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FT-IR spectroscopic investigation of ionic interactions in PPG 4000: $AgCF_3SO_3$ polymer electrolyte

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ABSTRACT

The effect of salt concentration on the ubiquitous ionic interactions observed in the case of the silver ion conducting polymer electrolyte system poly(propylene glycol) (PPG)–silver triflate has been investigated using Fourier transform infrared (FT-IR) spectroscopy as a probe for the characterization of the local environment of the triflate ion in PPG-based polymer electrolytes. The maximum free anion concentrations of symmetric and asymmetric SO_3 stretching modes in the case of poly(propylene glycol) complexed with silver triflate ($AgCF_3SO_3$) corresponding to the ether oxygen metal cation ratios from 2:1 to 6:1 have been investigated in detail. The present Fourier transform infrared spectral studies of the C—O—C stretching mode have shown reduction in the intensity, due to the decrease of salt concentration. The splitting of vibrational modes has been analyzed in terms of free ions, ion pairs and aggregates. The bands of SO_3 symmetric stretching mode appearing at 1032 and 1038 cm^{-1} in the chosen polymer electrolyte material have been assigned to free ions and ion pairs respectively.

1. Introduction

Much interest has been focused on the conduction mechanisms in solvent free, ion conducting polymers and their applications in various electrochemical devices such as batteries, electrochromic windows, displays, chemical sensors, and fuel cells range from sub-ambient to moderate temperatures [1,2]. The properties of solid electrolytes should allow for high ionic mobility, ionic transport in closely coupled to the high local flexibility and the segmental motion of the polymer chain. Consequently, fully amorphous low molecular weight liquid, like polymers which mimic the high molecular weight polymeric ion conductors complexes are commonly used as model systems [3,4]. A basic understanding has evolved regarding the salt and host structures that give rise to high ionic conductivity along with the requirements to obtain chemical and mechanical stability [5]. Ion mobility in a polymer matrix is fundamentally different from that in the case of an organic liquid or aqueous electrolyte where unconstrained solvent sheaths typically surround solvated ions, thus creating distinct kinetics entities [6]. The large amount of charged species introduces one of the most complex features in the cations coordinated to polar sites in the polymer host matrix forming more or less labile bonds or causing strong coulomb attractions between the dissociated salt ions, while the anions are not solvated by the aprotic host but occupy voids in the system which may result in the presence of free anions, ion pairs, solvated cations, triplets, multiplates or higher aggregates [7–10].

An understanding of the relationship between ionic conductivity and degree of solvation of cation as well as the influences of the anions on the physical state of the mixtures is crucial to the effort to discover new and more efficient electrolyte systems. It is well known that polyethylene oxide (PEO)-based polymer electrolytes containing lithium salts exhibit moderate ionic conductivities due to both the low lattice energy of lithium salt, which facilitates the solvation of lithium of the polyether, and exceptionally larger anion. Ion polymer interactions are manifested as changes in spectral regions associated with polar sites of the host polymer, ether oxygens and hydroxyl terminal groups in the case of poly(propylene glycol) (PPG) [11]. However, for electrolytes based on PPG in the literature studies [12–15] the ratio of OH end groups to ether oxygen is ∼1.35 and thus cation as well as anions, may also coordinate to these polar end groups. In fact, it has been reported that cations coordinated to OH terminal groups are more stable than cation coordinated to the ether oxygen in the polymer chain [16].

In the present study, an attempt to investigate the effect of silver salt concentration on poly(propylene glycol)-based polymer electrolyte by using vibrational spectroscopy has been undertaken. The triflate ion, in particular has a vibrational spectrum, which is very sensitive to its state of co-ordination, producing a series of different infrared (ir) active bands as its environment changes.

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2. Experimental

2.1. Preparation of polymer electrolyte samples

Specimens of silver polymer electrolytes were prepared by complexing poly(propylene glycol) (4000) (Polysciences Inc., USA) with varying concentrations of $AgCF_3SO_3$ (purity 99%, Aldrich) corresponding to compositions having ether oxygen to cation ratios of 2:1 to 6:1. The salt was dried on a vacuum line first at 348 K for 24 h and then dried at 363 K for another 24 h.The polymer was dried in a vacuum oven at room temperature for 24 h. The salts were then dissolved directly into the polymer at 343–353 K. Stringently drying the polymer clears ether oxygen salts so that it is easier for the extremely dry salt to dissociate and effect a solvation of the Ag^+ cation. The polymer–salt complexes of higher salt concentrations of O:M ratio of 2:1 and 3:1 were prepared in a similar fashion with the addition of acetonitrile in order to dissolve the large amounts of the salt. The solvent was eventually evaporated completely by vacuum drying at 333 K for 24 h. The anion does not in general solvate except possibly through hydrogen bonding with the OH terminal groups on the polymer chain. The prepared polymer electrolyte samples were all transparent and of high optical quality. The samples were stored in a dry desiccator for further measurements.

2.2. Fourier transform infrared studies

The Fourier transform infrared (FT-IR) spectra were recorded for all the specimens at room temperature using a PerkinElmer RX1 spectrophotometer. The polymer electrolytes were sandwiched between two KBr plates while recording the spectra with a wavenumber resolution of 2 cm^{-1} and in the range 4000–400 cm^{-1}.

3. Results and discussion

3.1. FT-IR studies

Vibrational modes are sufficiently localized to be used for analysis of common spectroscopic features in the polymer–salt complex. In a polymer, the free ions are more likely to be formed on dissociation of the salts when the cation–anion interaction is weak. Therefore, assessing the strength of these interactions is more important for the characterization of the ionic constituents, and consequently for developing an understanding of the interaction between silver ions and ether oxygen and also –OH end groups. The FT-IR spectroscopy has been used to study the polyether C—O—C and salt vibrations occurring within the poly(propylene glycol)–silver triflate-based electrolytes. It is generally believed that the solvation of the salt in poly(propylene glycol) involves coordination of the cation to the ether oxygens and OH terminal group of the polymer network. Owing to relatively high density of polar hydroxyl groups in poly(propylene glycol) host, it could be argued that the increase in free ions partly be attributed to a saturation of preferred coordination sites. As the basis for comparison and in the interest of understanding the spectroscopic data of Ferry et al. [17] for these vibrations are of $LiCF_3SO_3$ and $NaCF_3SO_3$/PPG (4000). In these studies the infrared spectrum of the SO_3 symmetric and asymmetric stretch mode has also been a subject of significant interest.

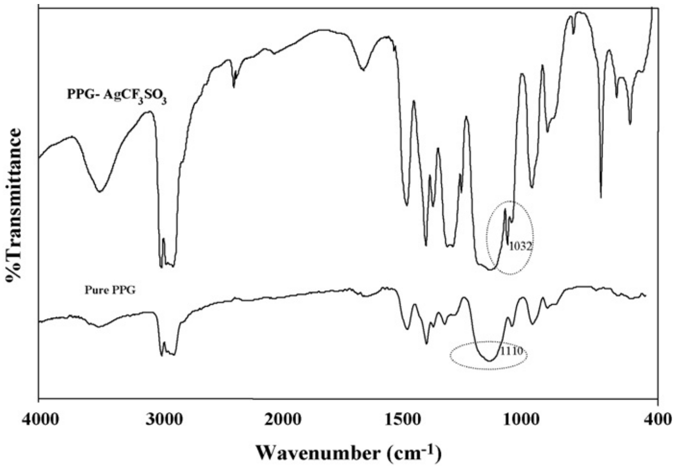

Fig. 1. FT-IR spectra of pure PPG and PPG–$AgCF_3SO_3$ complex.

Fig. 1 shows that the structural features of pure poly(propylene glycol) host, and the host complexed with silver triflate and their interactions are chosen for the comparison because of the major component of the triflate peak appears in complexation. The uncomplexed host polymer is found to exhibit structural features of C—O—C stretching, C—H stretching, C—H deforming, C—O—C in C—O stretching modes assigned at ~1110, ~2869, ~1454, ~1150–1070 cm^{-1}, respectively. The complexed poly(propylene glycol) having the single peak centered at ~1032 cm^{-1} which was assigned to the free symmetric SO_3 stretching mode tends to reflect the dissociation of silver salt and the very weak ion pairing between the silver cations and triflate anions. In the present investigation of silver ion conducting polymer electrolyte complexed with poly(propylene glycol) (PPG 4000) it is known to produce most evident changes of the spectrum when changing the composition in terms of the O:M ratio from 2:1 to 6:1 as shown in Table 1.

3.1.1. C—O—C region

The fact that the uncomplexed symmetric C—O—C stretching mode is noticed at ~1110 cm^{-1} and that it is shifted towards the lower wavenumber region appears to reveal the strength of interactions between silver cations, ether oxygen and also the –OH end groups. Both the regions of C—O—C symmetric and asymmetric vibrations observed at ~1110 and 625 cm^{-1} respectively are of particular interest in our studies. The changes in the intensity, shape and position of the C—O—C stretching mode are associated with oxygen–cation interactions whereas SO_3 symmetric stretching is associated with ion–ion interactions.

Fig. 2 shows that pure poly(propylene glycol) has a characteristic C—O—C vibration at ~1110 cm^{-1} and that the same group when most probably linked to the silver cations would have introduced a new ir vibration at ~1106 cm^{-1} in all those compositions of O:M ratio ranging from 2:1 to 6:1 of the PPG–$AgCF_3SO_3$ complexed polymer electrolyte. A careful evaluation of the spectra reveals further that the absorption intensity of C—O—C stretching mode observed at ~1106 cm^{-1} decreases with increasing ether oxygen to metal cation composition up to the O:M ratio of 4:1. It is confirmed that the free ion concentration increases due to increasing O:M ratio from 2:1 to 4:1 and consequently increasing the ion pairs in the compositions of 5:1 and 6:1.

Table 1
Vibrational frequency assignment of $AgCF_3SO_3$

Wavenumber (cm^{-1})	Assignment	Molecular ions
1272	Asymmetric SO_3	Free triflate ion
1257	Asymmetric SO_3	Free triflate ion
1225	Symmetric CF_3	Free triflate ion
1156	Asymmetric CF_3	Free triflate ion
1106	C—O—C	
1032	Symmetric SO_3	Free triflate ion
1038	Ag^+–$CF_3SO_3^-$	Ion pair
833	Ag^+–$CF_3SO_3^-$	Ion pair
756	Symmetric CF_3	Free triflate ion
638	Symmetric SO_3	Free triflate ion