The structure of associated ionic species in poly(propylene oxide)–alkali metal trifluoromethanesulphonate complexes

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This paper presents the results of Raman scattering and i.r. transmission investigations of poly(propylene oxide) ($\bar{M}_w = \sim 3000$) complexed with various concentrations of lithium, sodium and potassium trifluoromethanesulphonate. Analysis of the i.r. and polarized Raman spectra of the SO_3 stretching region, in conjunction with complementary data from other spectral regions, suggests the existence of three associated ionic species: two differently co-ordinated ion pairs and a triple ion. It is argued that the free ions which were previously postulated to exist in these polymer–salt complexes are really cation–anion pairs weakly interacting through the CF_3 end of the anion.

(Keywords: ion-conducting polymer; polymer–salt complex; ionic association; i.r. spectroscopy; Raman spectroscopy)

INTRODUCTION

Polymer electrolytes have been the focus of numerous investigations by physicists, chemists and engineers during the past decade[1,2]. Polyether and siloxane-based polymers complexed with inorganic salts have been shown to demonstrate significant levels of ionic conduction[3–6]. Potential applications of solvent-free polymer electrolytes with high ionic conductivities include high energy density batteries, specific ion electrodes, fuel cells and electrochromic displays[7].

While a great deal of progress has been made in the development of new polymer electrolytes with enhanced conducting properties, a detailed understanding of the underlying mechanism(s) of ionic conduction has lagged behind. The measurement of ionic conductivities in polymer electrolytes is relatively straightforward, yielding highly reproducible and reliable results. However, identification of each ionic species involved in charge transport and quantitative measurement of its contribution to the total ionic current have proven to be much more difficult tasks. The total ionic conductivity σ_T may be described by the relationship:

$$\sigma_T = \sum_i n_i v_i \mu_i$$

where n_i represents the number density, v_i the magnitude of charge and μ_i the mobility of charge carrier i, respectively. The counting index i runs over the number of available charge carriers present in the system. It is clear that other independent measurements must be made of n_i, v_i and μ_i in order to elucidate the separate contributions to σ from each species of charge carrier present in the system.

Cowie and Cree[8] have discussed some of the problems associated with the determination of transference numbers for the ionic species as well as the lack of consistency in those which have been reported. They also have noted that some techniques measure ion transport values from diffusional motion, which not only includes motions of the free ions but also those of ion pairs and more highly associated species. Knowledge of the microstructure of the electrolyte in the polymer is necessary to properly interpret measured transport values. Specifically, it is important to know what fraction of the complexed electrolyte is present as free ions, ion pairs, ion triplets or even more highly associated species.

In this paper, results are reported of detailed i.r. and polarized Raman spectroscopic investigations of low molecular weight poly(propylene oxide) (PPO) complexed with various concentrations of lithium, sodium or potassium trifluoromethanesulphonate ($LiCF_3SO_3$, $NaCF_3SO_3$ or KCF_3SO_3, respectively). Particular attention is focused on those regions of the spectra which display bands arising from internal vibrations of the trifluoromethanesulphonate anion. The goal of this work was to identify the number and type of ionic species present in the PPO–MCF_3SO_3 electrolytes. The PPO–MCF_3SO_3 system was chosen following the earlier work of Torell *et al.* who provided evidence of ion pairing and multiple ion aggregation in a comparative study of parallel-polarized Raman spectra of $NaCF_3SO_3$ complexed with PPO and dissolved in acetonitrile at a few concentrations[9–11].

EXPERIMENTAL

A PPO liquid polymer ($\bar{M}_w = \sim 3000$) manufactured by Dow Chemical Company was used. The polymer and

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polymer–salt complexes are viscous liquids at all temperatures and concentrations of complexed salt studied. The PPO and trifluoromethanesulphonate salts were dried under vacuum at elevated temperatures and allowed to cool in a desiccator.

Complexes were prepared by carefully weighing a small amount of PPO into a round-bottomed flask and then adding the appropriate mass of Alpha Reagent grade trifluoromethanesulphonate salt. A volume of high purity anhydrous acetonitrile approximately equal to that of the polymer was added as the secondary solvent. After dissolution, samples were heated to 80°C under vacuum for a minimum of 12 h to remove the acetonitrile and any residual water. The i.r. spectra of the resulting samples were examined to ensure that all acetonitrile had been removed.

Solvent-free PPO–MCF_3SO_3 (M = Li, Na, K) complexes were prepared in this manner with ether oxygen:metal ion ratios of 80:1, 40:1, 20:1, 15:1, 10:1, 7.5:1 and 5:1. The lower solubility of KCF_3SO_3 in PPO limited the highest concentration PPO–KCF_3SO_3 complex prepared to 10:1. Calculations of the ether oxygen:metal ion ratio were made based on an average of 50 ether oxygens per PPO molecule. All samples were colourless and of very high optical clarity.

Parallel- and perpendicular-polarized Raman spectra were collected for samples contained in capillary tubes using a standard 90° scattering geometry. Room temperature polarized Raman spectra were obtained for the uncomplexed PPO and all PPO–MCF_3SO_3 complexes. The 488.0 nm line of an argon ion laser was used for excitation at 500 mW output power. The spectra were measured at a 3 cm^{-1} spectral slit width using a system based on a 0.85 m Czerny-Turner double monochromator.

Mid i.r. transmission spectra of uncomplexed PPO and all PPO–salt complexes were acquired at room temperature on a Nicolet 200 SXV FTIR spectrometer equipped with a DTGS detector. Samples were pressed as a thin film between two potassium bromide plates using an appropriate spacer as necessary and measured by averaging 128 scans at a maximum resolution of 2 cm^{-1}.

VIBRATIONAL SPECTRA OF $CF_3SO_3^-$ IN PPO–MCF_3SO_3 COMPLEXES

The 'free' trifluoromethanesulphonate anion may be effectively described by the point group C_{3v} (assuming a staggered configuration), giving rise to $3N - 6 = 18$ normal vibrations belonging to the representations $5A_1 + A_2 + 6E$. The A_1 and E modes are both i.r. and Raman active, and bands arising from these vibrations may be easily distinguished by their characteristic depolarization ratios obtained from band intensities in perpendicular- and parallel-polarized Raman spectra. The A_2 mode is neither i.r. nor Raman active and results from the internal torsion of the anion. A normal co-ordinates analysis of the trifluoromethanesulphonate anion has been reported for the anion in concentrated (4 M) aqueous solution and mulls of the sodium and barium salts[12].

Bands arising from vibrations belonging to the A_1 and A_2 representations are non-degenerate, while those arising from vibrations belonging to the E representation are doubly degenerate. Since the observation of multiple bands arising from a single non-degenerate vibration may be interpreted as resulting from anions vibrating in distinguishably different potential energy environments, the integrated intensities of these bands may be used to determine the number of anions present in each environment.

When multiple bands are observed to arise from a degenerate vibration, the interpretation is not as straightforward. In addition to originating from anions in distinctly different environments, multiple bands may also arise from the lifting of degeneracy resulting from a breakdown in symmetry. As a consequence of this ambiguity, it is difficult to use bands arising from degenerate vibrations in a quantitative analysis; however the breakdown of symmetry observed through the splitting of bands can be an extremely powerful probe of each environment.

Bands corresponding to each of the $5A_1$ and $6E$ modes of the trifluoromethanesulphonate anion were observed in the vibrational spectra of the PPO–MCF_3SO_3 complexes. *Table 1* lists the frequencies and assignments[12] for these bands in the i.r. and polarized Raman spectra of the 10:1 PPO–MCF_3SO_3 complexes. Again, it is important to point out that bands arising from all active (A_1 and E) modes are observed. Many of the bands displayed concentration-dependent splittings and cation-dependent shifts which helped identify the number and type of ionic species present in the PPO–MCF_3SO_3 systems. Those spectral regions which were particularly useful in the identification of the ionic species present in the system are discussed in more detail in the following sections.

The $\nu_s(SO_3^-)$ region (1010–1070 cm^{-1})

Figure 1 displays the parallel-polarized Raman spectra of uncomplexed PPO and PPO–$LiCF_3SO_3$ complexes in the region in which bands arising from symmetric stretching motions of the SO_3^- end of the $CF_3SO_3^-$ anion [denoted as $\nu_s(SO_3^-)$] are observed. At low concentrations of complexed salt, the lowest frequency component at 1032 cm^{-1} provides the most intense contribution to the overall feature, and a second component at 1041 cm^{-1} may be clearly discerned on the high frequency side of the more intense component. With increasing concentration of complexed salt the relative intensity of the high frequency component is observed to increase in comparison to the intensity of the lower frequency component, and at higher concentrations of complexed salt, a third component grows in at 1050 cm^{-1} as a shoulder on the high frequency side of the second component. Only very slight shifts towards higher frequency are observed for these components with increasing concentration of complexed salt; similar shifts towards high frequency are common in the bands arising from the polymer and are believed to result from a constriction of the effective vibrational volume with increasing concentration of complexed salt. This is supported by the fact that the volume of the polymer–salt complexes has been found to decrease with increasing salt content[13–18]. Also shown in *Figure 1* are the i.r. spectra of uncomplexed PPO and each of the PPO–$LiCF_3SO_3$ complexes plotted on the same frequency scale.

Concentration profiles similar to those shown in *Figure 1* for the PPO–$LiCF_3SO_3$ complexes are observed in the corresponding spectra of the PPO–$NaCF_3SO_3$ and

Table 1 Observed frequencies and assignments for vibrational bands arising from the $CF_3SO_3^-$ anion in the 10:1 PPO-MCF_3SO_3 (M = Li, Na, K) complexes at room temperature

Frequency (cm^{-1})							
10:1 PPO-$LiCF_3SO_3$		10:1 PPO-$NaCF_3SO_3$		10:1 PPO-KCF_3SO_3			
Raman	I.r.	Raman	I.r.	Raman	I.r.	Symmetry	Assignment
208	209	207	208	208	208	*E*	$\rho_r(CF_3)$
312		312		312[a]		A_1	ν(C-S)
347	349	347[a]	349	347[a]	349[a]	*E*	$\rho_r(SO_3)$
517	517	517[a,b]	518	517	518[a]	*E*	$\delta_d(CF_3)$
573	573[a]	573	573[a]	573	574[a]	A_1	$\delta_s(SO_3)$
	640		639		639[a]	*E*	$\delta_d(SO_3)$
757	757	755	756	755	755	A_1	$\delta_s(CF_3)$
					765		
1032	1032	1032	1032	1032	1032	A_1	$\nu_s(SO_3)$
1041	1041	1038	1036	1035	1036		
1051				1046			
	1158[b]		1155[b]		1154[b]	*E*	$\nu_{as}(SO_3)$
1227	1226	1226	1225	1225	1225	A_1	$\nu_s(CF_3)$
	1257		1262		1257	*E*	$\nu_{as}(CF_3)$
	1293[b]		1288[b]		1285[b]		

[a] Band displays an unresolvable high frequency shoulder
[b] Band is difficult to resolve from underlying polymer bands

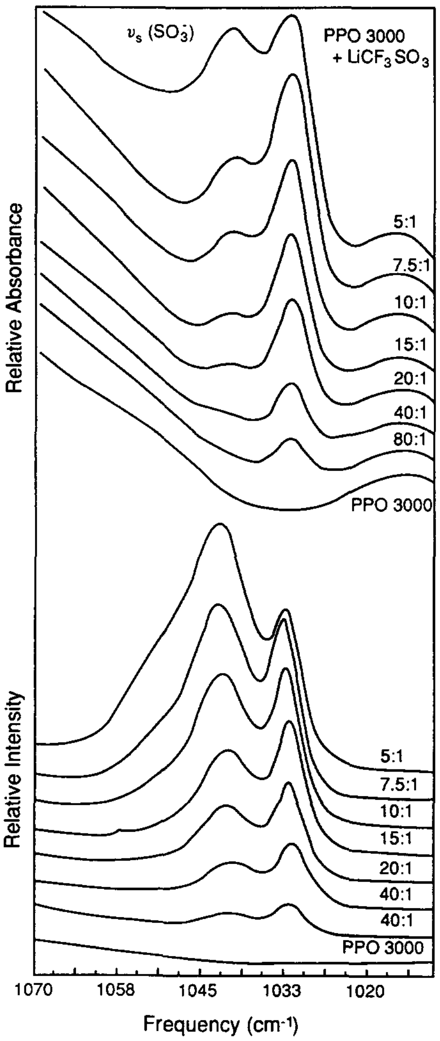

Figure 1 Comparison of room temperature parallel-polarized Raman scattering spectra and thin film i.r. transmission spectra of uncomplexed PPO and each of the PPO-$LiCF_3SO_3$ complexes in the $\nu_s(SO_3^-)$ spectral region

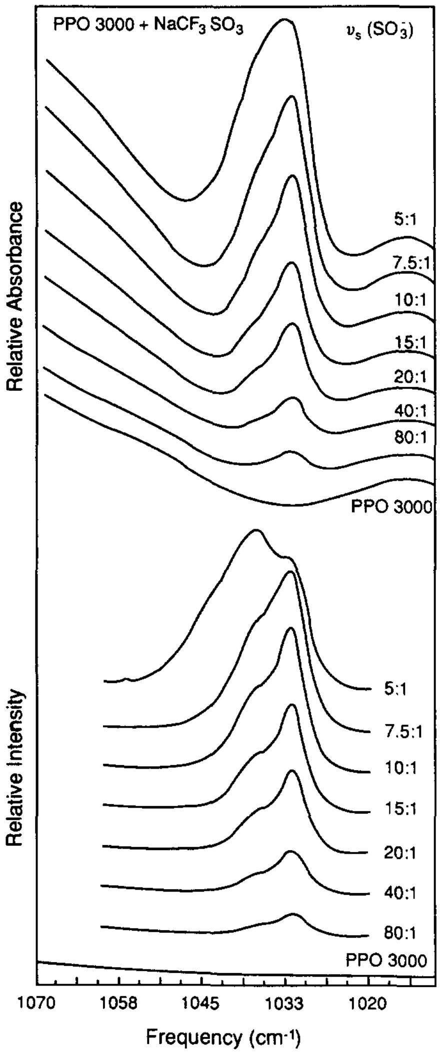

Figure 2 Comparison of room temperature parallel-polarized Raman scattering spectra and thin film i.r. transmission spectra of uncomplexed PPO and each of the PPO-$NaCF_3SO_3$ complexes in the $\nu_s(SO_3^-)$ spectral region

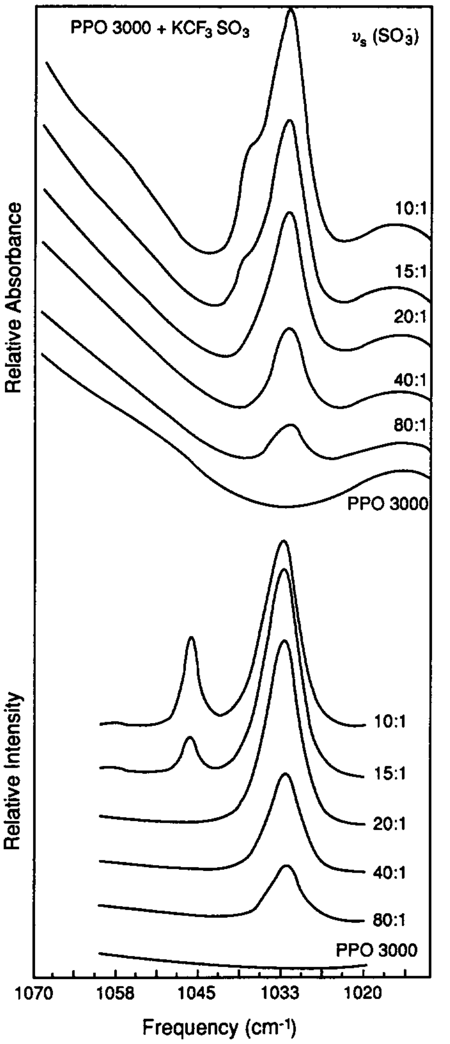

Figure 3 Comparison of room temperature parallel-polarized Raman scattering spectra and thin film i.r. transmission spectra of uncomplexed PPO and each of the PPO–KCF_3SO_3 complexes in the $\nu_s(SO_3^-)$ spectral region

PPO–KCF_3SO_3 complexes shown in *Figures 2* and *3*, respectively. It is significant that the i.r. spectrum of the 5:1 PPO–$NaCF_3SO_3$ complex in *Figure 2* displays no component corresponding to the highest-frequency component in the Raman spectrum. The absence of an i.r. feature coincident with the highest-frequency Raman feature is also noted in the i.r. spectra of the PPO–$LiCF_3SO_3$ complexes shown in *Figure 1* and is even more obvious in the i.r. spectra of the PPO–KCF_3SO_3 complexes shown in *Figure 3*. The Raman spectral data in *Figure 2* are similar to those previously reported by Schantz *et al.*[9]. *Figure 4* focuses on the $\nu_s(SO_3^-)$ region of 10:1 PPO–KCF_3SO_3, PPO–$NaCF_3SO_3$ and PPO–$LiCF_3SO_3$ complexes at room temperature and compares the parallel-polarized Raman spectra with the i.r. spectra.

The first thing to note in these data is that the low frequency component (at 1032 cm^{-1}), displays no shift with increasing salt concentration or upon substitution of the cation, while the higher frequency components display very striking cation-dependent shifts. It should also be pointed out that the highest frequency component in this region of the spectra of the PPO–KCF_3SO_3 complexes is extremely narrow and at a slightly higher frequency than would be expected if each of the complexes formed the same type of species giving rise to this band. In general, if identical types of associated species were formed, one would expect to see a cation dependence in which the frequency difference between the band arising from that associated species and the band arising from free ions would increase in the order $Li > Na > K$, consistent with the charge density and inverse mass of the cations. Exactly this behaviour is observed for the second band (1040 cm^{-1} in the Li complex, 1037 cm^{-1} in the Na complex and 1035 cm^{-1} in the K complex) which Torell *et al.*[9–11] have assigned in the sodium salt complex as arising from ion pairs, seeming to support this assignment.

The relative intensities of the second component are somewhat lower in the i.r. spectra shown in *Figures 1–3* than in the corresponding Raman spectra. It also appears that $\nu_s(SO_3^-)$ of the species giving rise to the highest-frequency component in the Raman spectra is either not observed or gives rise to a band which is shifted to significantly lower frequency in the i.r. spectra. These observations have consequences for the structure of the ionic species giving rise to the two higher-frequency components in the parallel-polarized spectra of this region.

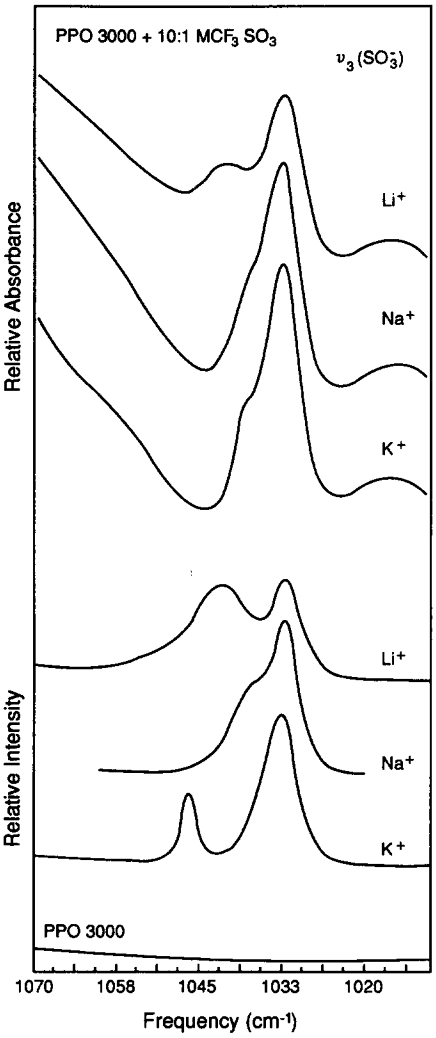

Figure 4 Comparison of room temperature parallel-polarized Raman scattering spectra and thin film i.r. transmission spectra of the 10:1 PPO–MCF_3SO_3 (M = K, Na, Li) complexes in the $\nu_s(SO_3^-)$ spectral region

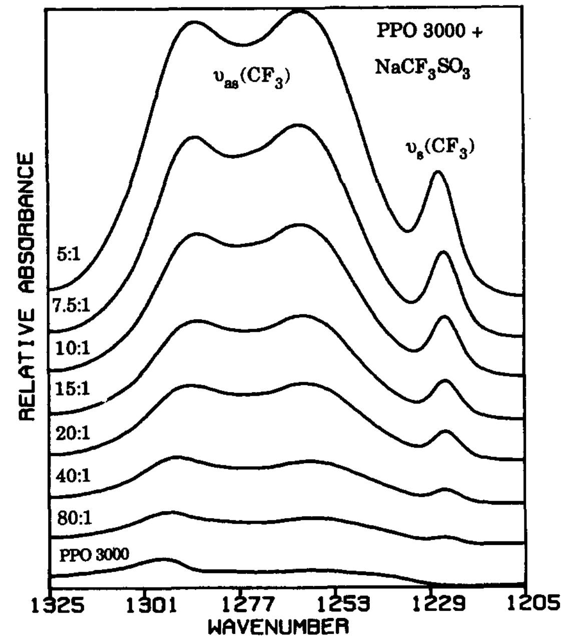

Figure 5 Thin film i.r. transmission spectra of uncomplexed PPO and each of the PPO–NaCF$_3$SO$_3$ complexes in the ν_{as}(CF$_3$) spectral region

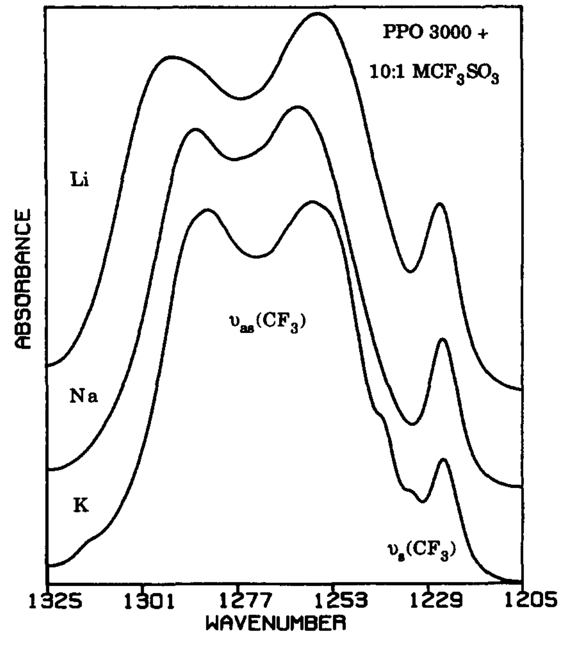

Figure 6 Thin-film i.r. transmission spectra of the 10:1 PPO–MCF$_3$SO$_3$ (M = K, Na, Li) complexes in the ν_{as}(CF$_3$) spectral region

The ν_{as}(CF$_3$) region (1205–1325 cm^{-1})

This mode results in relatively intense bands in the i.r. spectra of the PPO–MCF$_3$SO$_3$ complexes between 1205 cm^{-1} and 1325 cm^{-1}. *Figure 5* displays the i.r. spectra of uncomplexed PPO and each of the PPO–NaCF$_3$SO$_3$ complexes in this region. In the free ion this mode is doubly degenerate (belonging to the *E* representation), and would normally be expected to give rise to only one band. As may be seen in *Figure 5*, the degeneracy has been lifted, and two bands at 1262 and 1288 cm^{-1} result. It is important to note that the splitting is present and remains relatively unchanged throughout the entire range of concentration of complexed salt. The band at 1225 cm^{-1} arises from ν_s(CF$_3$) of the anion.

Figure 6 compares the i.r. spectra of the 10:1 PPO–MCF$_3$SO$_3$ (M = Li, Na, K) complexes in the ν_{as}(CF$_3$) region. The cation-dependent shifts observed for both bands resulting from ν_{as}(CF$_3$) strongly suggest that the degeneracy is broken by an interaction with the cation. These observations have very important consequences for the structure of the ionic species formed which will be discussed in greater detail in the following section.

PROPOSED STRUCTURES OF THE IONIC SPECIES

The key feature which first signalled the presence of different environments for the CF$_3$SO$_3^-$ anion in the PPO–MCF$_3$SO$_3$ complexes is the feature arising from ν_s(SO$_3^-$) of the anion which is depicted in *Figures 1–3*. This mode is non-degenerate (A_1 symmetry); therefore, the observation of multiple bands arising from this mode suggests that the anion (more particularly, the SO$_3^-$ end of the anion) vibrates in correspondingly distinct environments within the complex. Bandfitting procedures unambiguously resolve the spectra of this region for each of the PPO–MCF$_3$SO$_3$ complexes containing the highest concentration of complexed salt into three distinct bands. The results of bandfittings performed on the PPO–NaCF$_3$SO$_3$ Raman data are consistent with similar analyses presented by Schantz *et al.*[9] for this complex.

It is important to note that each of the component bands is relatively narrow. In the spectra of the PPO–NaCF$_3$SO$_3$ and PPO–LiCF$_3$SO$_3$ complexes, the lowest frequency band at 1032 cm^{-1} (which is unshifted upon substitution of the cation) is the narrowest band in the feature, and the two higher-frequency bands are somewhat broader, with the third band being slightly broader than the second. For example, in the parallel-polarized spectrum of the ν_s(SO$_3^-$) region of the 5:1 PPO–LiCF$_3$SO$_3$ complex, the first component band at 1032 cm^{-1} displays a half-width at half-maximum intensity of 2.8 ($\pm$0.1) cm^{-1}, compared to 5.2 ($\pm$0.1) and 5.5 ($\pm$0.1) cm^{-1} for the component bands at 1041 and 1050 cm^{-1}, respectively. The higher-frequency bands in the spectra of the PPO–KCF$_3$SO$_3$ complexes are much narrower than those observed in the PPO–LiCF$_3$SO$_3$ and PPO–NaCF$_3$SO$_3$ complexes, with the bandwidth of the third component at 1046 cm^{-1} being exceedingly narrow. In the parallel-polarized spectrum of the ν_s(SO$_3^-$) region of the 10:1 PPO–KCF$_3$SO$_3$ complex, the first component band at 1032 cm^{-1} displays a half-width at half-maximum intensity of 2.5 ($\pm$0.1) cm^{-1}, compared to 3.3 ($\pm$0.1) and 1.3 ($\pm$0.1) cm^{-1} for the component bands at 1035 and 1046 cm^{-1}, respectively.

To a first approximation, the breadth of each component band may be correlated to the distribution of environments for that species. This distribution must be rather narrow, since discrete bands corresponding to each species are observed rather than the broad featureless band which would most likely result if the anions existed in a broad continuum of environments. This is a very important observation, since it indicates that the anion forms only a few distinct species, and that the local environments of these species are rather homogeneous as evidenced by the bandwidths. To put this into perspective, the bandwidth of the component at 1032 cm^{-1} is four times narrower than the narrowest polymer band in the Raman spectra.

To properly consider the structures of each of the species formed, careful attention must be paid to the concentration-dependent changes in all of the anion bands. Concentration-dependent changes in bands other than those arising from $\nu_s(SO_3^-)$ may then be correlated to changes simultaneously occurring in the $\nu_s(SO_3^-)$ region of the spectra.

At very low concentrations of complexed salt, most of the anions are present in the form responsible for the band at 1032 cm^{-1}. Schantz *et al.* assigned this band to 'free' ions[9]. If only the bands arising from the SO_3^- end of the anion are considered (*Figure 4*), this seems perfectly correct. However, as shown in *Figure 5*, the i.r. spectra of the 80:1 and 40:1 PPO–MCF_3SO_3 complexes display two bands arising from $\nu_{as}(CF_3)$. The expected two-fold degeneracy of this feature has been broken. Further, as is evident in the figure, the frequency difference between the two bands is cation-dependent, necessarily requiring a weak and asymmetric interaction between the cation and the CF_3 end of the anion which lifts the degeneracy. This interaction is termed weak because the band arising from $\nu_s(CF_3)$ is not perturbed in a detectable manner. In contrast, the perturbation of the SO_3^- end is relatively strong, leading to three distinct bands in the $\nu_s(SO_3^-)$ region. Two of these bands originate from species in which the SO_3^- end of the anion interacts significantly with the cation. Therefore, the absence of discernible frequency shifts or multicomponent structure for the band arising from $\nu_s(CF_3)$ allows the assumption to be made that the perturbation at the CF_3 end of the anion is much weaker than that at the SO_3^- end.

Consequently, it appears that there really are no 'free' ions in the system; all of the anions appear to be weakly interacting with cations at the CF_3 end. The species giving rise to the band at 1032 cm^{-1} is then an anion interacting weakly with a polymer-bound cation in this fashion. *Figure 7* shows a schematic representation of this species, species A, which is the same in each of the PPO–MCF_3SO_3 (M = Li, Na, K) systems. Species A is perhaps best described as an F-co-ordinated, weak anion–cation pair.

This is indeed a surprising result. One would expect the SO_3^- end of the anion to be preferentially associated with the anion, since the negative charge of the anion is delocalized on this end. However, the spectroscopic evidence clearly shows that vibrations of the CF_3 end of the anion are perturbed in a cation-dependent manner. It is possible that steric factors underlie this observation. The cation is believed to be rather tightly solvated in a 'cage' formed by the oxygen atoms of one or more polymer chains. The smaller CF_3 end of the anion may be able to penetrate into the 'cage' more easily than the somewhat bulkier SO_3^- end. Electrostatic repulsions between oxygen atoms of the polymer and those on the SO_3^- end of the anion might also play a role.

The second ionic species, species B, is assigned by Schantz *et al.*[9] as an ion pair, a conclusion supported by the present study. Since a strongly absorbing band arising from C-O stretching motions of the polymer occurs at a frequency interferring with the observation of $\nu_{as}(SO_3^-)$, only one band could be discerned in the $\nu_{as}(SO_3^-)$ region; however, it is possible that additional band structure lies buried under the broad C-O absorption. Also, only a single very symmetric band is observed in the $\delta_d(SO_3^-)$ region of the i.r. spectra at 639 cm^{-1}. The lack of discernible splittings in these doubly degenerate features suggests a rather symmetric interaction at the SO_3^- end of the anion. The observation that the splitting in the bands arising from $\nu_{as}(CF_3)$ does not change appreciably with concentration (*Figure 5*) suggests that the second species also shares a weak interaction with a polymer-bound cation. A possible structure for the second species is proposed in *Figure 7*. Since the frequency of this second band exhibits appropriate cation-dependent shifts, it is likely that the structure of the second species is similar if not identical in all three PPO–MCF_3SO_3 systems. Species B might be described as an O-co-ordinated, relatively strong anion–cation pair.

Another important property of species B is that the molecular absorption coefficient arising from $\nu_s(SO_3^-)$ at 1036 cm^{-1} appears to be significantly reduced from that of the first species giving rise to the band at 1032 cm^{-1}. As will be discussed in the following section, the total intensity of the $\nu_s(SO_3^-)$ structure in the parallel-polarized Raman spectra was found to vary linearly with the concentration of complexed salt. Since the contribution to the total intensity arising from each band changed dramatically as a function of concentration, the effective scattering cross-sections for the $\nu_s(SO_3^-)$ vibration must be very similar if not identical for each of the three species. This was found to be true for all three PPO–MCF_3SO_3 systems. A comparison of the relative intensities of the second band to the first band in the spectra of *Figures 1–3* reveals that in all cases the i.r. intensity of the second band appears to be significantly reduced relative to the first band; this is particularly obvious in the PPO–$LiCF_3SO_3$ system.

The major clue to the identity of the third species, species C, is the absence of an i.r. band at the same frequency as the highest frequency component observed in the $\nu_s(SO_3^-)$ region of the Raman spectra. Instead, in the PPO–KCF_3SO_3 system, the concentration profiles of this region presented in *Figure 3* suggest that the shoulder observed at 1037 cm^{-1} in the i.r. spectra corresponds to the sharp band observed at 1046 cm^{-1} in the Raman spectra. Both features are first observable in the spectra of the 15:1 complex, have very similar bandwidths, and increase in relative intensity by roughly the same amount between the spectra of the 15:1 and 10:1 complexes. The most reasonable explanation for this behaviour identifies species C in the PPO–KCF_3SO_3 systems as containing a structure in which the metal ion is sandwiched between the SO_3^- ends of two trifluoromethanesulphonate anions. In this arrangement an inversion centre is introduced, establishing a mechanical coupling which splits this vibration into in-phase (i.r. active) and out-of-phase (Raman active) components. The simplest possible species consistent with this picture is the triple ion whose structure is schematically represented in *Figure 7*. However it is not possible from these data to distinguish between the triple ion and a larger aggregate containing the essential structural features previously described. Interestingly enough, another non-degenerate mode, $\delta_s(CF_3)$, displays behaviour similar to that seen in the $\nu_s(SO_3^-)$ region, but the highest-frequency feature is simultaneously observed in both the i.r. and Raman spectra. Internal rotation of the anions must limit the range of correlation introduced by the inversion centre, leaving the CF_3 groups on the two

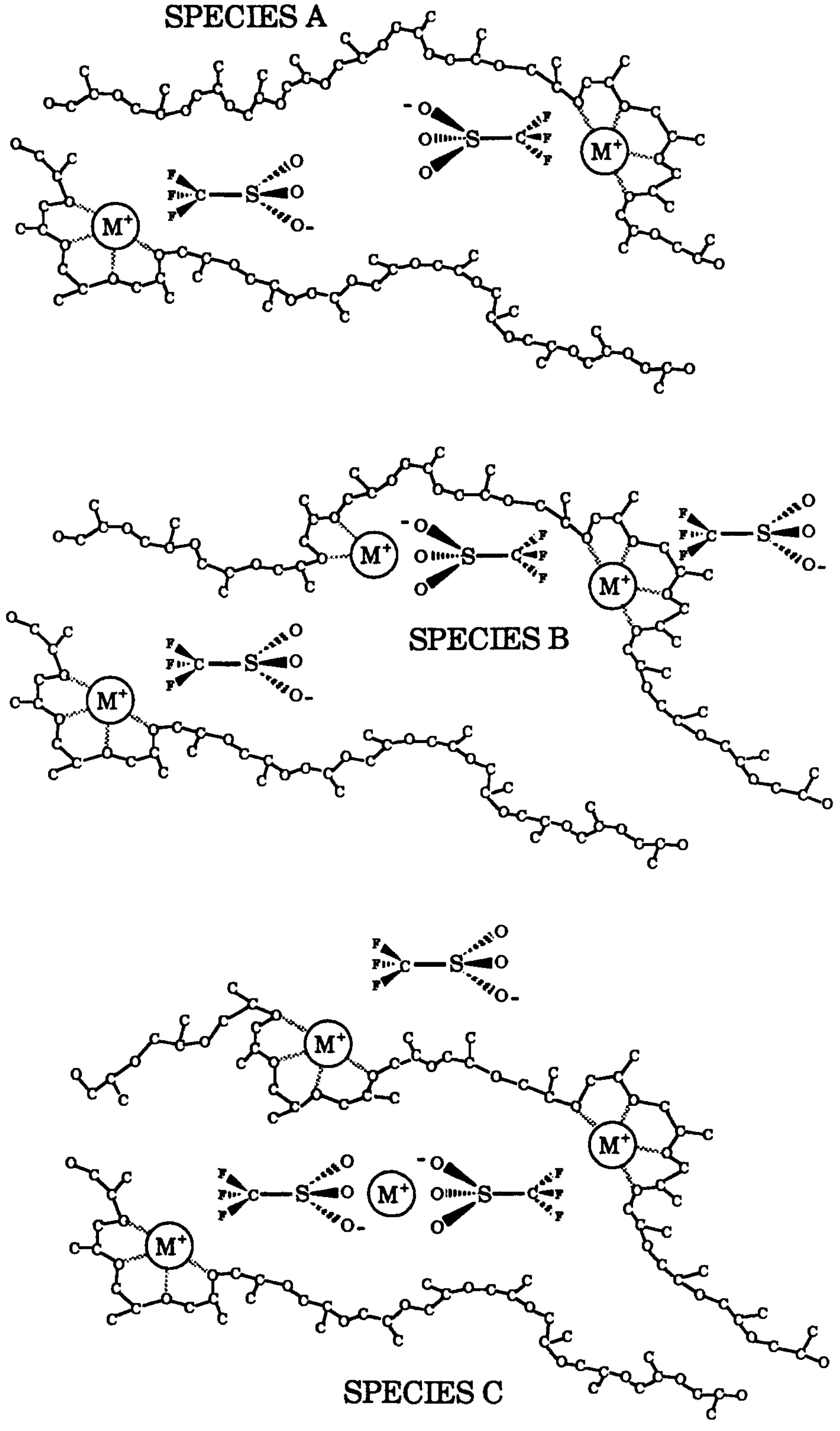

Figure 7 Schematic representations of the proposed structures for the triflate species observed in the parallel-polarized Raman spectra of the PPO–MCF_3SO_3 complexes. Species A is responsible for the $\nu_s(SO_3^-)$ band at 1032 cm^{-1} seen in all complexes at all concentrations. Species B is responsible for the $\nu_s(SO_3^-)$ band observed in the PPO–KCF_3SO_3 complexes at 1035 cm^{-1}, the PPO–$NaCF_3SO_3$ complexes at 1037 cm^{-1} and the PPO–$LiCF_3SO_3$ complexes at 1041 cm^{-1}. Species C is responsible for the $\nu_s(SO_3^-)$ band observed in the PPO–KCF_3SO_3 complexes at 1046 cm^{-1}, the PPO–$NaCF_3SO_3$ complexes at 1044 cm^{-1} and the PPO–$LiCF_3SO_3$ complexes at 1050 cm^{-1}

anions to vibrate as independent and indistinguishable units.

In the i.r. spectra of the PPO–$NaCF_3SO_3$ and PPO–$LiCF_3SO_3$ complexes, no band corresponding to species C could be unambiguously identified. For species B, $\nu_s(SO_3^-)$ is simultaneously observed at the same frequency in both the i.r. and Raman spectra. However, as argued earlier, the i.r. absorption coefficient of the second species seems to be reduced relative to that of the first species. It is entirely possible that the absorption coefficient for the third species C is further reduced, making any resulting band too weak to observe. In any case, the differences between the features observed in the Raman and i.r. spectra of the PPO–$LiCF_3SO_3$ and

PPO–$NaCF_3SO_3$ complexes are very suggestive of a highly symmetric structure similar to that of, or containing, species C suggested in *Figure 7* for the PPO–KCF_3SO_3 system.

One noteworthy point concerns the lack of a consistent frequency trend for the third species upon cation substitution (5:1 PPO–$LiCF_3SO_3$, 1050 cm^{-1}; 5:1 PPO–$NaCF_3SO_3$, 1044 cm^{-1}; 10:1 PPO–KCF_3SO_3, 1046 cm^{-1}). Also, the band at 1046 cm^{-1} in the PPO–KCF_3SO_3 systems is exceedingly narrow relative to the corresponding components in the spectra of the PPO–$NaCF_3SO_3$ and PPO–$LiCF_3SO_3$ systems. These observations seem to indicate that the structures of the third species are very similar or even identical in the PPO–$LiCF_3SO_3$ and PPO–$NaCF_3SO_3$ systems, but somewhat different in the PPO–KCF_3SO_3 system. The bandwidth of the third feature in the $\nu_s(SO_3^-)$ region of the parallel-polarized Raman spectra of the PPO–KCF_3SO_3 systems is surprisingly narrow when compared to the other component bands in this region. In fact, the bandwidth is only slightly broader than that encountered in the spectrum of microcrystalline KCF_3SO_3. However, assignment of the third band to microcrystalline KCF_3SO_3 dispersed in the polymer may be ruled out, since no corresponding band exists in the Raman spectrum of microcrystalline KCF_3SO_3. In other systems (PPO–MSCN and PPO–$NaClO_4$) we have observed that the spectrum of the microcrystalline precipitate dispersed in the complex is identical to the spectrum of the powdered microcrystalline salt[19,20]. Additionally, no evidence of a microcrystalline precipitate could be found by viewing a sample of the 10:1 PPO–KCF_3SO_3 complex under crossed-polarized light using a high-power optical microscope. Also, bands in the polymer which are very sensitive to complexation continue to change after the appearance of this extremely narrow feature. It seems clear that the salt has not precipitated out of the polymer complex. Instead, it appears that the species responsible for the very narrow third band is a highly ordered aggregate like the triple ion structure shown in *Figure 7*.

DISCUSSION AND SUMMARY

The $\nu_s(SO_3^-)$ region of the parallel-polarized Raman spectra of the PPO–MCF_3SO_3 (M = Li, Na, K) complexes displays a three-component structure attributable to three distinct environments for the $CF_3SO_3^-$ anion. A complete study of the i.r. and polarized Raman spectra leads to the suggested species shown in *Figure 7* as possible structures for the species responsible for each of the components in the $\nu_s(SO_3^-)$ region. A qualitative inspection of changes in the relative intensities of the component bands of this region with increasing concentration of complexed salt supports a stepwise equilibrium involving the three species in each of the PPO–MCF_3SO_3 systems.

In each of the PPO–MCF_3SO_3 systems, the concentration of species A reaches a maximum when the total concentration of complexed salt is between 10:1 and 7.5:1. Schantz *et al.*[9] report a similar observation in their study of the PPO–$NaCF_3SO_3$ system. This observation is particularly significant, since a maximum value in the conductivity of these systems has been observed in the same concentration range for the PPO–$LiCF_3SO_3$ and PPO–$NaCF_3SO_3$ systems[1]. Because species A would be expected to have the highest mobility of the three ionic species, it is the most efficient charge carrier in the system, and a decrease in its concentration would tend to decrease the measured conductivities. However, as pointed out by Schantz *et al.*[9], the magnitude of the observed decrease in conductivity is too large to be explained solely on the basis of a decrease in the number of charge carriers. Clearly the mobilities of the remaining charge carriers must also be greatly reduced at high concentrations of complexed salt.

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