. Ether oxygen co-ordination to a metal cation is likely to have a restricting effect on the backbone's local motional freedom, especially if the cation is simultaneously coordinated to a second or third ether oxygen on the same neighbouring backbone. The displacement of ether oxygen coordination by plasticizer co-ordination of the cations can thus be expected to have a strong effect on the local segmental mobility of the backbone. DMF is a clear case in point. PC, on the other hand, appears to be a less effective coordinating solvent than the ether oxygens and its presence at fixed salt concentration may cause more ether oxygens per unit volume (because there are less of them) to become involved in cation coordination. The polymer mobility therefore, which is reflected in T_1, is slightly decreased when PC is added whereas DMF increases the polymer segmental motion. The solvent–cation interactions also depend on the nature of the cation. This is seen in the relative increases of polymer ^{13}C T_1 when DMF is added to lithium-containing polyether as compared with sodium. The lithium ion appears to be coordinated more strongly by the DMF than the sodium ion and hence the polymer mobility increases more rapidly when LiClO$_4$ is present, upon addition of DMF.

Although both plasticizers decrease T_g and both increase the conductivity of the polymer electrolyte, their effect on the polymer in the presence of salt is quite distinct. In one case, the plasticizer competes with the polymer for the coordination of the alkali metal ion thereby increasing the ion and polymer mobility, whilst in the case of PC, which itself is a poor donor solvent and therefore is itself inefficient in alkali metal ion solvation, the addition of plasticizer enhances the coordination of the cation by the polymer and hence restricts polymer motion. It should be noted that both DMF and PC have considerably higher relative permittivities than the polymer and hence are expected to increase the number of charge carriers. Recent FTIR work[10] which has investigated the effect of adding tetraglyme and DMF to lithium triflate-containing polyether has shown that in the case of DMF the number of 'free' anions, that is, anions which are not coordinated by cations, increases as the concentration of DMF increases. This of course will result in an increased conductivity as given by the Nernst–Einstein expression. The combined increase in the number of charge carriers and the relative increase in polymer mobility upon addition of DMF is not, however, sufficient to explain the large increase in ionic conductivity. In addition, FTIR has shown that the addition of tetraglyme actually decreases the number of 'free' ions and hence the total number of available charge carriers. Since the total enhancement in conductivity is at least four times as large as the polymer T_1 enhancement, a further explanation is required to account for the conduction in the tetraglyme systems. Vincent *et al.*[30,31] have recently measured the diffusion coefficient of lithium and PF_6^- ions in a high molecular weight polyether by ^{7}Li and ^{19}F NMR. The addition of tetraglyme was also investigated and it appears that a 50% addition of tetraglyme results in approximately an 8-fold increase in diffusion coefficient at 80 °C. This accords with the approximately 8-fold increase in conductivity we have found in previous work.[2] It appears, therefore, that at least in the case of tetraglyme systems, the increased conductivity is predominantly a result of increasing mobility of the charge carriers. It remains then to explain what governs the increasing diffusion coefficients of the ions. In traditional polymer electrolytes, ionic conduction relies on high segmental motion of the polymer chains, however, in the presence of plasticizers the motion of the ions is likely to be complicated by the presence of the cosolvent.

If the absolute spin–lattice relaxation times for the plasticizer carbons are compared with those of the polymer it is clear that these can differ by more than an order of magnitude. The approximate motional quantity to compare in these circumstances is the correlation time τ for both plasticizer and polymer backbone. This would give a direct measure of the timeframe for plasticizer *versus* polymer motion. Unfortunately, this requires extensive temperature-dependent T_1 data. This was not possible to achieve in the present work since at the lower temperatures required to reach the T_1 minimum, the ^{13}C linewidth became too broad and the signal eventually was lost. Nevertheless, the absolute T_1 values for the polymer and plasticizers indicate that the plasticizer, although restricted in its mobility relative to its pure state, nonetheless maintains a higher degree of mobility as is evidenced by higher T_1 compared with the polymer. Thus the model suggested by this work for conduction in plasticized polyether electrolytes requires that ionic mobility is governed by both polymer and plasticizer mobility, however for that interval of time that the ions are completely within the plasticizer environment they move at a faster rate than those times when they are coordinated (in the case of cations) or in the vicinity of (in the case of anions) the polymer segments.

Conclusions

NMR ^{13}C spin–lattice relaxation time measurements have illustrated the effects of the incorporation of small molecules on the local polymer segmental motion in polyether–urethane networks both in the presence and absence of alkali metal salts. In the case of unsalted networks, large additions of all the plasticizers investigated result in an increasing T_1 consistent with an increased polymer mobility (assuming that the interactions which govern the relaxation are not significantly changing upon addition of plasticizer). In most cases, with the exception of higher DMF concentrations, the data gave an excellent fit to a single relaxation, the T_1 of which varies smoothly with composition, indicating a single phase system. In the case of DMF, at concentrations higher than 70% a decrease in the polymer T_1 is observed whilst the DMF T_1 times continue to increase. This is suggestive of phase separation, and is consistent with the observation of two T_g values in the thermal analysis experiments.

The degree to which the polymer relaxation time is affected is dependent upon the nature of the plasticizing molecule. In particular the molecules that are capable of strongly interacting with the polymer backbone, or which are themselves sterically hindered (or bulky) have less influence on the polymer relaxation rate and hence on the local mobility. Furthermore, certain plasticizers show distinct antiplasticization effects at low concentrations (less than 20%) as indicated by unchanging polymer ^{13}C T_1. PC additions seem to have the least effect on the polymer segmental motion whilst DMF has the greatest effect. This is in part due to the high mobility (higher fluidity) of the DMF molecule, however, a comparison of the fluidity of, for example tetraglyme and PC, indicates that these two should have comparable effects on polymer plasticization. The high relative permittivity may lead to strong plasticizer–polymer interactions (particularly at low PC contents) which restrict polymer segmental motion. This is even more noticeable in the case of alkali metal salt-containing polyether networks where PC additions lead to an increased polymer ^{13}C relaxation rate (decreasing T_1). This has been shown previously to be at least in part a result of stronger metal ion–polymer interactions as a result of an increased cation–anion screening provided by the high relative permittivity of PC.

Thermal analysis data also shows evidence of strong specific interactions in some plasticizer–polyether systems, with only DMF, NMF and the ether based systems showing linear Fox behaviour in the inverse T_g *versus* composition plots. The remaining plasticizers result in a higher T_g than would be predicted by the Fox equation, indicating strong polymer–plasticizer interactions. The differences observed between the plasticizers in their effects on T_1 are consistent with T_g. This therefore supports the notion that T_1 is a good local probe of polymer mobility.

This work was initiated from the desire to understand the effects of plasticization on the polymer mobility and hence on the conductivity behaviour of polymer electrolytes. The data presented here suggest that, on the basis of enhancement of polymer motion (T_1) in the absence of salt, DMF should have the greatest effect on conductivity enhancement followed by NMF, triglyme, tetraglyme and γ-butyrolactone, whilst PC should have the least effect on the conductivity. Indeed, a comparison of the effects of PC and DMF on the polymer ^{13}C T_1 times in salt-containing systems would suggest that PC restricts polymer segmental motion and hence would not have a positive effect on ionic conductivity in these systems. This is not the case, however. Although DMF does give a greater enhancement than PC when added to polyether–urethane polymer electrolytes, NMF gives the greatest enhancement and PC still improves the conductivity to a larger degree than do triglyme and tetraglyme.[2] In addition, the relative increase of polymer mobility as indicated by the increased T_1 is not as great as the relative conductivity enhancements. These results therefore indicate that the role of the plasticizer in improving ionic conductivity in polymer electrolytes is not simply in improving the polymer segmental motion and decreasing T_g. The specific interactions between plasticizer molecules, polymer segments and ionic species will affect the final conduction mechanism and the magnitude of the conductivity in polymer electrolytes. For example the DMF–cation interactions and the PC shielding will have an influence on, and determine the number and nature of, the major charge-carrying species. The mobility of the plasticizer molecules themselves must also play a large role in the conduction mechanism. Although T_1 of the polymer is increased, indicating greater polymer segment mobility, the plasticizer molecules will still be more mobile and hence ions which are in the vicinity of the plasticizer molecules will have a higher mobility and result in higher conductivities.

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