Vibrational spectroscopic studies of low molecular weight poly(propylene oxide)–sodium thiocyanate complexes

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This paper presents the results of room temperature Raman scattering and infra-red transmission studies of a poly(propylene oxide), PPO, of average molecular weight approximately 450, complexed with varying concentrations of sodium thiocyanate, NaSCN. Observed changes in the polarized Raman and infra-red spectra of the polymer and polymer–salt complexes permit some insight into the basic nature of the complexes which are formed and the effect of successive complexation on polymer dynamics. In addition, characteristic frequencies observed for the thiocyanate anion in these complexes indicate that the thiocyanate anion is involved in contact ion pairing with the sodium cations at the nitrogen end of the anion.

(Keywords: ion-conducting polymer; polymer–salt complex; Raman spectroscopy; infra-red spectroscopy)

INTRODUCTION

Solid materials exhibiting unusually high ionic conductivities which approach liquid electrolyte values are of interest because of their potential applications in high energy density batteries, fuel cells, specific ion electrodes, gas sensors and numerous other devices[1]. Although these fast-ion-conducting solids are usually crystalline or glassy inorganic materials, solid polyethers complexed with inorganic salts have been shown to exhibit significant levels of ionic conduction[2–4] and, thus, have become the subject of increasing scientific interest. The most widely studied polyether–salt complexes are poly(ethylene oxide), PEO[5,6], or poly(propylene oxide), PPO, complexed with various inorganic salts of low lattice energies[3,6]. Although the ionic conductivity of PPO complexes is slightly lower than that of comparable PEO complexes[7], in some ways PPO is a more tractable system to study, since it can be obtained in a completely amorphous form[8], unlike PEO, which contains regions of crystallinity[9]. This paper reports the results of a detailed vibrational spectroscopic study at room temperature of a low molecular weight PPO complexed with sodium thiocyanate, NaSCN, at various concentrations. The molecular weight of the PPO used in this study is sufficiently low that the polymer and the polymer–salt complexes are viscous liquids under the conditions of the study. The relative simplicity of this system permits some insight into the basic nature of the complexes which are formed, and the effect of successive complexation on polymer dynamics.

EXPERIMENTAL

A PPO liquid polymer of average molecular weight approximately 450 manufactured by Dow Chemical Co. was used in these studies. The polymer was dried under vacuum at elevated temperatures and then mixed with appropriate amounts of Alpha Reagent grade sodium thiocyanate, NaSCN, which had been dried similarly. A volume of spectroscopic grade acetone approximately equal to that of the polymer was added to lower the intrinsic viscosity of the polymer–salt system, facilitating easier stirring and greater homogeneity. These samples were then heated to 60°C under vacuum with stirring for no less than 12 h to remove the acetone and any residual water. Five different PPO–NaSCN complexes were prepared in this manner with ether oxygen:sodium ion ratios of 40:1, 20:1, 10:1, 6:1 and 4:1. Calculations of the ether oxygen:sodium ion ratio were made based upon an average of six ether oxygens per PPO molecule.

Raman spectra were recorded at room temperature with a spectrometer system based on a 0.85 m Czerney–Turner double monochromator equipped with a thermoelectrically cooled RCA C31034 photomultiplier tube for detection. Data were collected at a spectral bandpass of 2.0 cm^{-1} using the 488.0 nm line of an argon ion laser for excitation at 500 mW. Parallel and perpendicularly polarized Raman spectra were collected of samples contained in quartz cuvettes using a standard 90° scattering geometry.

Infra-red transmission spectra were collected at room temperature on a Nicolet 200 SXV Fourier transform

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infra-red (*FT*i.r.) system equipped with an evacuable bench. Samples in the mid-infra-red spectral region were pressed as a thin film between two KBr plates.

O–H STRETCHING REGION

Polarized Raman spectra of uncomplexed PPO, as shown in *Figure 1*, contain three easily discernible features in the region between 3100 and 3700 cm^{-1}. The first feature at 3588 cm^{-1} exhibits a measured depolarization ratio of 14% and is believed to be an O–H stretching band originating from 'free' O–H groups. The broad feature centred at 3463 cm^{-1} exhibits a measured depolarization ratio of 17% and is believed to represent those O–H groups which participate in some degree of hydrogen bonding between the alcoholic proton and an ether oxygen or the oxygen of another O–H group. The band observed at 3197 cm^{-1} is not believed to result from an O–H stretch, but rather an overtone, since the same band has been shown to exhibit almost no temperature dependence in earlier studies of a PPO of molecular weight approximately 3000. The observation of an O–H stretching band at a frequency as low as 3197 cm^{-1} would most certainly require that the O–H group from which it originates be involved in extensive hydrogen bonding, causing the observed band to be much broader and demonstrate a marked temperature dependence.

Parallel polarized Raman spectra of 20:1, 10:1 and 4:1 PPO–NaSCN complexes are also shown in *Figure 1* for the region between 3100 and 3700 cm^{-1}. As the concentration of sodium ions in the complex increases, the feature at 3463 cm^{-1} becomes even broader and shifts to lower frequency. The highest frequency band at 3588 cm^{-1} decreases in intensity, almost completely disappearing into the broad centre feature in the spectrum of the 4:1 complex. The low frequency band at 3197 cm^{-1} does not appear to shift in frequency or broaden significantly, further supporting its assignment as an overtone. The low frequency shift and broadening observed in the O–H stretching bands are characteristic of increased association of the O–H group and suggest that sodium ions interact strongly with the alcoholic endgroups upon increasing concentration of complexed NaSCN. From studies of higher molecular weight systems it is clear that complexation in higher molecular weight polyethers occurs primarily through interaction of the sodium ions with ether oxygens; however, these data indicate that in the low molecular weight complexes the alcoholic oxygens also interact strongly with the sodium ions as the complex is formed.

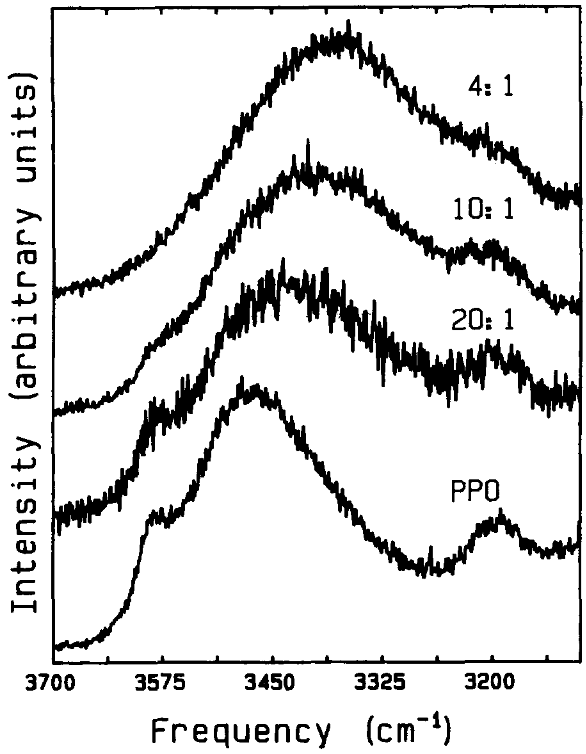

Figure 1 Parallel polarized Raman scattering spectra of uncomplexed PPO and the 20:1, 10:1 and 4:1 PPO–NaSCN complexes over the region between 3100 and 3700 cm^{-1}

Table 1 Frequencies, calculated depolarization ratios, and assignments for the C–H stretching region of the spectra of uncomplexed PPO

Frequency (cm^{-1})	$100(I_\perp/I_\parallel)$ (%)	Assignment[10]
2873	12	$\upsilon_s(CH_3)$
2902	16	$\upsilon_s(CH_2)$
2933	2	υ(CH) – tertiary carbon
2979	65	$\upsilon_{as}(CH_2)$, $\upsilon_{as}(CH_3)$

C–H STRETCHING REGION

Vibrational spectra of uncomplexed PPO contain four C–H stretching bands between 2800 and 3050 cm^{-1} which have been assigned in an earlier normal coordinate analysis[10]. Band positions, assignments, and calculated depolarization ratios in the C–H stretching region of the polarized Raman spectra of uncomplexed PPO are given in *Table 1*.

Figure 2 compares the parallel and perpendicularly polarized Raman spectra of the 4:1 complex with those of uncomplexed PPO in the region between 2800 and 3050 cm^{-1}. Using spectral deconvolution techniques, the two lowest frequency bands assigned to $\upsilon_s(CH_2)$ and $\upsilon_s(CH_3)$ were shown to be the most affected upon complexation, displaying striking shifts to higher frequency upon increasing concentration of complexed NaSCN (5 cm^{-1} shift between the spectrum of uncomplexed PPO and that of the 4:1 complex), while the two highest frequency bands shift to only slightly higher frequency (1 cm^{-1} shift between the spectrum of uncomplexed PPO and that of the 4:1 complex). This shift can be easily seen in the perpendicularly polarized Raman spectra, where the band assigned to $\upsilon_s(CH_2)$, which is too weak to be seen in the pure PPO Raman spectrum, begins to shift to higher frequency and grow in intensity with increasing salt concentration until it is the second most intense feature in the perpendicularly polarized Raman spectrum of the C–H stretching region. It is interesting to note that in the C–H stretching region, bands assigned to symmetric vibrations are the most affected upon increasing complexation.

Figure 3 compares the infra-red transmission spectrum of the 4:1 complex with that of uncomplexed PPO over the same region as that in *Figure 2*. The infra-red spectra complement the Raman spectra by clearly establishing the presence of the band assigned to the CH_2 symmetric stretching vibration, while allowing easier observation of the high frequency shifts that occur upon increasing concentration of complexed NaSCN.

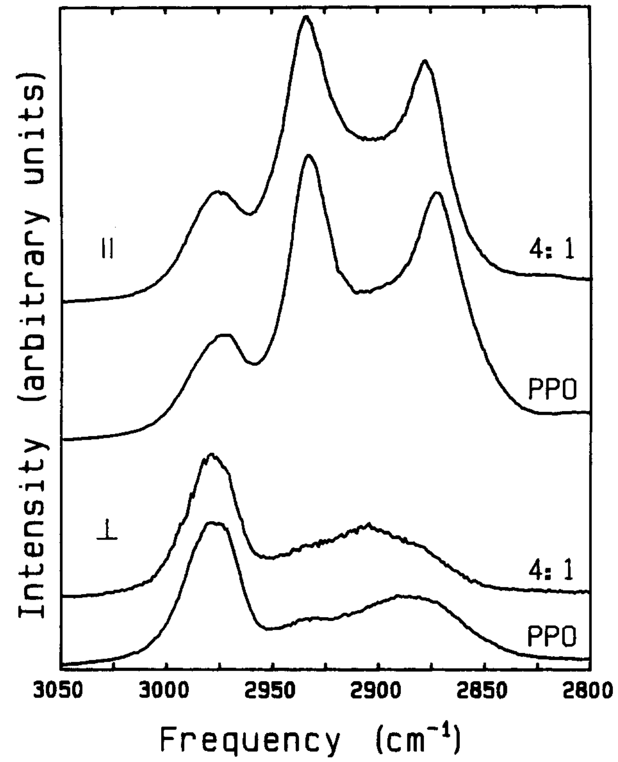

Figure 2 Parallel (upper) and perpendicularly (lower) polarized Raman scattering spectra of uncomplexed PPO and the 4:1 PPO–NaSCN complex over the region between 2800 and 3050 cm^{-1}. The intensities of the perpendicularly polarized spectra are greatly enhanced (approx. × 10), and are, therefore, not comparable with those of the parallel polarized spectra

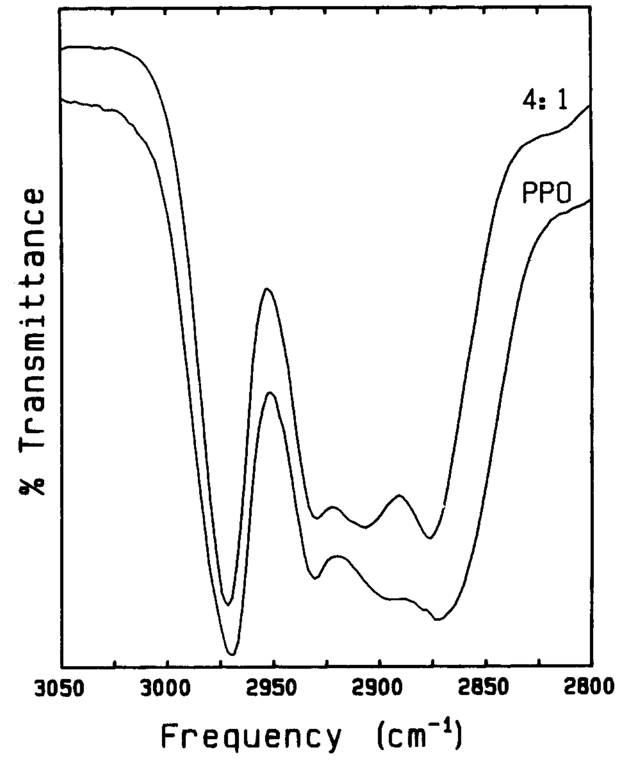

Figure 3 Thin-film infra-red transmission spectra of uncomplexed PPO and the 4:1 PPO–NaSCN complex over the region between 2800 and 3050 cm^{-1}

MID-REGION

Parallel polarized Raman spectra of uncomplexed PPO and the 20:1, 10:1 and 4:1 complexes are shown in *Figure 4* for the region between 700 and 1500 cm^{-1}. Most bands in this region exhibit slight shifts to higher frequency and small changes in relative intensity upon increasing concentration of complexed NaSCN. However, there are several features in the parallel polarized Raman spectra which exhibit more dramatic changes upon increasing complexation, and will, therefore, be discussed in greater detail.

The region between 900 and 950 cm^{-1} contains a feature which appears to consist of two bands that have been assigned to CH_2 twisting motions of the methyl group[10]. In the spectrum of uncomplexed PPO, this feature resembles a single, fairly broad band, but in the spectrum of the 4:1 complex, the higher frequency component shifts no less than 15 cm^{-1} from its position in the uncomplexed PPO, revealing that this feature truly consists of at least two bands.

Another broad feature which lies between 800 and 900 cm^{-1} is apparently composed of no fewer than three bands which differ considerably in relative intensity. The frequency and intensity of the highest frequency component at 866 cm^{-1} seems to be unaffected by complexation with NaSCN. The behaviour of the other two component bands is somewhat unusual in that they are observed in the spectrum of uncomplexed PPO, smeared out in the spectra of less concentrated complexes, and then, once again, become resolved in the spectra of the 6:1 and 4:1 complexes. The two lowest frequency component bands apparently shift approximately 10 cm^{-1} to lower frequency between the spectra of uncomplexed PPO and the 4:1 complex.

There is a polarized band at 751 cm^{-1} in the spectrum of the 4:1 complex which is absent in the spectrum of uncomplexed PPO. This band grows in intensity upon increasing concentration of NaSCN in the complex and is assigned as the S–C stretching vibration of the thiocyanate anion.

The broad feature which lies between 1050 and 1200 cm^{-1} in the parallel polarized Raman spectrum of

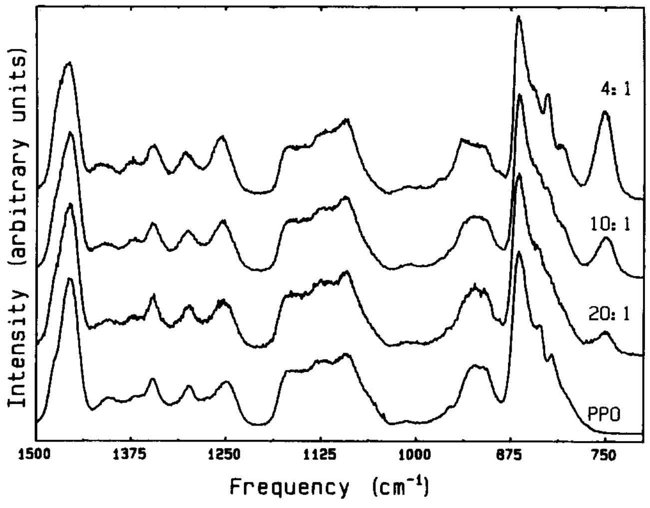

Figure 4 Parallel polarized Raman scattering spectra of uncomplexed PPO and the 20:1, 10:1 and 4:1 PPO–NaSCN complexes over the region between 700 and 1500 cm^{-1}

uncomplexed PPO consists of three discernible bands which have been assigned to skeletal vibrations of the polymer backbone arising from a combination of C–C and C–O stretching motions[10]. In the polarized Raman spectra, the three component bands which compose this feature show almost no frequency shifts, but do show some small variation in relative intensities.

Figure 5 compares the infra-red transmission spectrum of the 4:1 complex with that of uncomplexed PPO. The infra-red spectra contain a number of bands which are also observed in the Raman scattering spectra shown in *Figure 4*. The infra-red spectra reveal a remarkable splitting of the broad feature between 1050 and 1200 cm^{-1} upon increasing concentration of complexed NaSCN. The splitting does not seem to result from frequency shifts, but appears as though one or more of the component bands has narrowed upon increasing complexation. The observation that bands in the same region of the polarized Raman spectra exhibit very little change is very surprising in light of the splitting displayed by the infra-red spectra; however, failure to observe frequency shifts in the polarized Raman spectra is consistent with the suggestion that the observed splitting in the infra-red spectra originates in the narrowing of one or more of the component bands composing this feature.

LOW FREQUENCY REGION

Parallel polarized Raman spectra of uncomplexed PPO and the 20:1, 10:1 and 4:1 complexes are shown in *Figure 6* for the region between 100 and 600 cm^{-1}. The spectrum of uncomplexed PPO has a band centred at roughly 504 cm^{-1} which undergoes an apparent growth in intensity on its high frequency side upon complexation and increasing concentration of NaSCN in the complex. This apparent increase in high frequency intensity is the result of the growth of a new feature centred at 524 cm^{-1} which may be assigned as the band arising from the internal bending motion of the thiocyanate anion. This assignment is supported by the relatively strong scattering intensity displayed by this band in the perpendicularly polarized Raman spectra of the PPO–NaSCN complexes.

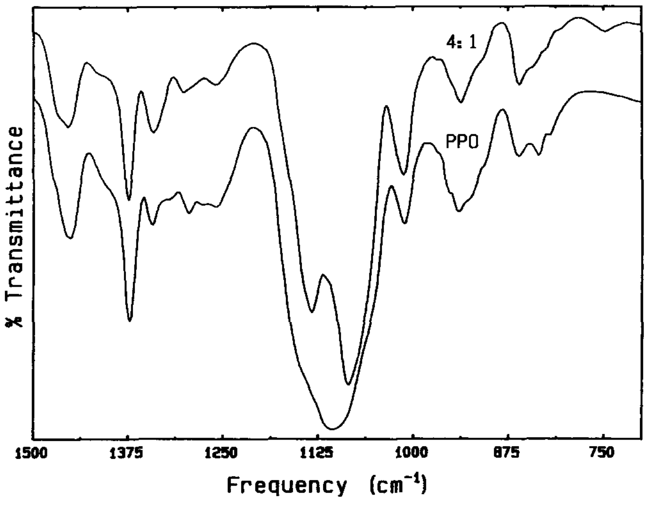

Figure 5 Thin-film infra-red transmission spectra of uncomplexed PPO and the 4:1 PPO–NaSCN complex over the region between 700 and 1500 cm^{-1}

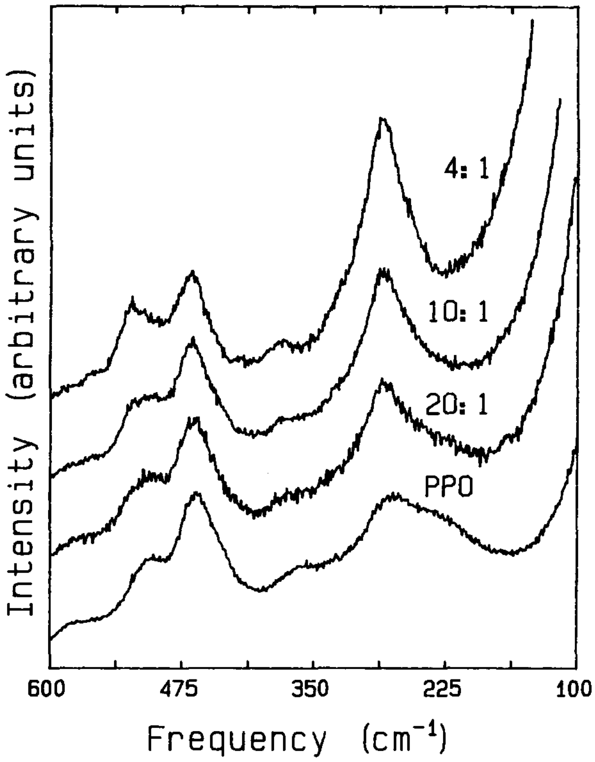

Figure 6 Parallel polarized Raman scattering spectra of uncomplexed PPO and the 20:1, 10:1 and 4:1 PPO–NaSCN complexes over the range between 100 and 600 cm^{-1}

In the spectrum of uncomplexed PPO, the region between 150 and 350 cm^{-1} is dominated by a very broad band centred at roughly 255 cm^{-1} with a high frequency shoulder at 282 cm^{-1}. As the concentration of NaSCN in the complex is increased, the entire feature appears to narrow and display a corresponding increase in intensity. Deconvolution analysis shows that the apparent narrowing of the entire feature results from the growth in intensity of a band centred at 287 cm^{-1} in the spectrum of the 4:1 complex. This region of the parallel polarized Raman spectra was best described in the band deconvolution procedure using an exponential function to model the behaviour of the apparent laser wing and Gaussian functions to model both the underlying broad band and the somewhat narrower band which grows into the spectra upon increasing complexation with NaSCN.

The growth in intensity appears at a frequency very near that of the original high frequency shoulder at 282 cm^{-1} in the spectrum of uncomplexed PPO. Since most bands in the Raman spectra have demonstrated a high frequency shift upon increasing concentration of NaSCN in the complex, it seems reasonable that the band responsible for the high frequency shoulder in the spectrum of uncomplexed PPO would display a similar shift. In this case, it is possible that the observed growth in intensity results from an increase in the Raman scattering intensity of this band.

It is important to note that this feature, which is introduced upon complexation of the polymer, does not result from the metal–oxygen stretching mode which is observed at roughly 190 cm^{-1} in far-infra-red transmission spectra. Although bands in the vicinity of 287 cm^{-1} have not been assigned for PPO, bands very near this frequency have been assigned to a combination of C–C–O and C–O–C bending motions coupled with torsions along the polymer backbone for PEO[11]; an analogous assignment seems reasonable for PPO. Assignment of bands appearing in this region to vibrations of this type is further supported by our observation that the broad low frequency feature appears to be the superposition of a large number of component bands. The parallel polarized Raman spectrum of propylene glycol contains one relatively narrow band in this region, and the parallel polarized Raman spectra of dipropylene glycol and tripropylene glycol contain two and three bands, respectively.

THIOCYANATE ANION INTERNAL VIBRATIONS

Three bands observed in Raman scattering spectra of the 4:1 complex at 2062, 751 and 524 cm^{-1} may be assigned to the υ_1, υ_3 and υ_2 (doubly degenerate) vibrational modes of the thiocyanate anion, respectively. The three modes υ_1, υ_3 and υ_2 have also been labelled υ_{CN}, υ_{SC} and δ_{SCN^-} in group frequency terminology representing the internal coordinate most displaced by the normal mode of vibration. These assignments are supported by the observation that the band at 751 cm^{-1} is completely polarized, whereas the two bands appearing at 2062 and 524 cm^{-1} are not polarized, as would be expected. In fact, the band appearing at 524 cm^{-1} is not easily seen in the parallel polarized Raman spectra shown in *Figure 6*, but its relatively strong scattering intensity in perpendicularly polarized Raman spectra allows its easy assignment. Throughout the spectra of the PPO–NaSCN complexes, bands arising from the thiocyanate anion displays no asymmetries or shoulders, and between the spectra of the 40:1 and 4:1 complexes, υ_1 and υ_3 display small high frequency shifts of 2 cm^{-1}, while υ_2 displays a greater high frequency shift of approximately 10 cm^{-1}.

A number of authors have recently probed the structure of solvated NaSCN in media of low permittivity[12–14], and characteristic vibrational frequencies for free thiocyanate anions (υ_1, 2053; υ_3, 735; υ_2, 465 cm^{-1}), NaSCN contact ion pairs (υ_1, 2056; υ_3, 760; υ_2, 475 cm^{-1}) and dimers (υ_1, 2052; υ_3, 772; υ_2, 489 and 478 cm^{-1}) have been reported[13]. In addition, the thiocyanate anion is known to be ambidentate, and certain shifts in frequency relative to the free anion may be used as an accurate means of determining its mode of coordination. Specifically, coordination at the nitrogen end of the anion increases υ_1 and υ_3, while coordination at the sulphur end of the anion increases υ_1, but decreases υ_2 and υ_3[13,15,16].

Based upon the above criteria, it seems fairly clear that the only thiocyanate anion species which is spectroscopically detected in the PPO–NaSCN complexes is the $Na^+ \cdot NCS^-$ contact ion pair coordinated at the nitrogen end of the anion. There is no evidence of bands arising from either the free anion or the dimer. The existence of NaSCN as contact ion pairs is further supported by our unreported observation of cation ($M^+ = Li^+, Na^+, K^+$) dependent shifts in the characteristic vibrational frequencies of the thiocyanate anion in PPO–MSCN complexes.

SUMMARY

The guiding idea behind this work was to characterize the nature of interactions between the complexed salt, NaSCN, and its polymer host, PPO. In this study, vibrational spectroscopy was used to follow changes in the vibrational dynamics of PPO, which are introduced upon complexation with NaSCN. Those PPO bands which were affected by complexation were carefully studied over a wide range of concentrations of complexed NaSCN. In addition, the polyatomic thiocyanate anion possesses internal vibrational degrees of freedom, giving rise to bands which were used to probe the environment and structure of the complexed NaSCN.

In higher molecular weight polyethers, it is clear that complexation results from coordination between ether oxygens along the polymer backbone and metal cations, but in lower molecular weight polyethers, the O–H termini play a very important role in the complexation process. In fact, the O–H stretching region is one of the first regions in the vibrational spectra of PPO to display discernible changes upon complexation with NaSCN. Since the oxygen atoms of O–H termini are expected to be considerably more basic than ether oxygens, it is possible that O–H termini are preferentially coordinated. At the very least, one would expect that the interaction between the more basic oxygen atoms of O–H termini and sodium cations would be stronger than similar interactions between ether oxygens and sodium cations. These data are insufficient to conclude that the O–H termini are preferentially coordinated, but very significant changes observed in the O–H stretching region of low concentration complexes clearly indicate that there is a substantial interaction between the O–H termini and sodium cations in the low molecular weight PPO–NaSCN complexes.

The four discernible bands in the C–H stretching region demonstrate high frequency shifts upon increasing complexation. The two bands which are most affected are those which have been assigned to symmetric stretches of CH_2 and CH_3. It is not surprising that the symmetric stretch of the CH_2 group would be perturbed by coordination of an adjacent ether oxygen with a sodium cation, but it is surprising that the symmetric stretch of the CH_3 group displays a greater frequency shift than the tertiary CH stretch of the chiral carbon atom, which is also adjacent to an ether oxygen.

Splitting of the broad feature between 1050 and 1200 cm^{-1} in the infra-red spectra is very interesting, since polarized Raman spectra of this region contain three overlapping, but discernible bands which demonstrate almost no changes upon increasing complexation with NaSCN. Careful study of the infra-red spectra indicates that the observed splitting is not the result of frequency shifts. The idea that the splitting does not result from frequency shifts is further supported by a very close correlation between the two bands which split out of the broad feature in the infra-red spectra and the two lowest frequency bands in the same region of the Raman spectra. It seems likely that these bands are simultaneously observed in both infra-red and Raman spectra of PPO. In this case, the splitting may result from a narrowing of the bandwidths of these two bands in the infra-red spectra.

Bands in the region between 1050 and 1200 cm^{-1} have been attributed to combinations of C–C and C–O stretching vibrations along the polymer backbone. Those vibrations in which the C–O bond distance is most displaced result in the largest change in the dipole moment, causing bands arising from these vibrations to be relatively strong absorbers in infra-red spectra. Since the two bands which split out of the broad feature are the strongest absorbers in the infra-red spectra of PPO, they result from normal modes of vibration containing rather large C–O stretching components. If bandwidth narrowing is responsible for the splitting of the two bands, it may be caused by sodium cations which coordinate ether oxygens forming regions of greater local symmetry and homogeneity. Greater local homogeneity would lessen the diversity of potential energy environments for C–O stretching leading to narrowing of the bands and the observed splitting.

The idea of increased local homogeneity is also suggested by deconvolution analyses of the polymer bands most affected by complexation. Many of the polymer bands are best described by Gaussian bandshapes, particularly those bands which are most affected upon complexation. The observation that bands most affected by complexation become more Gaussian in shape upon increasing complexation is extremely suggestive of a more normal (Gaussian) distribution of potential energy environments for the vibrational modes from which these bands arise.

Finally, observed vibrational frequencies of the thiocyanate anion in the PPO–NaSCN complexes indicate that the thiocyanate anion is contact ion paired with a sodium cation at the nitrogen end of the anion. Since the υ_1 and υ_3 vibrational modes of the anion were observed as single, symmetric features, in all concentrations studied, neither the free anion or any other associated species was detected. The bending mode υ_2 at 524 cm^{-1} is observed at a much higher frequency than previously reported for thiocyanate salts dissolved in media of low permittivity[12–14].

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