OH end-group coordination to cations and triflate ions in PPG systems

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In poly(propylene glycol) (PPG) the polymer chains are terminated by hydroxy groups. These polar ends are capable of coordinating to both cations and anions when a salt is dissolved in the polymer. This coordination has been monitored using shifts in the OH stretching vibration band at about 3400 cm^{-1}, as measured by Fourier transform infra-red spectroscopy. In the $LiCF_3SO_3$–PPG(3000) system, the Li^+ ions preferred to coordinate to OH groups rather than to ether oxygens; at the composition $LiCF_3SO_3PPG_{10}$, all OH groups were coordinated by both lithium and triflate ions, suggesting that the properties of these electrolytes depend to a large extent on metal ion to OH end-group interactions. Solvent-shared ion pairs, where the ions are separated by an OH group rather than free triflate ions, are present in these samples. The triflate ions in the solvent-shared ion pairs are suggested to have a $\nu(SO_3)_s$ absorption band at 1032 cm^{-1}, i.e. at the same position as has been found for non-coordinated triflate ions.

(Keywords: poly(propylene glycol); infra-red spectroscopy; hydroxy end-group)

INTRODUCTION

Polymers are widely used as matrices in which different salts are dissolved to form ionically conducting polymer electrolytes. Several polymer–salt blends have been investigated over the last 20 years; the most common have involved poly(ethylene oxide) (PEO) and poly(propylene glycol) (PPG) complexed with different metal trifluoromethanesulfonates ('triflates'). The cations of the salt are generally believed to be coordinated to the ether oxygens of the polymer chain; the anions are either coordinated to the cations or are non-coordinated[1]. In several of these studies, the polymer chains were terminated by hydroxy end-groups which can coordinate to the cations via the oxygen atoms and to the anions via hydrogen bonding.

Cation dependent shifts in the OH stretching band have been detected by Raman spectroscopy[2] for PPG(425) containing dissolved MSCN, where M = Li, Na and K; hydrogen bonding to the anions has also been suggested by Schantz *et al.*[3] for salts dissolved in PPG(4000). The ether oxygen to OH ratio for the medium-length polymer PPG(3000) is about 25. Only a small fraction of the metal ions are coordinated by the end-groups in a randomly coordinated situation. The properties of the polymer electrolyte would then be largely determined by metal ion to ether oxygen interactions. However, a preferential coordination to the end-groups would lead to a drastically different situation since the ether oxygen to metal ion ratios normally used are of the same order of magnitude as the end-group to ether oxygen ratios. The properties of the system would then be largely dominated by the end-group coordination.

Metal triflates dissolved in PPG have been investigated extensively by Raman[3–7] and infra-red[7,8] spectroscopy. Concentration and temperature have been varied. Free triflate ions, ion pairs and, in some cases, higher aggregates have been proposed on the basis of shifts in the symmetric SO_3 stretching vibration $\nu(SO_3)_s$ observed in the Raman spectra. In the infra-red spectroscopic investigation[8] of $LiCF_3SO_3PPG_n$, it was observed that the antisymmetric SO_3 stretching vibration $\nu(SO_3)_a$ remained split into two components for all concentrations and temperatures studied. This was interpreted as indicating that no free triflate ions exist in these systems, contrary to the interpretations of the Raman results[3–6]. The present investigation was partly undertaken to resolve this problem.

In the work described in this paper, we used Fourier transform infra-red (*FT*i.r.) spectroscopy to investigate the OH and SO_3 stretching regions in MCF_3SO_3–PPG systems as a function of concentration, temperature, cation type and polymer chain length.

EXPERIMENTAL

MCF_3SO_3 salts, where M = Li, Na and K, were prepared from dilute triflic acid and Li_2CO_3, NaOH and KOH, respectively. The salts were first dissolved in the acid until a pH of around 4 was reached; the solution was then filtered and allowed to evaporate at 100°C for Li and 60°C for Na and K. Since the $LiCF_3SO_3$ salt was still not water-free, it was heated overnight in a vacuum oven at 240°C. Tetrabutylammonium triflate, $(C_4H_9)_4NCF_3SO_3$, was prepared from dilute triflic acid and a 20% tetrabutylammonium hydroxide solution. Tetrabutylammonium triflate salt was precipitated after mixing the two solutions to pH 5 and waiting for 15 min. The salt was first filtered by suction and then dried overnight in air at 70°C. *FT*i.r. measurements were made to check the dryness of all salts.

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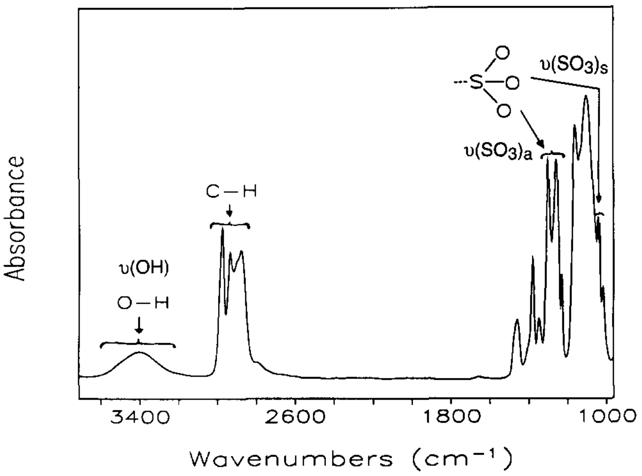

Figure 1 *FT*i.r. absorption spectrum of $LiCF_3SO_3PPG(2000)_{10}$ showing the regions of interest

Polymer electrolytes were made by dissolving stoichiometric amounts of poly(propylene glycol) (PPG) (Aldrich; molecular weights of 4000, 3000, 2000, 1000, 725 and 425) and the salt in anhydrous acetonitrile (Merck; spectroscopic grade). For the blends containing alkali metal triflates, the solvent was first allowed to evaporate in a desiccator connected to a water suction pump. A small amount of the viscous solution was then spread over a KRS5 (TlI + TlBr) (Harrick) or CaF_2 window creating a film about 0.5 μm thick. For blends containing tetrabutylammonium triflate, the salt precipitated out when the solvent was allowed to evaporate. A very thin polymer film (about 0.05 μm thick) was therefore cast directly from the acetonitrile solution on a BaF_2 window to create a supersaturated polymer film. Such thin polymer films showed no salt crystals even after heating to 100°C, as confirmed using a polarization microscope, but gave low signal to noise ratios in the *FT*i.r. measurements.

The samples were prepared and stored in a drybox (relative humidity ~3%) and the *FT*i.r. measurements were made in a vacuum cell equipped with a heating element. Prior to the measurements, the samples were heated to 45°C and cooled when in place in the spectrometer to ensure that all water and solvent had evaporated. This was checked in the OH and CN stretching regions.

Absorbance spectra were recorded on a Digilab/BioRad FTS-45 *FT*i.r. spectrometer in the range 400–4000 cm^{-1} with a resolution of 1 cm^{-1} for the $\nu(SO_3)_s$ and $\nu(SO_3)_a$ regions and a resolution of 8 cm^{-1} for the OH stretching region ν(OH). The lower resolution in the ν(OH) region gave a better signal to noise ratio for the comparatively weak OH bands. The absorbances of the OH stretching bands were typically around 0.3 for the thick samples and 0.03 for the thin samples containing tetrabutylammonium triflate.

RESULTS AND DISCUSSION

An overview of the spectrum for the polymer electrolyte $LiCF_3SO_3PPG(2000)_{10}$ is presented in *Figure 1*; the regions of particular relevance to this work are indicated. Coordination of the OH end-groups can be detected in the ν(OH) region at 3000–3600 cm^{-1}. The OH stretching bands are known to shift to lower wavenumbers compared to the ideal gas-phase value both for OH groups involved in hydrogen bonding and in metal ion coordination[9–11]. It has also been found that the effect on the positions of the bands is cooperative; the combined effect of hydrogen bonding and metal ion coordination is larger than the sum of the individual contributions[12].

The non-coordinated, 'free' triflate ion is assumed to have the point group symmetry C_{3v}, where $\nu(SO_3)_a$ is a doubly degenerate E mode and $\nu(SO_3)_s$ is a non-degenerate A_1 mode. Both modes are infra-red active. When coordinated, the symmetry of the triflate ion is lowered, causing a splitting of the antisymmetric SO_3 stretching mode into two components and a shift of the symmetric SO_3 stretching mode. The $\nu(SO_3)_a$ region is located at 1200–1320 cm^{-1} and the $\nu(SO_3)_s$ region at 1010–1060 cm^{-1} (*Figure 1*).

In previous model studies of lead, zinc[13] and lithium[8] triflates dissolved in acetonitrile, the $\nu(SO_3)_a$ and $\nu(SO_3)_s$ vibrations for the free triflate ion were assigned to bands at 1272 and 1032 cm^{-1}, respectively. The same assignments were found from studies using ^{18}O-labelled and ^{13}C-labelled samples[14,15]. On coordination, a splitting of the degenerate $\nu(SO_3)_a$ band is found for all metal ions investigated, while in the $\nu(SO_3)_s$ region shifts to higher wavenumbers are observed for lithium, to lower wavenumbers for lead and zero shift for zinc. These observations are valid also for the polymer electrolytes, where lead and zinc triflates were dissolved in PEO[13] and lithium triflate in PPG[8]. For Yb(III)triflate dissolved into PEO, shifts were found to both higher and lower wavenumbers in the same spectrum for the $\nu(SO_3)_s$ band[16].

OH stretching in the pure polymer

The appearance of the ν(OH) region for the pure polymers is dependent on the chain length (*Figure 2*). Spectra from the two longest polymer chains investigated, PPG(3000) and PPG(4000), are practically identical, with a large absorption band at 3483 cm^{-1}. In the spectra for the shorter polymers, this band is broadened and shifted to lower wavenumbers. Since the number of hydroxy end-groups per ether oxygen increases with decreasing polymer length, the 3483 cm^{-1} band is assigned to hydroxy end-groups that are hydrogen bonded to ether oxygens (A; *Figure 3*), while the shift for the shorter chains is caused by an overlap with new bands from OH groups

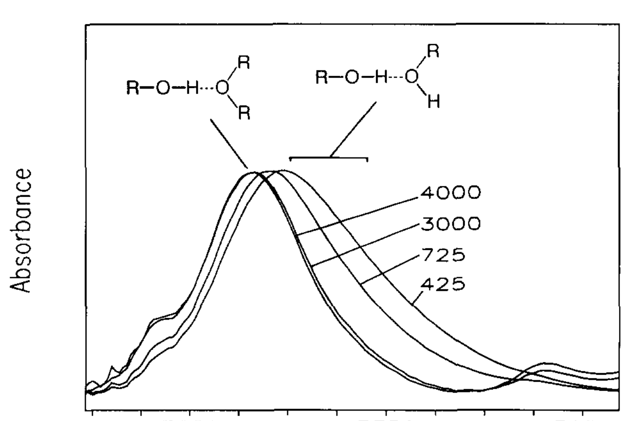

Figure 2 *FT*i.r. absorption spectra in the ν(OH) region for the pure polymers PPG(X) (X = 4000, 3000, 725 and 425). The spectra are scaled to the maximum absorption in the region shown

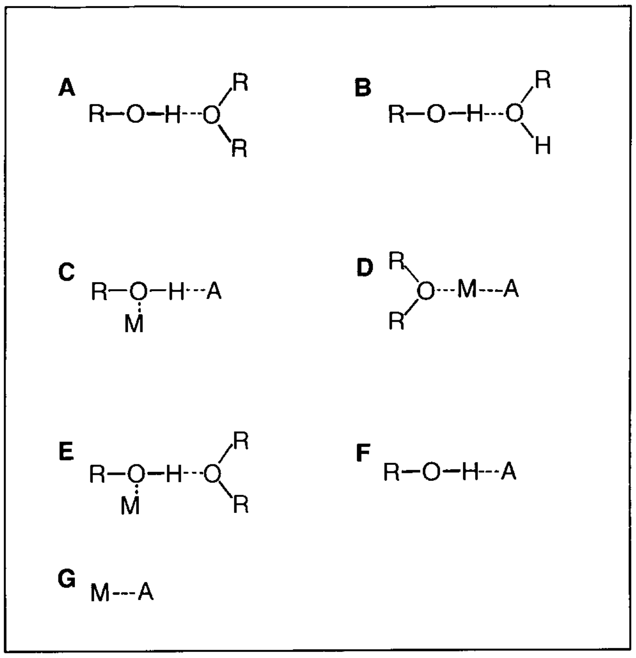

Figure 3 Different local structural arrangements discussed in the text (M = metal ion, A = anion)

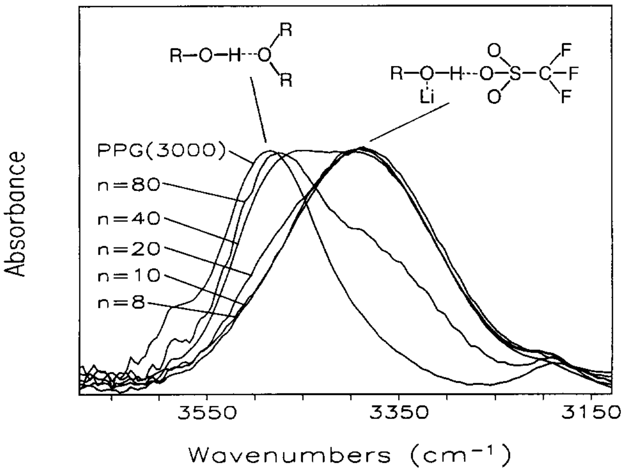

Figure 4 *FT*i.r. absorption spectra in the ν(OH) region for pure PPG(3000) and $LiCF_3SO_3PPG(3000)_n$ ($n = 8$, 10, 20, 40 and 80). The spectra are scaled to the maximum absorption in the region shown

that are hydrogen bonded to other OH groups (**B**; *Figure 3*). The small band at about 3200 cm^{-1} appearing in the spectrum of PPG(4000) has been assigned as an overtone band[17], and the shoulder at about 3590 cm^{-1} was found in the present study to be independent of temperature and therefore assigned as a combination band.

Concentration dependence for $LiCF_3SO_3$–PPG

The ν(OH) region was investigated for samples with different concentrations of $LiCF_3SO_3$ (*Figure 4*). For low concentrations, the spectrum is dominated by the pure polymer band at 3483 cm^{-1}, while a shoulder develops on the low wavenumber side for intermediate concentrations. This shoulder grows to a new band for higher concentrations, and the pure polymer band at 3483 cm^{-1} disappears. The new band is centred at 3385 cm^{-1} and is both cation dependent, as discussed below, and anion dependent[18]. We therefore conclude that this band corresponds to OH end-groups which are coordinated both to lithium ions (through the oxygens) and to triflate ions (through hydrogen bonds), thus creating solvent-shared or solvent-separated ion pairs (**C**; *Figure 3*).

For an ether oxygen to metal ion ratio of 20 ($n = 20$), only a very small fraction of the pure polymer band remains. A random coordination of lithium ions to oxygen atoms would require that only about 5% of the OH end-groups be coordinated. Since almost all OH groups are, in fact, found to be coordinated, there must be a strong preference for lithium ion coordination to the OH end-groups.

The SO_3 stretching vibrations were investigated earlier by infra-red[8] and Raman spectroscopy[4]. A $\nu(SO_3)_a$ band was found split into two components at 1299 and 1255 cm^{-1} in the infra-red spectra for all concentrations investigated, while two bands were found in the $\nu(SO_3)_s$ region at about 1032 and 1041 cm^{-1} in both the infra-red and Raman spectra. On increasing the salt concentration, the 1041 cm^{-1} band was found to increase relative to the 1032 cm^{-1} band. Assignments will be discussed further below.

Chain length and temperature dependence

The number of hydroxy end-groups per metal ion increases as the polymer chain length decreases for a constant ether oxygen to metal ion ratio. The spectra in the OH stretching region will thus be an overlap of bands from situations **A**, **B**, **C** and **E** (*Figure 3*), and therefore not very informative.

The effect of varying the polymer chain length on the $\nu(SO_3)_a$ and $\nu(SO_3)_s$ regions is illustrated in *Figures 5* and *6*, respectively. A reduced splitting of $\nu(SO_3)_a$ is observed for the shorter chain lengths, i.e. the splitting decreases from 45 cm^{-1} for PPG(4000) to 37 cm^{-1} for PPG(425). At the same time, the intensity of the band at 1032 cm^{-1} in the $\nu(SO_3)_s$ region increases compared to that of the 1041 cm^{-1} band.

The temperature dependence of the OH stretching bands in $LiCF_3SO_3PPG(3000)_{20}$ is illustrated in *Figure 7*. At 25°C, the spectrum is dominated by the OH stretching band at 3385 cm^{-1} (**C**; *Figure 3*), as discussed above. On increasing the temperature, an absorption band associated with **A** (*Figure 3*) develops. This indicates that the lithium and triflate ions are displaced from the OH groups as the temperature is increased.

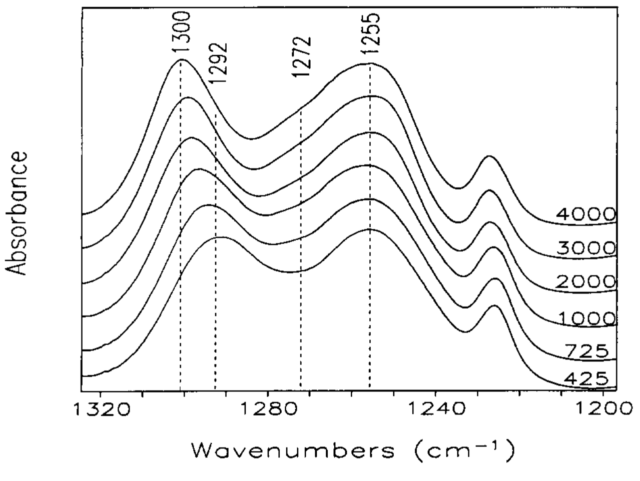

Figure 5 *Ft*i.r. absorption spectra in the $\nu(SO_3)_a$ region for $LiCF_3SO_3PPG(X)_{10}$ ($X = 4000$, 3000, 2000, 1000, 725 and 425)

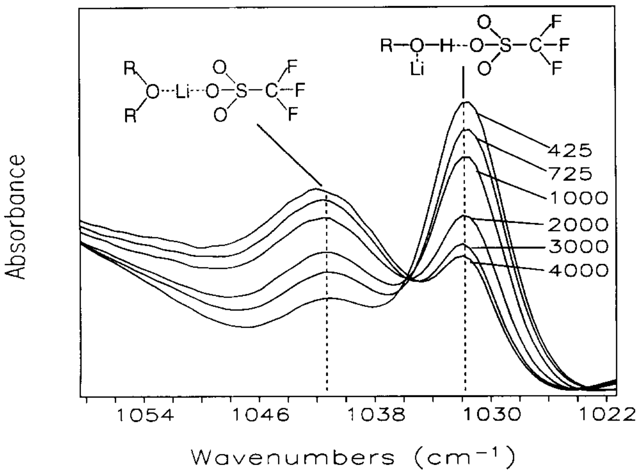

Figure 6 *FT*i.r. absorption spectra in the $\nu(SO_3)_s$ region for $LiCF_3SO_3PPG(X)_{10}$ ($X = 4000$, 3000, 2000, 1000, 725 and 425). The spectra are scaled to a polymer band

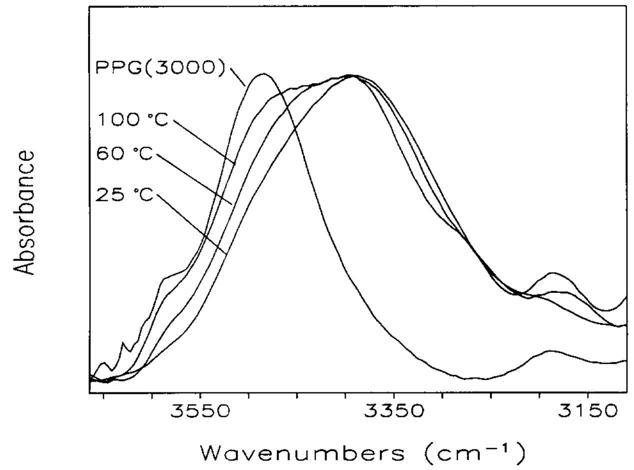

Figure 7 *FT*i.r. absorption spectra in the $\nu(OH)$ region for pure PPG(3000) at 25°C and $LiCF_3SO_3PPG(3000)_{20}$ at 25, 60 and 100°C. The spectra are scaled to the maximum absorption in the region shown

The temperature dependence of the $\nu(SO_3)_a$ and $\nu(SO_3)_s$ regions for $LiCF_3SO_3PPG(3000)_{20}$ was investigated earlier[8]. On increasing the temperature the 1032 cm^{-1} $\nu(SO_3)_s$ band decreases and a new band appears at 1039 cm^{-1} alongside the 1041 cm^{-1} band and its intensity increases. The $\nu(SO_3)_a$ components become only slightly more separated as the temperature is increased.

The existence of solvent-shared ion pairs involving the OH end-groups was proposed in an earlier section. Since a preferential coordination of Li^+ to the end-groups was also found, the number of solvent-shared ion pairs must increase as the number of OH groups increases. In the $\nu(SO_3)_s$ region, the intensity of the band at 1032 cm^{-1} also increases with decreasing chain length. These observations suggest that for triflate ions in solvent-shared ion pairs, $\nu(SO_3)_s$ is found at 1032 cm^{-1} and $\nu(SO_3)_a$ is split, but with a somewhat smaller splitting than for contact ion pairs. The band at 1041 cm^{-1} has been assigned as $\nu(SO_3)_s$ for contact ion pairs[19]; the 1039 cm^{-1} band, observed on increasing the temperature[8], is here also assigned as $\nu(SO_3)_s$ for contact ion pairs. We suggest that this latter type of contact ion pair is formed when the solvent-shared ion pairs at the OH end-groups dissociate. A possible structural distinction between the two types of contact ion pair would then be that those ion pairs associated with $\nu(SO_3)_s$ at 1041 cm^{-1} are also coordinated to the ether oxygens of the polymer (D; *Figure 3*), while the other ion pairs are not polymer coordinated (G; *Figure 3*).

Cation dependence

Cation dependent shifts for $\nu(OH)$ relative to the pure polymer band are observed on dissolving MCF_3SO_3, where M = Li, Na and K, in PPG(3000) (*Figure 8*). The largest shift appears for lithium and the smallest one for potassium, as expected from the difference in their ionic radii. A similar cation dependence was found by Manning *et al.*[2] for MSCN in PPG(425).

Samples of tetrabutylammonium triflate dissolved in PPG(3000) were studied for ether oxygen to cation ratios of 10, 20 and 40 (*Figure 9*) in order to locate the OH stretching band from an OH group hydrogen bonded to a triflate ion (**F**; *Figure 3*). Only one band is observed for all concentrations at approximately the same position as the band in the pure polymer (3485 cm^{-1}). This indicates the similar strengths of hydrogen bonds between OH groups and ether oxygens (**A**) or triflate ions (**F**). The same result was obtained in a study[18] of the anion dependence of the OH stretching band in LiX–PPG(3000) systems, where $X = PF_6^-$, BF_4^-, ClO_4^-, $CF_3SO_3^-$, I^- and Br^-.

Raman and infra-red spectra of $MCF_3SO_3PPG(4000)$ and $MCF_3SO_3PPG(3000)$ systems, where M = Li, Na and K, were studied earlier in the $\nu(SO_3)_a$ and $\nu(SO_3)_s$ regions[7,19]. One cation independent $\nu(SO_3)_s$ band was found at 1032 cm^{-1}, and one cation dependent band at higher wavenumber. The band at 1032 cm^{-1} was assigned to free triflate ions, and the band at higher wavenumber to ion pairs. The splitting of $\nu(SO_3)_a$ was found to be cation dependent, with the largest value for Li and the smallest for K.

In the spectrum of tetrabutylammonium triflate dissolved in PPG(3000), the $\nu(SO_3)_a$ region contains two components approximately 10 cm^{-1} apart at all concentrations (*Figure 10*), suggesting a weak interaction at the SO_3 end, whereas only one band (at 1032 cm^{-1}) is found in the $\nu(SO_3)_s$ region. Similar results for tetrabutylammonium triflate dissolved in 2-propanol have recently been obtained by Frech and Huang[20]. This must then be the behaviour for an OH group hydrogen bonded to

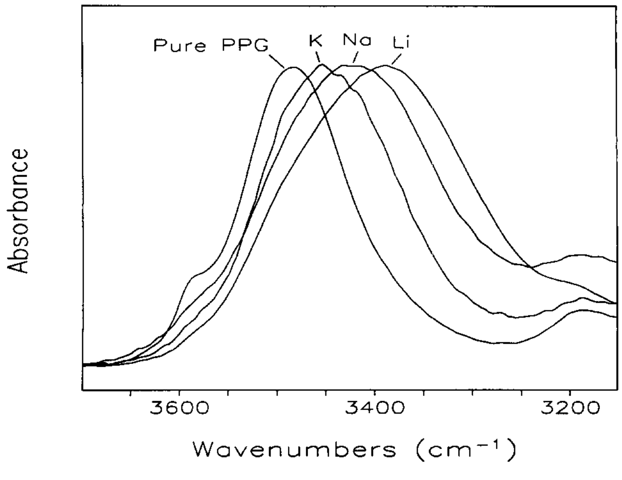

Figure 8 *FT*i.r. absorption spectra for pure PPG(3000) and $MCF_3SO_3PPG(3000)_{20}$ (M = Li, Na and K). The spectra are scaled to the maximum absorption in the region shown

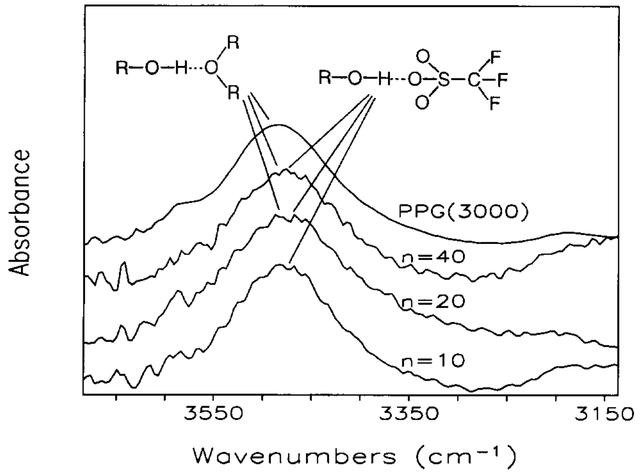

Figure 9 *Fti.r.* absorption spectra in the ν(OH) region for pure PPG(3000) and $(C_4H_9)_4NCF_3SO_3PPG(3000)_n$ ($n = 10$, 20 and 40) (very thin samples cause the low signal to noise ratios for the tetrabutylammonium triflate samples)

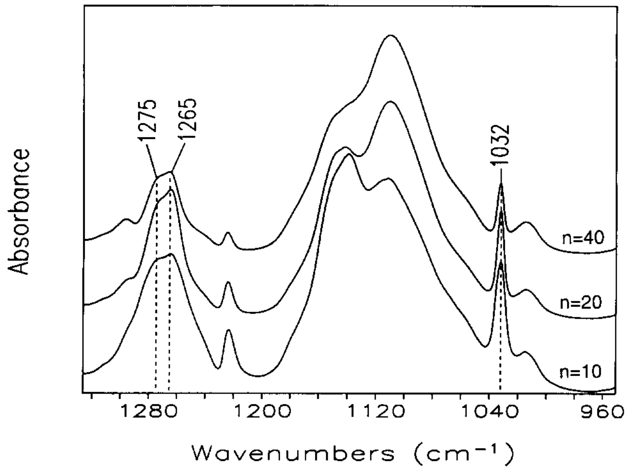

Figure 10 *FTi.r.* absorption spectra for $(C_4H_9)_4NCF_3SO_3PPG(3000)_n$ ($n = 10$, 20 and 40)

the anion (**F**) with little or no interaction with the cation, as would be the case for the bulky tetrabutylammonium cation.

$\delta(CF_3)_s$ modes

Frech and coworkers have recently, in a number of articles[20–23], studied the effect of different solvents and cations on a mixed band, referred to as the $\delta(CF_3)_s$ band, in the region 750–770 cm^{-1}. They have found that this band is sensitive to environmental changes around the triflate ion, and therefore serves as a good complement to the SO_3 bands in determining the coordination of the triflate ions. They found three bands in the $\delta(CF_3)_s$ region for lithium triflate dissolved in a PPO trimer: one small band at 752 cm^{-1} assigned to 'free' triflate ions, a large band at 758 cm^{-1} assigned to ion pairs and a small band at 763 cm^{-1} assigned to a higher aggregate ('aggregate 1')[23]. We have also studied this $\delta(CF_3)_s$ region; spectra for $LiCF_3SO_3PPG(425)_{10}$ and $(C_4H_9)_4NCF_3SO_3PPG(3000)_{10}$ (each with large absorption bands at 1032 cm^{-1} in the $\nu(SO_3)_s$ region) are presented in *Figure 11*. One rather broad band is found at 757 cm^{-1} for $LiCF_3SO_3PPG(425)_{10}$, whereas a sharper band is found at 753 cm^{-1} for $(C_4H_9)_4NCF_3SO_3PPG(3000)_{10}$. A band at 740 cm^{-1} was also found in the spectrum of the sample containing tetrabutylammonium triflate, and corresponds to an absorption band from the tetrabutylammonium ion. The observation of two separate absorption bands for $\delta(CF_3)_s$ means that the CF_3 group experiences at least two different structural situations. This strengthens our earlier suggestions of at least two different structural origins for the $\nu(SO_3)_s$ band at 1032 cm^{-1}. An analogous observation was, in fact, made by Frech and Huang[20] for tetrabutylammonium triflate in 2-propanol and triglyme solutions, where $\delta(CF_3)_s$ was found at 758 and 754 cm^{-1}, respectively, while only one band at 1034 cm^{-1} was found in the $\nu(SO_3)_s$ region.

Concluding discussion

A major issue of debate has been as to whether the $\nu(SO_3)_s$ band at 1032 cm^{-1} corresponds to free triflate ions alone or whether other structural arrangements can give an absorption band at the same wavenumber. It has been suggested above that solvent-shared ion pairs (**C**; *Figure 3*) as well as triflate ions hydrogen bonded to OH groups with no cation influence (**F**; *Figure 3*) can have $\nu(SO_3)_s$ absorption bands at 1032 cm^{-1}. In both these cases (particularly **C**), however, $\nu(SO_3)_a$ is split, indicating a definite interaction with the SO_3 end.

In a recent *ab initio* study of the vibrational frequencies of Li^+–$CF_3SO_3^-$ ion pairs[24], $\nu(SO_3)_s$ was found to shift to higher wavenumbers when involved in monodentate coordination and to lower wavenumbers for bidentate coordination; the bond angle Li···O–S is 180° for the monodentate case and about 90° for the bidentate case (*Figure 12*). The $\nu(SO_3)_s$ frequency was also investigated as a function of this angle. For Li···O–S angles close to 120°, $\nu(SO_3)_s$ did not shift, whereas $\nu(SO_3)_a$ was still split. The angle H···O–S falls in the range 112–143° in several crystalline hydrates containing the triflate ion[25–29]. We therefore suggest that the bond angles $ROH\cdots O\text{–}SO_2CF_3$ in the present cases also have values in the vicinity of 120° (see, for example, *Figure 4*, coordination geometry **C**). This would explain the zero shift for the $\nu(SO_3)_s$ band for situations involving solvent-shared ion pairs and OH end-groups hydrogen bonded to the triflate ions, and why no cation effect has been found for the 1032 cm^{-1} band.

Of course, free triflate ions also absorb at 1032 cm^{-1}; in systems containing no OH groups (such as aprotic

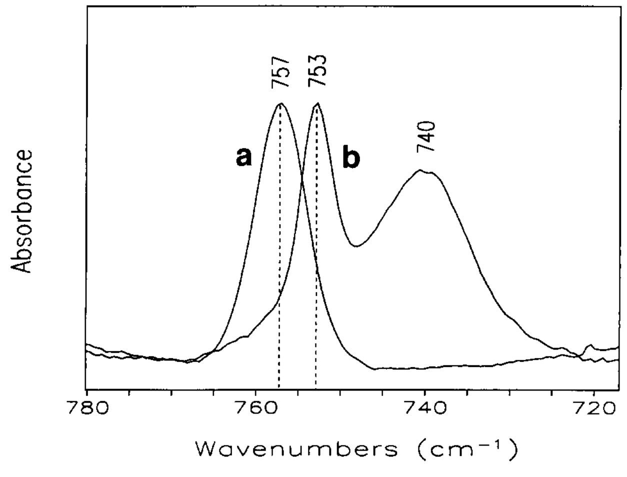

Figure 11 *FTi.r.* absorption spectra in the $\delta(CF_3)$ region for (a) $LiCF_3SO_3PPG(425)_{10}$ and (b) $(C_4H_9)_4NCF_3SO_3PPG(3000)_{10}$

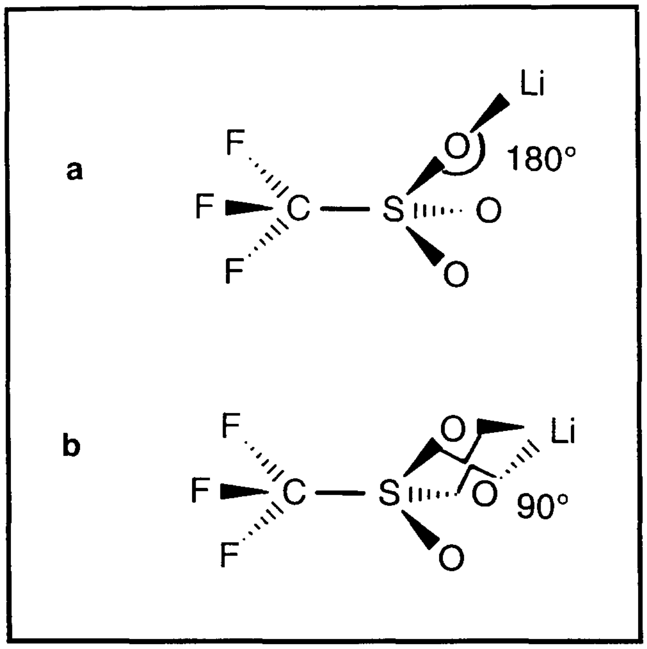

Figure 12 Local structures for (a) monodentate coordination and (b) bidentate coordination of Li^+

organic solvents or methyl-capped polyethers), a $\nu(SO_3)_s$ absorption band is found at 1032 cm^{-1} corresponding to free triflate ions. In such cases[20,30], however, this band is always accompanied by a $\nu(SO_3)_a$ absorption band at 1272 cm^{-1}.

Poly(propylene glycol) (molecular weight of 4000) has been suggested as an amorphous single-phase model system for high molecular weight poly(ethylene oxide)-based electrolytes[19]. The low OH end-group to ether oxygen ratio is not considered to influence the properties of the electrolyte significantly. This would indeed be a reasonable assumption if there were a random distribution of metal ion to OH end-group and ether oxygen contacts, or preferential metal ion to ether oxygen contacts. We have shown here, however, that quite the opposite is true; there is, in fact, a strong preference for OH end-group to metal ion coordination. The ether oxygen to end-group ratio for PPG(3000) is 26, and for PPG(4000) 34. Since these ratios are of the same order of magnitude as the ether oxygen to metal ion ratios commonly used, the properties of these electrolytes should depend to a large extent on the metal ion to OH end-group interactions.

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