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Complex impedance, differential scanning calorimetry (DSC) and ^{7}Li nuclear magnetic resonance (NMR) studies have been carried out on electrolytes such as poly(propylene glycol) (PPG) and poly(ethylene glycol) mono-methyl-ether (PEG) containing lithium salts. The impedance studies were made over a range of frequencies, temperatures and pressures and were used to obtain values of electrical conductivity. It is shown that the Bendler-Shlesinger (BENSH) formalism is a better representation of the data than the Vogel-Tammann-Fulcher (VTF) equation (or mathematically equivalent Williams-Landel-Ferry (WLF) equation). For both the PEG- and PPG-based electrolytes the electrical conductivity decreases as pressure increases and the activation volume decreases strongly as temperature increases. However, the activation volume is smaller for the PEG-based material and the curvature is opposite for the two materials. All results for the electrolytes are explained qualitatively in terms of free volume.

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Electrical Conductivity and NMR Studies of PEG and PPG Containing Lithium Salts

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Complex impedance, differential scanning calorimetry (DSC) and ^{7}Li nuclear magnetic resonance (NMR) studies have been carried out on electrolytes such as poly(propylene glycol) (PPG) and poly(ethylene glycol) mono-methyl-ether (PEG) containing lithium salts. The impedance studies were made over a range of frequencies, temperatures and pressures and were used to obtain values of electrical conductivity. It is shown that the Bendler-Shlesinger (BENSH) formalism is a better representation of the data than the Vogel-Tammann-Fulcher (VTF) equation (or mathematically equivalent Williams-Landel-Ferry (WLF) equation). For both the PEG- and PPG-based electrolytes the electrical conductivity decreases as pressure increases and the activation volume decreases strongly as temperature increases. However, the activation volume is smaller for the PEG-based material and the curvature is opposite for the two materials. All results for the electrolytes are explained qualitatively in terms of free volume.

Keywords: Electrical Conductivity, Lithium Electrolytes, Activation Volume, High Pressure

Chemical Compounds: poly(propylene glycol), poly(ethylene glycol) mono-methyl-ether, $LiCF_3SO_3$

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1. Introduction

Lithium battery materials continue to be widely studied and ion conducting polymers are of interest as possible electrolytes. Two polymers which have received a great deal of attention are poly(propylene glycol) (PPG) and poly(ethylene glycol) (PEG), the former being of fundamental interest and the latter having possible applications. While there have been a great many studies of various properties of these materials, there remain a number of unanswered questions and one approach which can be used to answer such questions is to compare the results for solids and liquids [1]. In fact, both PPG and PEG are excellent candidates for such studies since they exist both as solids and liquids. In the past, several of the authors have reported work on the solid (or rubbery) forms of these materials [2,3]. The purpose of the present work is to extend the measurements to lower equivalent weight, liquid polymer electrolytes in an attempt to determine the extent to which solid polymer electrolytes exhibit liquid-like behavior. Towards this end, differential scanning calorimetry (DSC), electrical conductivity and nuclear magnetic resonance (NMR) studies have been undertaken.

2. Experimental

PPG (average MW 4000) and PEG (poly(ethylene glycol mono-methyl ether) average molecular weight 350) were obtained from Poly Sciences Inc. $LiCF_3SO_3$ was added to the polymers in an approximately 20:1 repeat unit:lithium ion ratio (1M solution) using techniques described elsewhere [4]. The equipment and remaining techniques used to measure the electrical conductivity and its variation with pressure and temperature are also described there along with the details of the DSC measurements [4]. Finally, ^{7}Li NMR measurements on the PEG and PPG materials (as well as 1M $LiPF_6$:PEG for comparison) were performed at 117 MHz between 125 and 425K.

3. Results

For all electrical experiments a complex impedance diagram consisting of a slightly depressed semicircular arc and/or slanted line was observed. Those features are usually observed in ion conducting polymers with blocking electrodes and an example for a closely related material, PPG-1025, is given in fig. 1 of Ref. 4. The bulk resistance, R, was obtained from the intercept of the arc and/or slanted line with the Z' axis and the resistance was transformed to the electrical conductivity, σ, at all temperatures using procedures described elsewhere [4].

It was found that the atmospheric pressure, room temperature conductivities of the as-received PPG and PEG were about 1.2×10^{-10} and 2.2×10^{-7} S/cm, respectively, and those for PPG:$LiCF_3SO_3$ and PEG:$LiCF_3SO_3$ were about 2.6×10^{-6} and 3.4×10^{-4} S/cm, respectively.

The results for the variation of the conductivity with temperature for the materials are shown in fig. 1. The DSC data for PEG:$LiCF_3SO_3$ are shown in fig. 2 and the NMR linewidth results are presented in fig. 3.

4. Discussion

4.1. *Temperature Effects*

Fig. 1 shows that PEG:$LiCF_3SO_3$ exhibits smooth, non-Arrhenius behavior at high temperatures accompanied by a large decrease in the conductivity for temperatures below about 260K. The discontinuity is attributed to crystallization which is confirmed by the DSC results in fig. 2. The data exhibit a glass transition at about 203K (Tg) followed by a crystallization exotherm with the maximum at about 223K and finally there is a melting endotherm at about 267K. Because of the effects of crystallization, no further analysis of the electrical data for PEG:$LiCF_3SO_3$ are reported.

On the other hand, fig. 1 shows that the electrical conductivity of PPG:$LiCF_3SO_3$ is smooth at all temperatures. This is consistent with the DSC results where all that is found for PPG:$LiCF_3SO_3$ is an endotherm with a central temperature of about 219K. However, the endotherm was broadened on the high temperature side which may be an indication of the phase separation which is known to exist in this material [5]. Confirmation of the different glass transitions between samples can be seen in the NMR linewidth data of fig. 3. The maximum-slope temperatures, demarcating the onset of segmental motions associated with the glass transition, are 214K (±8K) and 239K (±10K) for PEG:$LiCF_3SO_3$ and PPG:$LiCF_3SO_3$ respectively. (Pure PPG-4000 exhibits a well-defined glass transition at about 206K.)

The data were analyzed using the Vogel-Tammann-Fulcher (VTF) [6] equation:

$$\sigma = \sigma_0 \exp\left(\frac{-B}{T - T_0}\right) \qquad (1)$$

A non-linear least squares fit of Eq. (1) to the data was carried out for PPG:$LiCF_3SO_3$ and the resultant best-fit parameters are $\log_{10}\sigma_o$=-1.21 , B=1210K and T_0=176.1K with an RMS deviation of 8.4×10^{-3}.

These values are typical for these types of materials [2]. However, it has become apparent that Eq. (1) gives an inadequate representation of the data, particularly near Tg [7]. This has been discussed in detail elsewhere for a similar material, PPG1025 containing $LiCF_3SO_3$ [4]. In fact, it has been shown that the BENSH equation:

$$\sigma = D\exp\left(\frac{-B''}{(T-T_c)^{1.5\gamma}}\right) \qquad (2)$$

which is based on the phenomenological model of Bendler and Shlesinger [8] gives an improved fit to the data. Setting γ=1, the resultant best-fit parameters for PPG:$LiCF_3SO_3$ are $\log_{10}$(D)=-2.05, B"=14240 and T_c=150.9K with an RMS deviation of 6.2×10^{-3}. On the basis of the RMS deviation, the BENSH equation once again provides a better representation of the temperature dependence of the electrical conductivity.

4.2. Pressure Effects

In all cases, the pressure variation of the electrical conductance is similar to fig. 3 of ref. 4 and was well-represented by:

$$\ln G = \ln G_0 + ap + bp^2 \qquad (3)$$

The best-fit values of a and b are listed in Table 1.

4.2.1. Activation Volume

The values of a were converted to the pressure dependence of the electrical conductivity as described elsewhere [4]. The results were used to calculate an apparent activation volume using

$$\Delta V = -kT\,[\partial \ln\sigma/\partial p]_T. \qquad (4)$$

and the values of ΔV are listed in Table 1. The results are plotted in fig. 4 along with recent results for PPG1025:$LiCF_3SO_3$ [4].

Two features are apparent. First, ΔV for the PPG-based electrolytes is much larger than ΔV for PEG:$LiCF_3SO_3$. Second, all activation volumes decrease strongly as temperature increases. These results are straightforward to interpret in terms of free volume, at least qualitatively. Specifically, since free volume is the volume *available* for motion and since the activation volume is the volume *change* required for motion, they behave oppositely i.e. large activation volumes are associated with small free volumes and vice versa. Consequently, the larger values of ΔV for the PPG vs. the PEG electrolytes can be thought of as a consequence of smaller free volume due greater space-filling by the PPG molecules. Further, the decrease in activation volume with temperature, which is observed for all materials, is explained at least in part by the fact that the free volume increases as temperature increases. Further discussion of the relationship between free volume and the activation volume is given elsewhere [4].

4.2.2. Curvature

The curvature, as represented by b in eq. (3), is also of interest. In particular, it is noted that all of the values reported to date for PPG-based materials, those listed in Table 1 and those reported in ref. [4], are negative while those for PEG-based materials are positive. Other recent data for a PEG-based electrolyte also show positive curvature [fig. 2 of ref. 11].

Following the argument presented above, the activation volume would be expected to increase as pressure increases because the free volume should decrease with pressure. In other words, the compressibility of the activation volume would be expected to be negative and, as a consequence, the curvature would be expected to be negative. This explains the results for the PPG-based electrolytes. (Further discussion is given elsewhere [4]). The opposite result for the PEG-based electrolyte is explained if the compressibility of the activation volume is positive. This is consistent with the theories of Varotsos [12]. It also may be that the difference in curvature is a consequence of the pressure dependence of Tg since it has been shown that the pressure dependence of Tg is quite large (about 170 K/GPa) for PPG-based materials [2,13] while that for the PEG-based materials is about half that [14]. Clearly, further work is necessary for a complete understanding of this interesting phenomenon.

5. Summary

In summary, several results have been obtained via DSC, electrical conductivity and NMR studies of PEG and PPG containing $LiCF_3SO_3$. First, it is shown that once again, the BENSH equation is a better representation of data for glass-forming materials than the widely used VTF equation. For both the PEG and PPG-based electrolytes the electrical conductivity decreases as pressure increases and the activation volume decreases strongly as temperature increases. However, the activation volume is smaller for the PEG-based material and the curvature is opposite for the two materials. Finally, it is pointed out that the curvature in the variation of the electrical conductivity is different for PEG and PPG containing salts. A qualitative explanation of all results is given in terms of free volume.

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Table 1. Effect of pressure on the electrical conductivity for PEG:$LiCF_3SO_3$ and PPG:$LiCF_3SO_3$ and other materials from the literature.

T (K)	a $(GPa)^{-1}$	b $(GPa)^{-2}$	$\chi_T/3^a$ $(GPa)^{-1}$	$\frac{\partial \ln\sigma}{\partial p}$ $(GPa)^{-1}$	ΔV (cm^3/mol)
PPG:$LiCF_3SO_3$					
299	-19.9	-0.77	0.16	-19.7	49.0
323	-13.7	-3.47	0.12	-13.8	36.5
PEG:$LiCF_3SO_3$					
295	-8.91	+2.04	0.16	-8.75	21.5
308	-7.56	+1.46	0.14	-7.42	19.0
323.2	-6.39	+0.95	0.12	-6.27	16.9
343.3	-5.17	+0.75	0.11	-5.06	14.4
363.2	-4.51	+1.21	0.10	-4.41	13.3

Figure Captions

Figure 1. Electrical conductivity vs. reciprocal temperature for: (a) Circles, PEG:$LiCF_3SO_3$ and (b) Squares, PPG:$LiCF_3SO_3$ The host liquids are PPG-4000 and PEGMME-350 and the concentration is approximately 20:1 repeat units per lithium for each material.

Figure 2. DSC thermograms for PEG and PEG:$LiCF_3SO_3$.

Figure 3. Full width at half maximum (FWHM) vs. temperature for ^{7}Li NMR in various polymer electrolytes.

Figure 4. Apparent activation volume vs. reduced temperature ($T-T_g$) for various PPG-based materials.

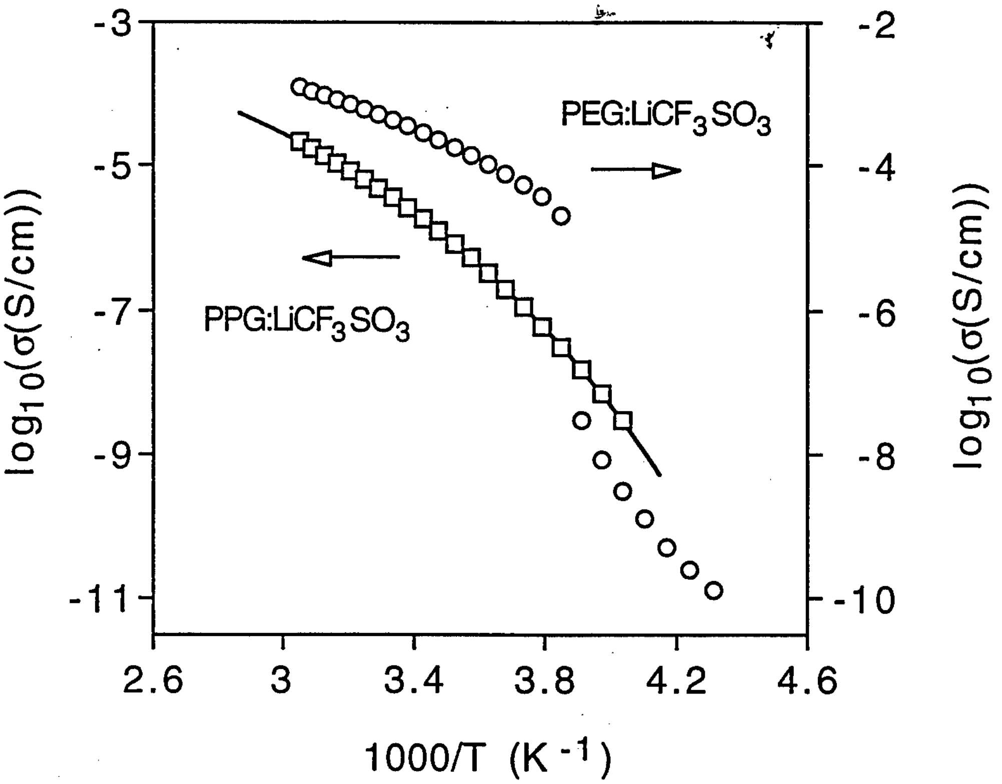

Figure 1

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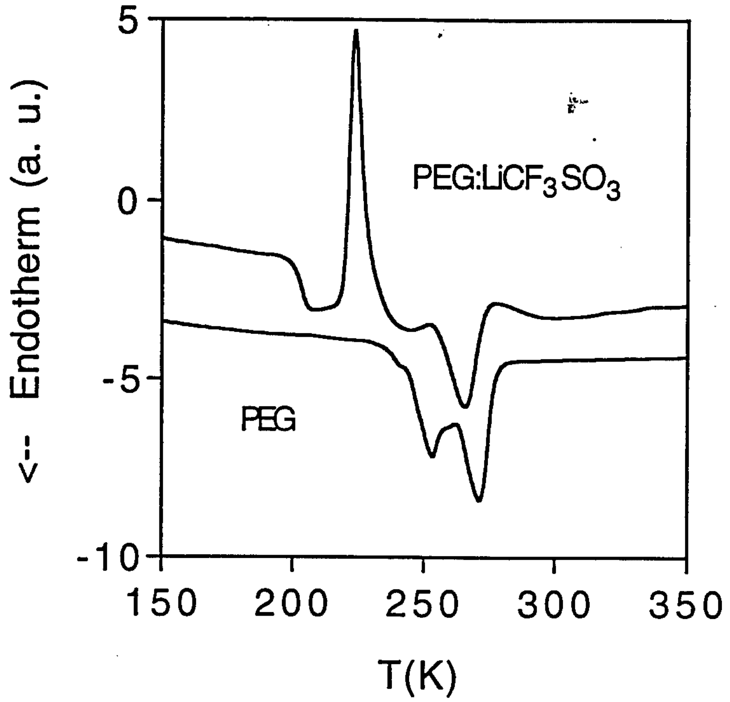

Figure 2

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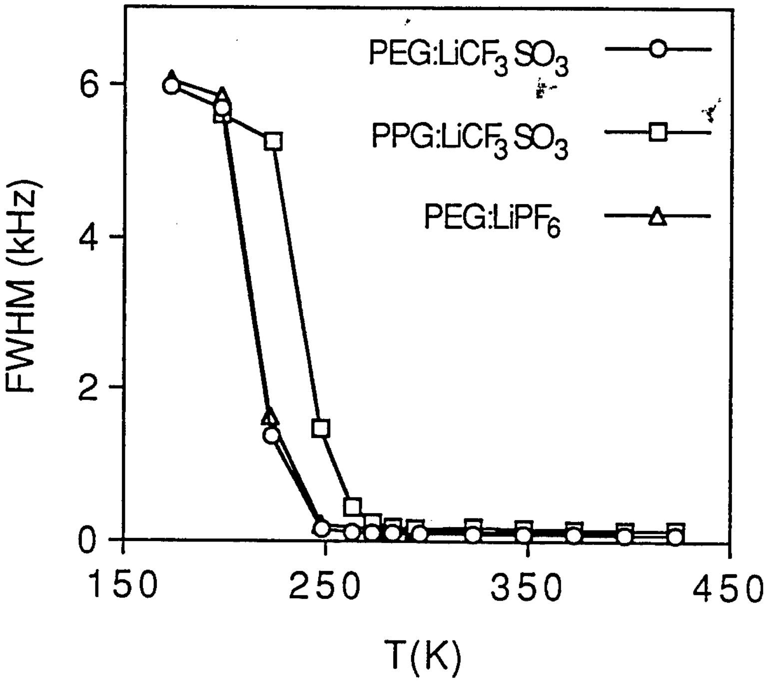

Figure 3
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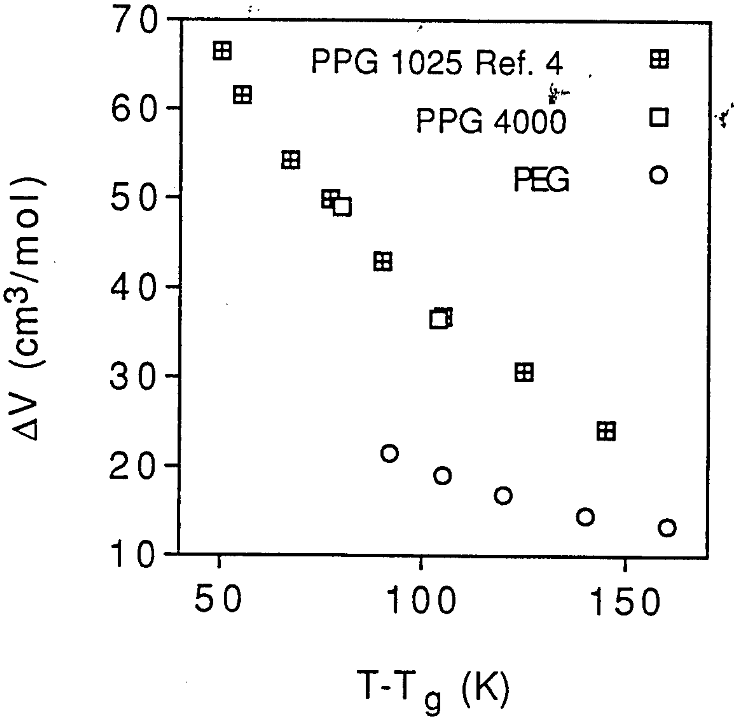
70
60
50
40
30
20
10
50
100
150
ΔV (cm^3/mol)
T-T$_g$ (K)
PPG 1025 Ref. 4 ⊞
PPG 4000 □
PEG ○

Figure 4

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