Dependence of ionic association on polymer chain length in poly(ethylene oxide)–lithium triflate complexes

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Ionic association in complexes of lithium trifluoromethanesulfonate with low-molecular-weight poly(ethylene oxide) dimethyl ethers was studied using Raman and infra-red vibrational spectroscopy. The relative concentrations of ion pairs and more highly associated ionic species are quite dependent on chain length. This dependence was measured in both the CF_3 symmetric deformation mode and the SO_3 symmetric stretching mode. The effect of the terminating group was considered by comparing the dimethyl ethers with hydroxy-terminated poly(ethylene oxide) at comparable chain lengths. Hydrogen bonding effects in the hydroxy-terminated poly(ethylene oxide) compounds were also found to depend on chain length.

(Keywords: ionic association; polyether; triflate)

INTRODUCTION

Ionically conducting polymers[1] are currently of intense technological interest for a wide variety of potential applications, particularly in high-energy density batteries and electrochromic devices[2]. It is well known that the spacing of the ether oxygens along the polymer backbone is critical for the coordination of the cations, with the most effective coordination observed in polyethers in which the ether oxygens are separated by two carbon atoms[3]. Consequently, most of the ionically conducting polymers are based primarily on poly(ethylene oxide) (PEO) and to a lesser extent, poly(propylene oxide) (PPO). These polymers are complexed with lithium, sodium or potassium salts of low lattice energy; the counter anions are usually trifluoromethanesulfonate ('triflate', $CF_3SO_3^-$), perchlorate (ClO_4^-), thiocyanate (SCN^-) and iodide (I^-).

A general picture of the mechanism of ion transport in these polymer–salt complexes has emerged. Conduction occurs primarily through amorphous regions of the polymer[4,5] with ionic association and segmental motion of the polymer backbone playing a major role. The two effects are not completely separable, since the segmental motion depends to a large extent upon the ionic interactions with the ether oxygen atoms in the backbone and these interactions, in turn, depend to some extent upon the degree of ionic association.

Vibrational spectroscopy has been successfully used to examine fundamental questions of ionic association in polymer–salt complexes[6]. In general, ionic aggregation increases with increasing temperature[7,8] or increasing salt concentration. In salts such as perchlorate and triflate it is possible to identify the presence of ion pairs and higher ionic aggregates[9–11] such as triple ions[12]. An extreme case of increasing ionic aggregation with increasing temperature is occasionally observed as phase separation at sufficiently high temperatures, where the complexed salt precipitates out as a microcrystalline powder[13].

The effect of polyether chain length on ionic conductivity has been studied. Nagaoka *et al.*[14] considered block copolymers of short PEO chains segmented by dimethyl siloxane units which created sufficient disorder in the chain to prevent crystallization. The authors examined the effect of PEO chain length on the conductivity and found a maximum in σ for a chain length of about eight PEO units. The conductivity maximum was explained in terms of two competing effects: the increase in cation solubility with increasing chain length, n, counterbalanced by a decrease in degree of segmental motion as evidenced by an increase in T_g with increasing n. It is known from other studies that the cation solubility increases in $CH_3O\text{–}(CH_2CH_2O)_n\text{–}CH_3$ with increasing values of n up to a limit, depending on the particular cation[15]. In fact, this limit has been used to deduce the cation coordination number in polyether–salt complexes.

However, few systematic studies of the effect of polymer chain length on ionic association have been performed. The complexation of fluorenyllithium, -sodium and -potassium in PEO dimethyl ethers of the formula $CH_3O\text{–}(CH_2CH_2O)_n\text{–}CH_3$ in dioxane and tetrahydrofuran as solvents has been investigated using optical and n.m.r. spectroscopy. It was found that the ratio of solvent-separated ion pairs to contact ion pairs increased with increasing chain length of the polyether for chain lengths from 1 to 4 for the lithium salt and 3 to 6 for the sodium salt[16]. Schantz *et al.*[17] noted that the concentration of associated ions relative to that of free ions decreased with increasing chain length (molecular weight) in a Raman spectroscopic study of sodium triflate and lithium perchlorate in poly(propylene glycol) with molecular

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weights ranging from 400 to 4000. Petersen *et al.*[18] examined the chain length dependence of ionic association in complexes of lithium triflate with CH_3 end-capped PEO with chain lengths 1–4 and (approximately) 8 units. They observed a chain length dependence only for $n > 4$, with an increasing amount of 'free' ions in the longer chain system ($n = 8$) relative to the short chain system. In the same study, the authors also described the effect of polyether chain end-capping on ionic association. The amount of free ions present is reduced in CH_3 end-capped PEO relative to OH end-capped PEO at comparable chain lengths while the temperature dependence of ionic association is increased. The latter effect was attributed to hydrogen bonding between anions and OH groups on the ends of the polymer chains.

EXPERIMENTAL

Sample preparation

PEO dimethyl ethers with the formula $CH_3O{-}(CH_2CH_2O)_n{-}CH_3$ where n ranges from 1 to 4 were purchased from Aldrich. The monomer (h.p.l.c. grade, 99.9%) and dimer (anhydrous, 99 + %) were used without further purification. However, the trimer (99%) and tetramer (99 + %) were distilled with CaH_2 under vacuum to remove the traces of water before use. Compounds of α,ω-hydroxy PEO with the formula $HO{-}(CH_2CH_2O)_n{-}H$ (Aldrich, $\geqslant 99\%$, $n = 1$, 3, 5, 6 and 8.5; Fluka, 99 + %, $n = 4$) were used without further treatment. Lithium triflate (97%) was purchased from Aldrich and dried at 130°C under vacuum for 24 h before use. The polymer complexes were prepared under a dry nitrogen atmosphere in a glove box. No solvent was used in the complexation process.

Raman spectra

Parallel polarized Raman spectra of samples contained in a capillary were recorded at room temperature using a standard 90° scattering geometry. A 0.85 m Czerney–Tuner double monochromator equipped with a thermoelectrically cooled RCA (31034) photomultiplier tube was used for data collection. The light source was the 488 nm line excited at 400 mW from a Spectra Physics argon ion laser. A scanning step of 0.2 cm^{-1} and a data collecting time of 4 s for each data point were used in data collection in the spectral region from 1000 to 1065 cm^{-1}. In the other spectral regions the scanning step was 1.0 cm^{-1} and the collection time for each data point was 2 s. The polymer bands in the spectral region between 1000 and 1065 cm^{-1} were subtracted from the spectra of the polymer–salt complexes. Then the remaining bands due to the polymer–salt complexes were fit to a trial function consisting of a linear baseline and Gaussian–Lorentzian functions. A non-linear least-squares strategy was used in fitting the trial function to the experimental Raman intensity.

Infra-red spectra

Infra-red spectra were collected on a Nicolet 200 SXV *FT*i.r. system at 1 cm^{-1} resolution. Silver bromide plates were used as windows for the polymer complexes and solutions of lithium triflate in water. In the figures, the infra-red spectra of the polymer bands have been subtracted from the infra-red spectra of the polymer complexes for clarity of presentation.

RESULTS

Effect of chain length on ionic association

Triflate ion $\nu_s(SO_3)$ stretching mode. In the first part of this study, complexes of $CH_3{-}(OCH_2CH_2)_n{-}OCH_3$ and lithium triflate were prepared at three concentrations (expressed as the ether oxygen:cation ratio), 80:1, 20:1 and 5:1. Lithium triflate was slightly saturated in the 5:1 complex with the tetramer ($n = 4$). Raman scattering spectra of the $\nu_s(SO_3)$ stretching mode are shown in *Figures 1a, 1b* and *1c* for the 80:1, 20:1 and 5:1 complexes, respectively. The structure in this spectral region originates from contributions from triflate ions in various states of ionic association. The assignment of the 1033 cm^{-1} band to 'free' ions, the 1043 cm^{-1} band to ion pairs and the 1052 cm^{-1} band to ion aggregates follows from previous studies[9–12]. The intensity contribution from each species was resolved by curve fitting as described above, and the ratio of each species' intensity contribution to the total intensity was calculated. These data are plotted as a function of chain length n for the three salt concentrations and are shown in *Figures 2a, 2b* and *2c*, corresponding to the spectra in *Figures 1a, 1b* and *1c*, respectively.

Several trends are apparent. At each salt concentration the largest increase in the relative percentage of 'free' ions occurs between $n = 1$ and $n = 2$, followed by a relative insensitivity to the value of n. Also at each concentration the relative percentage of ion pairs is largest, and tends to increase with n. The rate of increase appears to be larger at higher salt concentration. Finally, the concentration of ionic aggregates decreases with increasing n. The concentration dependence of the data can be examined at each chain length n. At each value of n the relative amount of 'free' ions decreases with increasing concentration while both the ion pair and ionic aggregate concentrations increase. This concentration dependence is consistent with similar studies of longer chain polyether complexes.

The effect of chain length can also be seen in the infra-red transmission spectra of the $\nu_s(SO_3)$ stretching mode as shown in *Figure 3*. The increase of 'free' ions and corresponding decrease of aggregates with chain length as seen in the Raman spectra are noted here. However, there are weak infra-red-active polymer bands in this region and so the spectra were not fit due to the relatively larger error introduced by the change in the baseline with different chain lengths. The band centre frequencies for the 'free' ions, ion pairs and aggregates are 1033, 1041 and 1051 cm^{-1}, respectively.

The effect of chain length on the strength of the ion pair interaction was examined through the splitting of the antisymmetric stretching mode, $\nu_{as}(SO_3)$, in a series of infra-red transmission measurements. As shown in the bottom spectrum of *Figure 4*, the interaction of the cation with the triflate ion lifts the double degeneracy of this mode and results in two distinct bands at 1301 and 1260 cm^{-1}. For the sake of comparison, spectra of lithium triflate in water at 0.02 m and 20:1 concentration are shown in the upper and middle spectra, respectively. Water has a high static dielectric constant ($\varepsilon = 78$) and the triflate ion remains dissociated even at high salt concentrations. The nature of the interaction between cation and anion responsible for the splitting of the antisymmetric stretching mode (presumably the formation of ion pairs) appears to be completely

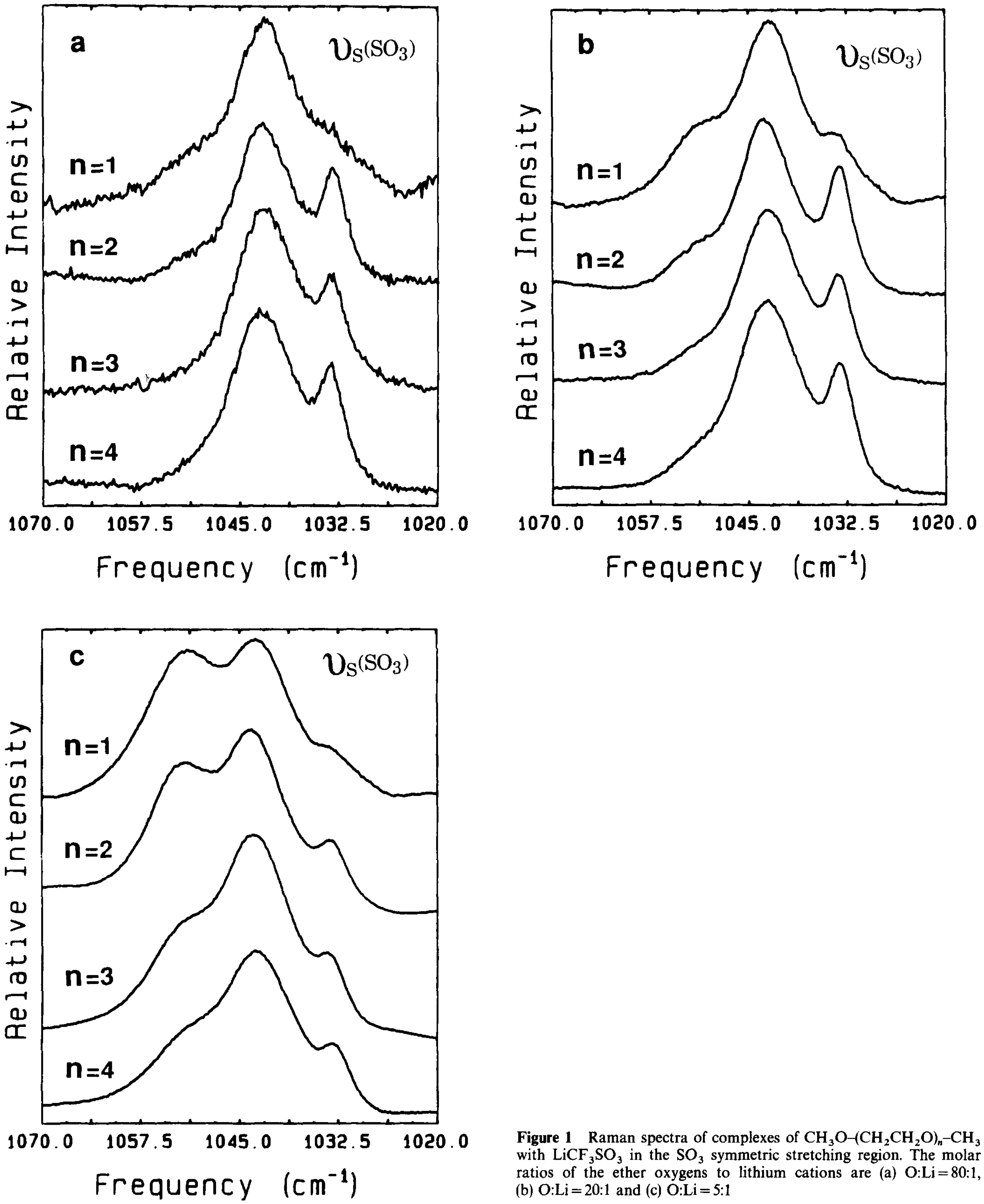

Figure 1 Raman spectra of complexes of CH_3O–$(CH_2CH_2O)_n$–CH_3 with $LiCF_3SO_3$ in the SO_3 symmetric stretching region. The molar ratios of the ether oxygens to lithium cations are (a) O:Li = 80:1, (b) O:Li = 20:1 and (c) O:Li = 5:1

independent of chain length over the range of *n* examined in this study.

Triflate ion $\delta_s(CF_3)$ deformation mode. The vibrational mode at approximately 760 cm^{-1} has been the subject of some disagreement in the literature. In ammonium triflate this has been assigned as a symmetric deformation mode[19,20], while a study in sodium triflate describes this as a mixture of the symmetric CF_3 stretching motion and the symmetric C–S stretching motion[21]. Bürger *et al.*[22] assigned this as a mixture of CF_3 symmetric deformation and C–S stretching in silver triflate. The most complete assignments are found in a recent study of both normal isotopic and partially ^{18}O labelled tetrabutylammonium

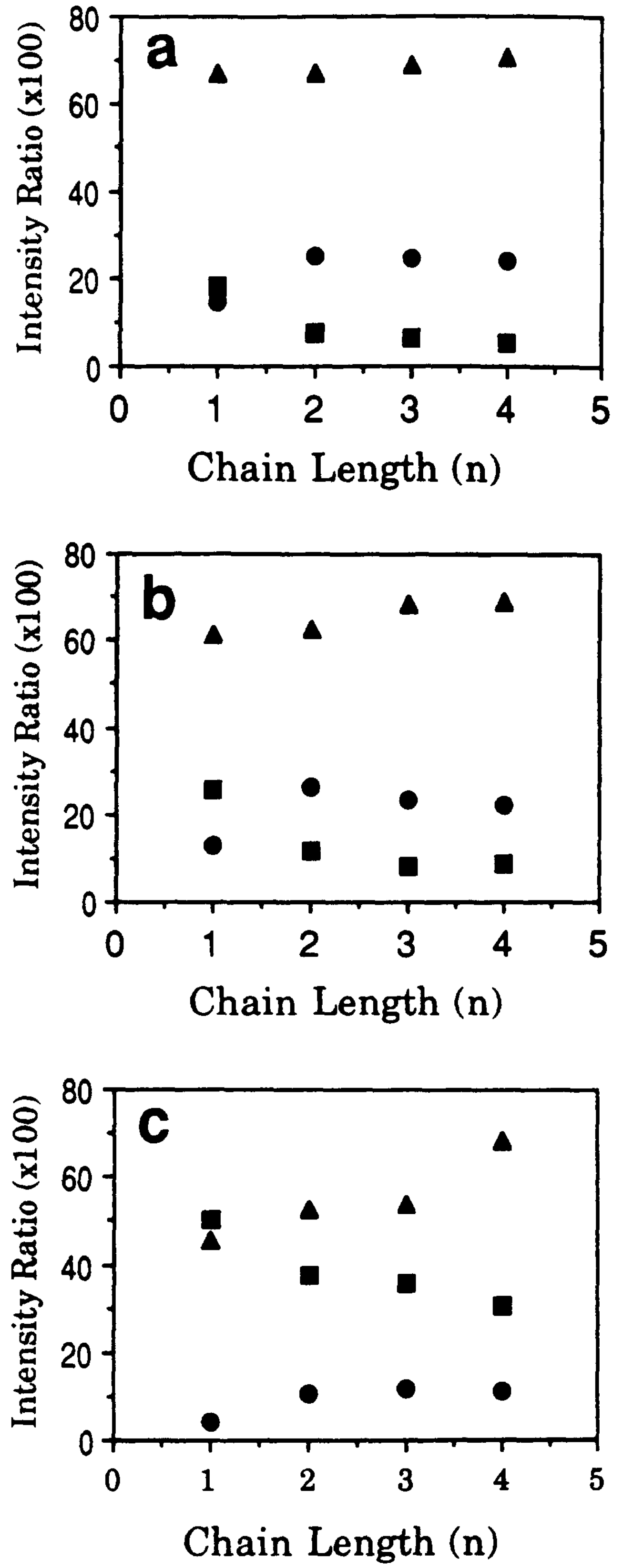

Figure 2 Relative intensities of triflate ionic species obtained from curve fitting the ν(SO_3) bands shown in *Figures 1a*, *1b* and *1c*: (●) 'free' ions; (▲) ion pairs; (■) aggregates

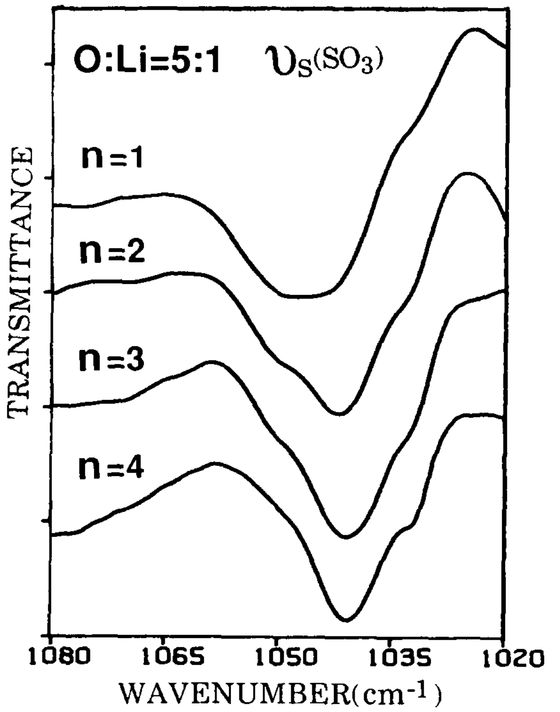

Figure 3 *FT*i.r. spectra of the 5:1 complexes of $CH_3O{-}(CH_2CH_2O)_n{-}CH_3$ with $LiCF_3SO_3$ in the SO_3 symmetric stretching region

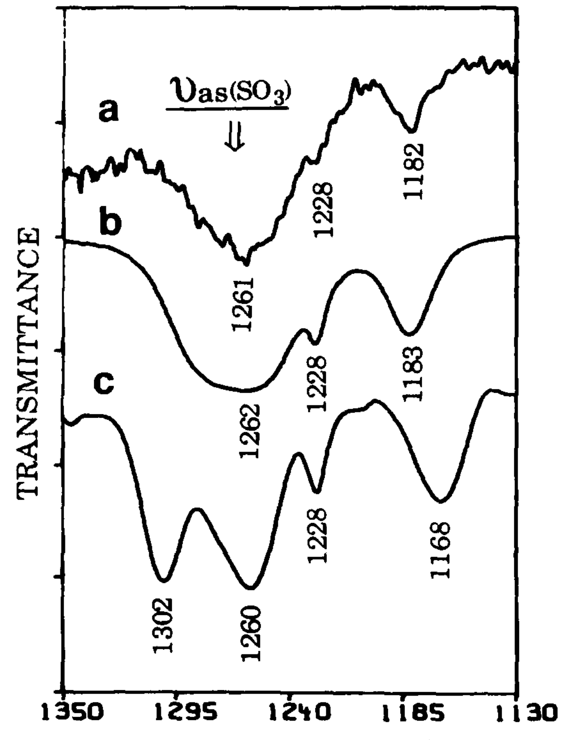

Figure 4 *FT*i.r. spectra of the H_2O and $LiCF_3SO_3$ solutions (spectrum a = 0.01 m, spectrum b = 2.30 m) and the 7.5:1 complex of $CH_3O{-}(CH_2CH_2O)_4{-}CH_3$ with $LiCF_3SO_3$ (spectrum c) between 1130 and 1350 cm^{-1}

triflate by Johnston and Shriver^{23}. They described the mode as a CF_3 symmetric deformation containing a significant amount of C–S stretching motion. In our work it is interesting to note that the structure of the bands in this region reflect the concentrations of the various triflate ion species. This is particularly evident when comparing *Figure 5*, which shows the chain length dependence of the Raman spectra of the 20:1 complex with *Figure 1b*, which shows equivalent data in the SO_3 symmetric stretching region. Raman spectra in this region of

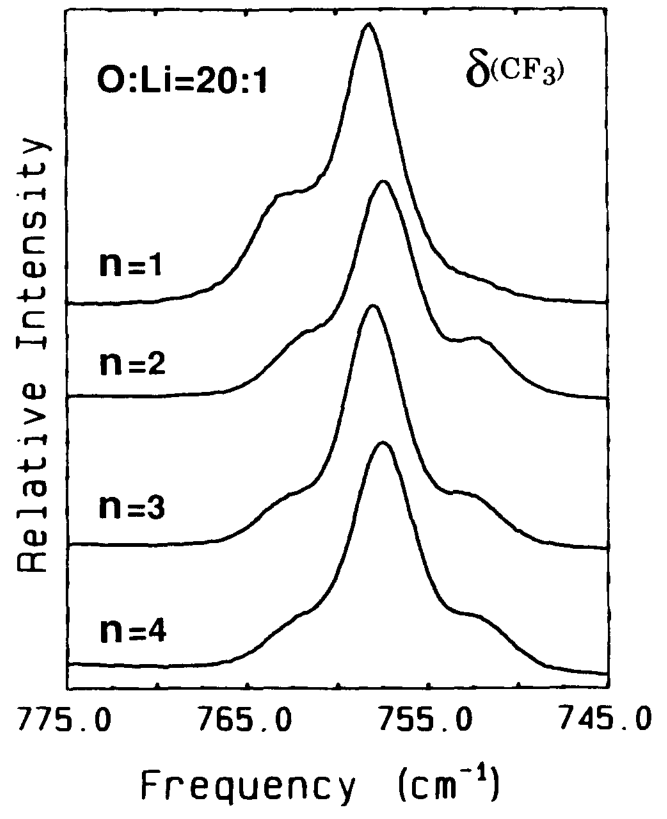

Figure 5 Raman spectra of the 20:1 complexes of $CH_3O\text{-}(CH_2CH_2O)_n\text{-}CH_3$ with $LiCF_3SO_3$ in the CF_3 symmetric deformation region

the 80:1 and 5:1 complexes (not shown) exhibit the same trends in chain length dependence as do the corresponding spectra in the SO_3 symmetric stretching region. However, the Raman spectral data in this region were curve-fitted as previously described and the separate contributions of the various ionic species were calculated at each concentration as a function of chain length. *Figures 6a, 6b* and *6c* show the analyses of the 80:1, 20:1 and 5:1 complexes, respectively, in the 760 cm^{-1} spectral region and should be compared to equivalent analyses of SO_3 symmetric stretching bands of *Figures 2a, 2b* and *2c*.

Effect of end-group on ionic association

Triflate ion $\nu_s(SO_3)$ stretching mode. In this part of the study, complexes of $H\text{-}(OCH_2CH_2)_n\text{-}OH$ and lithium triflate were prepared at a 20:1 ether oxygen:cation ratio. Raman scattering spectra of the $\nu_s(SO_3)$ stretching mode are shown in *Figure 7* for chain lengths n of 1–6 and 8.5. Most significantly, in this system the 'free' ions are the dominant species while the ion pairs are present in relatively smaller numbers. This is exactly opposite to the behaviour seen in the dimethyl ethers, where the ion pairs are the dominant species. The concentration of ionic aggregates was found to be negligible and was ignored in the subsequent band-fitting analysis. This analysis (*Figure 8*) shows that between $n=1$ and $n=2$ the relative free ion concentration increases and the ion pair concentration decreases. However, for chain lengths greater than 2 this behaviour reverses; the relative concentration of 'free' ions decreases while that of the ion pairs increases with increasing chain length. This general behaviour was also noted in the CH_3 end-capped PEO (see *Figures 2b* and *6b*); however, it is particularly clear in the OH capped material.

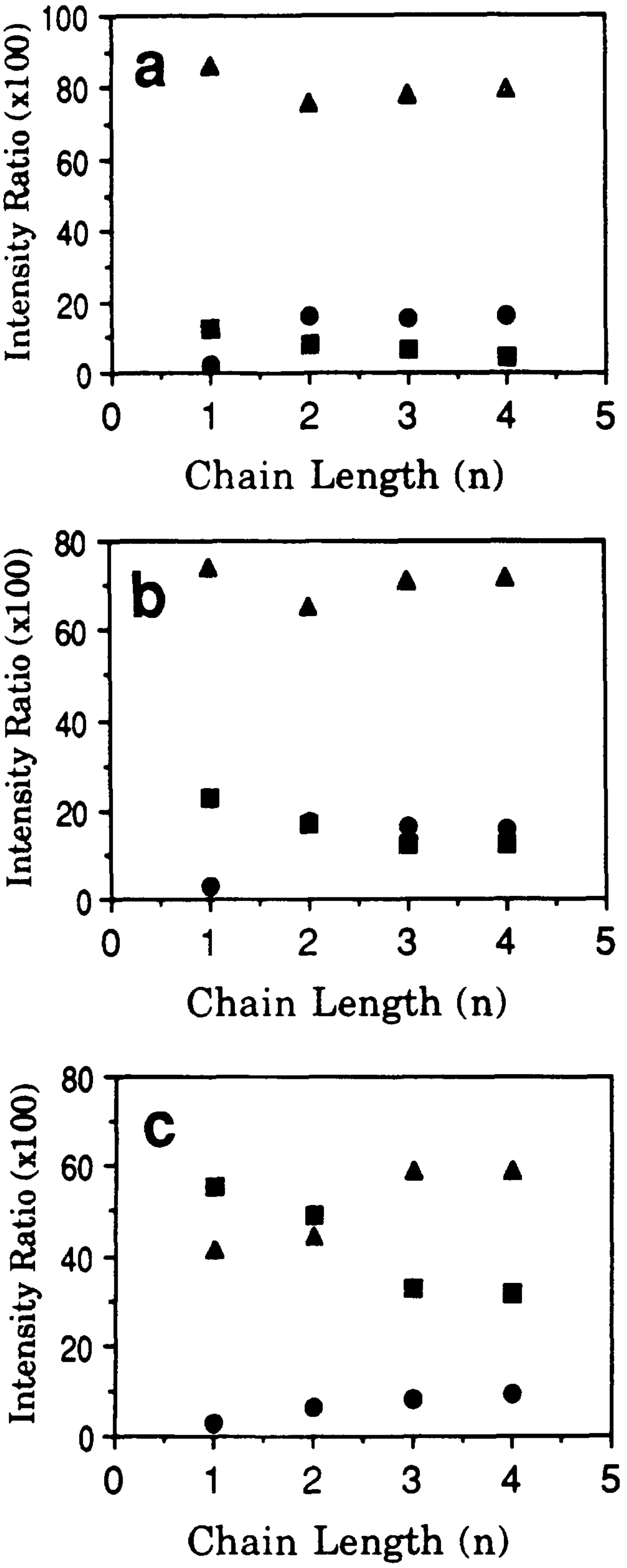

Figure 6 Relative intensities of triflate ionic species obtained from curve fitting of the $\delta(CF_3)$ bands for complexes of $CH_3O\text{-}(CH_2CH_2O)_n\text{-}CH_3$ with $LiCF_3SO_3$: (●) 'free' ions; (▲) ion pairs; (■) aggregates. The molar ratios of the ether oxygens to lithium cations are (a) O:Li = 80:1, (b) O:Li = 20:1 and (c) O:Li = 5:1

Triflate ion $\delta_s(CF_3)$ deformation mode. Raman scattering spectra of the $\delta_s(CF_3)$ deformation mode are shown for the 20:1 complexes of the OH capped material in *Figure 9* for chain lengths n of 1–6 and 8.5. Previously in the dimethyl ethers, this spectral region reflected the

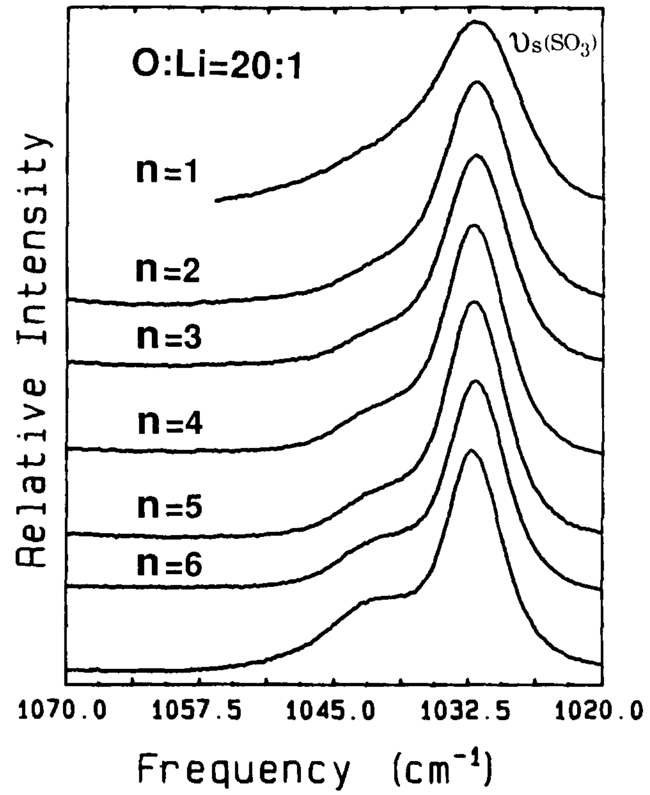

Figure 7 Raman spectra of the 20:1 complexes of HO–(CH$_2$CH$_2$O)$_n$–H with LiCF$_3$SO$_3$ in the SO$_3$ symmetric stretching region

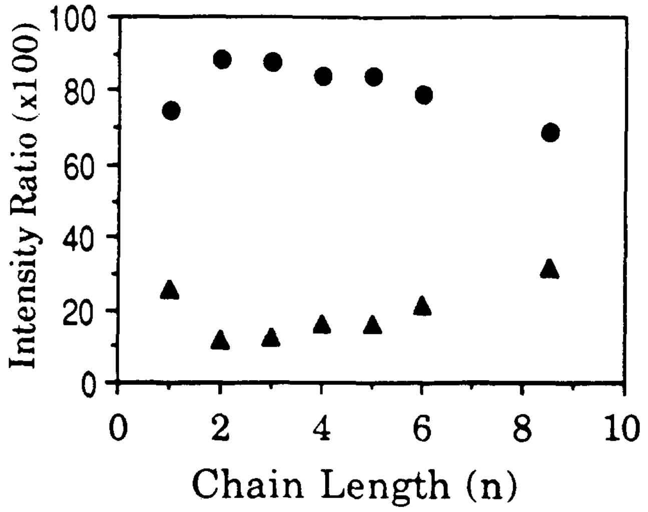

Figure 8 Relative intensities of triflate ionic species obtained from curve fitting of the ν(SO$_3$) bands for the 20:1 complexes of HO–(CH$_2$CH$_2$O)$_n$–H with LiCF$_3$SO$_3$: (●) 'free' ions; (▲) ion pairs

distribution of triflate ion species seen in the $\nu_s(SO_3)$ stretching mode (compare with *Figure 5*). However, in the diols there is a single, fairly broad band whose frequency decreases with increasing chain length until $n=4$. Above this length the frequency appears to be independent of n. In a study of the effects of various solvents on ionic association in lithium triflate[24], we postulated an interplay between anion–cation interactions and anion–solvent interactions. The strengths of these interactions are quite different between the CH$_3$ end-capped and the OH capped polyethers used in this study.

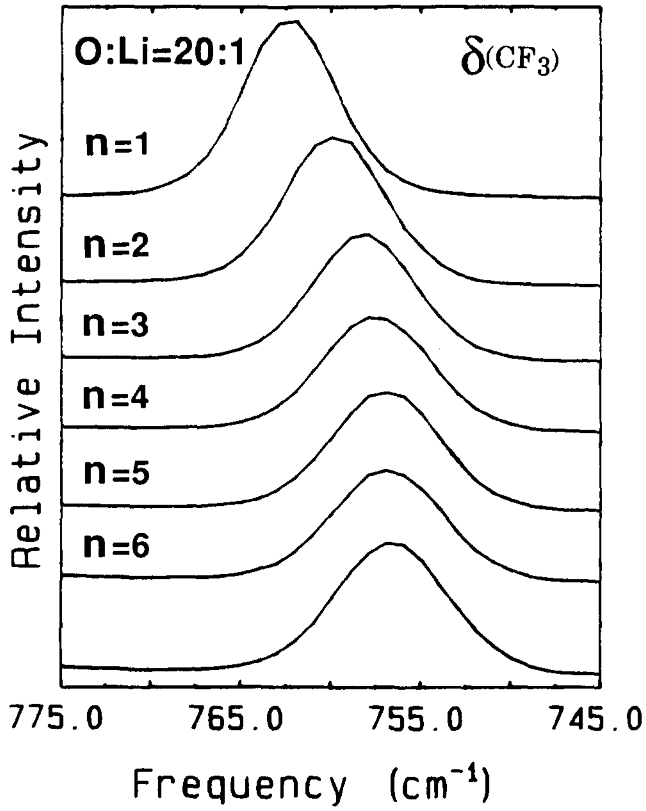

Figure 9 Raman spectra of the 20:1 complexes of HO–(CH$_2$CH$_2$O)$_n$–H with LiCF$_3$SO$_3$ in the CF$_3$ symmetric deformation region

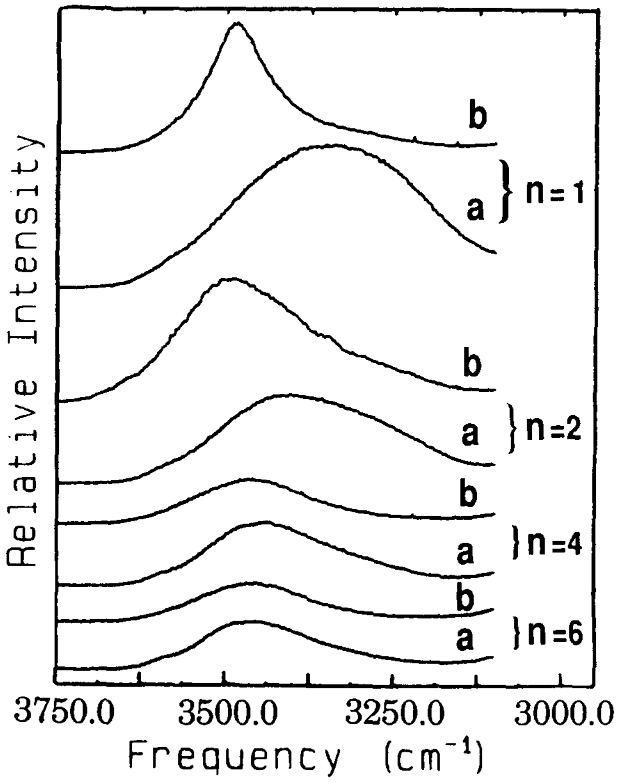

Figure 10 Raman spectra of (a) the pure diol HO–(CH$_2$CH$_2$O)$_n$–H and (b) the 3:1 complexes of HO–(CH$_2$CH$_2$O)$_n$–H with LiCF$_3$SO$_3$ in the O–H stretching region at chain lengths $n=1$, 2, 4 and 6

A quantitative measure of the electron-donating or electron-accepting properties of a solvent is the electron-pair acceptance polarity index $E_T(30)$, which is the lowest energy transition of the indicator solute 2,6-diphenyl-4-

(2′,4′,6′-triphenyl-1-pyridino)phenoxide dissolved in the solvent of interest[25]. Using this scale to estimate the relative size of the nucleophilic solvent–anion interaction, the values[26] for diethylene glycol, triethylene glycol and tetraethylene glycol are 53.8, 53.5 and 52.2 kcal mol^{-1}, respectively. The corresponding value for diethylene glycol dimethyl ether is 38.6 kcal mol^{-1}. Some idea of the significance of these differences can be gained by examining these solvents on the E_T^N scale[27], which is normalized to water and tetramethylsilane (TMS) as reference solvents according to

$$E_T^N = [E_T(\text{solvent}) - E_T(\text{TMS})]/[E_T(\text{water}) - E_T(\text{TMS})]$$

The value for diethylene glycol is 0.713 compared with 0.244 for diethylene glycol dimethyl ether. Therefore, the stronger interaction of the glycol polyethers with the triflate anion is manifested in a significantly larger bandwidth of the CF_3 symmetric deformation mode, masking the structure normally present in this region due to the various triflate ion species.

O–H stretching mode. *Figure 10* shows the O–H stretching region of the diols used in this study, comparing the pure diol (curve a) with the 3:1 diol complex (curve b) as a function of chain length. The presence and degree of hydrogen bonding in each sample is easily recognized by the shift to lower frequency and the increase in bandwidth[28]. The difference in degree of hydrogen bonding between the pure diol and the corresponding complex is seen to decrease with increasing *n*. In part this trend is due to decrease of hydrogen bonding in the pure diol with increasing chain length (see spectral curves labelled ‘a’). The same comparison of the spectra of the complex shows a somewhat smaller dependence of the band centre frequency on chain length.

DISCUSSION

In the CH_3 end-capped polyethers, the concentration of ‘free’ ions remains relatively constant after the initial increase from $n=1$ to $n=2$. However, the concentrations of the associated ionic species exhibit a marked dependence on chain length; in particular, the concentration of ion pairs increases while the concentration of aggregates decreases with increasing chain length. This pattern becomes much more pronounced at higher salt concentrations. These data suggest that the equilibrium between ion pairs and aggregates is more dependent on chain length than any equilibrium involving free ions.

The concentration dependence of ionic association is noteworthy. At each chain length, the relative concentrations of free ions, ion pairs and aggregates change somewhat between the 80:1 and 20:1 complexes. However, the greatest change is between the 20:1 and 5:1 complexes. This is not unexpected, since the 5:1 complex is a saturated system in the sense that there is approximately one lithium ion for each one or two dimethyl ether molecules. In contrast, in the 80:1 and 20:1 complexes there are a significant number of uncoordinated molecules in the system.

The effect of the end-group in these short chain polyethers is quite striking although this comparison was only made at one concentration. In the 20:1 diol complex there was no significant concentration of aggregate species as noted earlier. The dominant species is the ‘free’ ions, in contrast to the dimethyl ether system in which the dominant species are the ion pairs. However the general trend in the glycol complexes is that the relative concentration of free ions decreases and that of the ion pairs increases with increasing chain length. The dependence of the relative concentrations on chain length in *Figure 8* closely resembles the dependence of the relative concentrations on temperature, e.g. as shown in Figure 3 of reference 11. Although that study used 4000 molecular weight, hydroxy-terminated PPO complexed with sodium triflate at a 30:1 ratio, the pattern of increasing ionic association with increasing temperature is a general trend of many polymer–salt complexes. A Brillouin study of the molecular-weight dependence of structural relaxation in low-molecular-weight poly(propylene glycol) concluded that the flexibility of the chain decreases as the molecular weight of the chains decreases[29]. Hydrogen bonding interactions were assumed to play a significant role in the flexibility of the chain[29,30].

There appear to be several effects which are important in considerations of the hydrogen bonding in low-molecular-weight glycols. First, the degree of hydrogen bonding in the pure glycol depends critically upon the chain length, since the strength of the interaction markedly decreases with increasing chain length, as shown in *Figure 10*. This decrease in hydrogen bond strength argues for intermolecular rather than intramolecular hydrogen bonding. Second, complexation with a salt tends to disrupt the hydrogen bonding. In the 3:1 complex the hydrogen bonding is almost completely suppressed as deduced from insensitivity of the band centre frequency to the chain length. The interference with the formation of hydrogen bonds probably originates in the interaction between the cation and the alcoholic oxygen of the glycol. In an earlier study of low-molecular-weight PPO complexed with alkali metal thiocyanates[31,32] the cation dependence of the hydrogen-bonding frequency shift established that the cation plays the major role in the hydrogen bonding interaction.

The appearance of bands originating in the triflate ion $\delta_s(CF_3)$ deformation mode which reflect the distribution of triflate ionic species in the dimethyl ethers was noted earlier. The relatively small frequency shifts accompanying the observed band structure necessarily imply a small but non-negligible redistribution of charge within the bonding framework of the triflate ion. Since the cation interacts with the oxygen atom(s) of the triflate anion in the associated species, this in turn suggests that the π electron framework of the SO_3 end is involved in an extended bonding structure. These frequency shifts also support Shriver's contention that this mode contains a significant contribution from the C–S stretching motion.

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