

Vibrational spectroscopic studies of cation effects in low molecular weight poly(propylene oxide) complexed with lithium, sodium and potassium thiocyanate

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This paper presents the results of room temperature Raman scattering and infrared transmission investigations of an approximately 450 average molecular weight poly(propylene oxide), PPO, complexed with varying concentrations of lithium, sodium and potassium thiocyanate. The strength of interaction between the metal cation and the polymer is observed to increase in the order $\text{Li} > \text{Na} > \text{K}$. Spectral changes in the O–H stretching region show that the cations interact with the alcoholic oxygen atoms as well as the ether oxygen atoms. Frequency shifts in the C–H stretching region combined with the growth of splittings and structure in lower frequency bands suggest that increasing complexation is accompanied by changes in the polymer backbone dynamics and structure. The metal–oxygen stretching band is easily identified in the infrared transmission spectra. Finally, cation-dependent frequency shifts of the thiocyanate ion bands indicate the formation of contact ion pairs coordinated at the nitrogen end of the anion.

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

INTRODUCTION

Polymer electrolytes have been the focus of numerous investigations by physicists, chemists, and engineers during the past ten years^{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 displays⁷. A fundamental understanding of the mechanisms of ion transport in polymers is required for the intelligent development of new polymer electrolyte systems.

A variety of physical and spectroscopic techniques have been used in the quest for insight into these systems, including audio-frequency electrical conductivity⁸, differential scanning calorimetry^{8,9}, thermo-mechanical analysis⁸, dielectric relaxation¹⁰, X-ray absorption¹¹, infrared and Raman spectroscopy^{12–14}, and nuclear magnetic resonance (n.m.r.)^{6,8,9,15–19}. Systems based on poly(ethylene oxide), PEO, poly(propylene oxide), PPO, and polyether block copolymers of poly(dimethylsiloxane), PDMS, complexed with low lattice energy salts have been widely investigated. Spectroscopic investigations of PEO are complicated by regions of crystallinity in the polymer²⁰. The ionic conductivity of PPO complexes is slightly lower than that of comparable complexes of PEO or PDMS blends²¹; however, PPO can be obtained as a completely amorphous material²².

This fact, combined with the relatively simple polymer backbone structure, renders the PPO–salt systems ideal for fundamental investigations of conducting polymer systems.

Recently, we presented changes in regions of the vibrational spectra which are introduced upon formation of low molecular weight PPO complexes with NaSCN¹⁴. This effort provided some insight into the nature of the complexes formed and the effect of successive complexation on polymer dynamics. In addition, it was observed that considerable association of the sodium cation and thiocyanate anion are implied by the frequencies of bands arising from the thiocyanate anion internal vibrations.

This paper reports the results of detailed room temperature infrared and polarized Raman spectroscopic investigations of low molecular weight PPO complexed with various concentrations of lithium, sodium, and potassium thiocyanate. Particular attention is focused on those regions of the spectra which display differences upon substitution of one alkali metal cation for another, providing considerable insight into the cation dependence of the dynamics and structural changes in PPO–salt complexes. Another feature that may be studied in these cation substitution experiments is the nature of ionic association in these polymer–salt systems. The thiocyanate anion was chosen as the common counterion because of our previous experience with it^{12–14}.

EXPERIMENTAL

An approximately 425 average molecular weight PPO liquid polymer manufactured by Dow Chemical Company

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was used in these studies. The molecular weight is sufficiently low that the polymer and polymer-salt complexes are viscous liquids at all temperatures and concentrations of complexed salt studied. The PPO and thiocyanate 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 bottom flask and then adding the appropriate mass of Alpha Reagent grade lithium thiocyanate, LiSCN, sodium thiocyanate, NaSCN, or potassium thiocyanate, KSCN. A volume of spectroscopic grade acetone approximately equal to that of the polymer was added to lower the viscosity of the polymer-salt system, to facilitate easier stirring and greater homogeneity. Samples were stirred at room temperature for at least 1 h, allowing adequate time for all of the salt to dissolve. After dissolution, samples were heated to 60°C under vacuum for a minimum of 12 h to remove the acetone and any residual water. To ensure that all acetone and residual water were removed, infrared spectra of the samples were checked for bands arising from either compound.

Solvent-free PPO-MSCN ($M = \text{Li, Na, K}$) complexes were prepared in this manner with ether oxygen:sodium ion ratios of 40:1, 20:1, 10:1, and 5:1. Due to the lower limiting solubility of KSCN in PPO, the highest concentration PPO-KSCN complex prepared was 8:1. 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 Czerny-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 capillary tubes using a standard 90° scattering geometry. Polarized Raman spectra were obtained for the uncomplexed PPO, PPO-NaSCN complexes and PPO-KSCN complexes. All PPO-LiSCN complexes were clear, but slightly yellow in colour, causing them to be unstable in the laser beam at the two wavelengths (488.0 and 514.5 nm) of the argon ion laser.

Mid-infrared transmission spectra were acquired at room temperature using a Nicolet 200 SXV FTi.r. system equipped with an evacuable bench and DTGS detector. Mid-infrared spectra were collected over the range $4000\text{--}400 \text{ cm}^{-1}$ by averaging 128 scans at a maximum resolution of 2 cm^{-1} . Samples in the mid-infrared spectral region were pressed as a thin film between two potassium bromide plates. Mid-infrared spectra of uncomplexed PPO and all PPO-salt complexes were obtained.

Far-infrared transmission spectra were acquired at room temperature using a Nicolet 20F FTi.r. equipped with a proprietary silicon beamsplitter and DTGS detector. During data acquisition, the optics of the 20F bench were held under an 80 mtorr* vacuum, while the sample was contained in a small chamber purged with dry nitrogen gas. Far-infrared spectra were collected over the range $650\text{--}50 \text{ cm}^{-1}$ by averaging 128 scans at a maximum resolution of 4 cm^{-1} . Samples in the far infrared spectral region were pressed between two 2 mm

polyethylene plates using an appropriate spacer. Far infrared spectra of uncomplexed PPO and all PPO-salt complexes were obtained.

O-H STRETCHING REGION

In the earlier study of the vibrational spectra of complexes of PPO and NaSCN¹⁴, it was observed that, upon complexation with NaSCN, the O-H stretching region of PPO displays low frequency shifts and broadening of all bands assigned to O-H stretching. These frequency shifts and band broadenings are characteristic of increased association of the O-H group and suggest that sodium ions interact strongly with the alcoholic end groups upon increasing concentration of complexed NaSCN.

In the present study, it was observed that the vibrational spectra of PPO-LiSCN and PPO-KSCN complexes display effects almost identical to those observed in the spectra of PPO-NaSCN complexes. Figure 1 compares the infrared transmission spectra of uncomplexed PPO and the PPO-MSCN complexes containing the highest concentration of each thiocyanate salt under study. Only small differences in the position and breadth of the band resulting from O-H stretching of associated alcoholic termini can be discerned from spectra of the three highest concentration PPO-MSCN complexes. The associated O-H stretching bands show slight trends of broadening and shifting to lower frequency in the order $\text{Li} > \text{Na} > \text{K}$.

It is likely that effects due to the relative strength of interactions with the cations provide the dominant contribution to the cation-dependent changes observed in the O-H stretching bands. In this case, it would be expected that a lithium cation would interact more strongly with the alcoholic oxygen than a sodium cation and, similarly, sodium more strongly than potassium. Trends observed in the vibrational spectra of the O-H

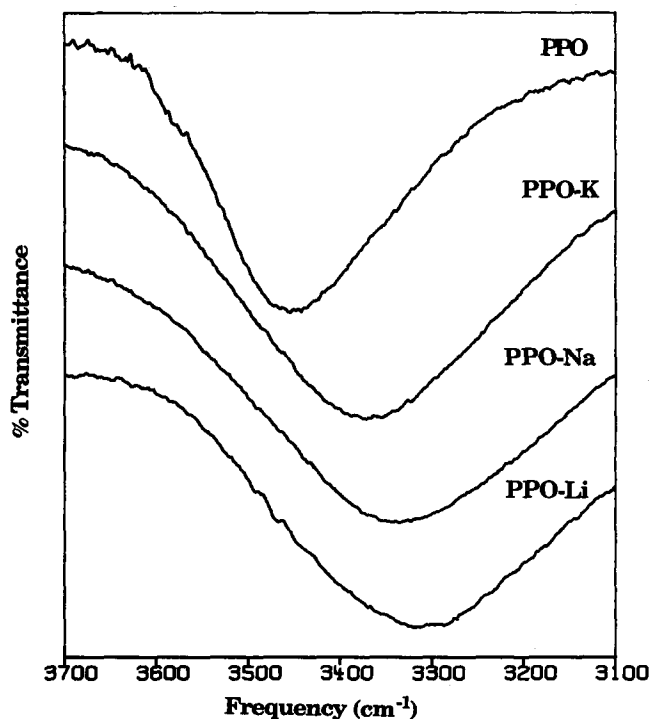


Figure 1 Thin-film infrared transmission spectra of uncomplexed PPO and the highest concentration PPO-MSCN complexes over the region $3100\text{--}3700 \text{ cm}^{-1}$

* 1 torr \approx 133 Pa

stretching region are certainly consistent with the behaviour expected based on the cation charge density.

C-H STRETCHING REGION

Vibrational spectra of uncomplexed PPO contain four discernible C-H stretching bands between 2800 and 3050 cm^{-1} which have been assigned in an earlier normal coordinate analysis²³. In the previous study of the vibrational spectra of complexes of PPO and NaSCN¹⁴, it was observed that, upon complexation with NaSCN, all bands in the C-H stretching region of PPO shift to slightly higher frequencies. Using spectral deconvolution techniques, it was shown that the two lowest frequency bands assigned to symmetric stretches of the methylene (CH_2) and methyl (CH_3) groups were the most affected upon complexation. The two lower frequency bands display shifts of $\approx 5 \text{ cm}^{-1}$ between spectra of uncomplexed PPO and the 4:1 PPO-NaSCN complex, while the higher frequency bands assigned to asymmetric C-H stretching show only small ($\approx 1 \text{ cm}^{-1}$) shifts.

In the present study, the extent of the changes observed in the vibrational spectra are found to be highly cation dependent. Figure 2 presents infrared transmission spectra of uncomplexed PPO, and the highest concentration PPO-MSCN complexes over the region 2800–3050 cm^{-1} . The effects of successive complexation observed in the C-H stretching region of the vibrational spectra are very similar for each polymer-salt complex. However, comparison of the spectra shown in Figure 2 demonstrates that the effect of complexation with MSCN becomes stronger in the order $\text{Li} > \text{Na} > \text{K}$. These observations

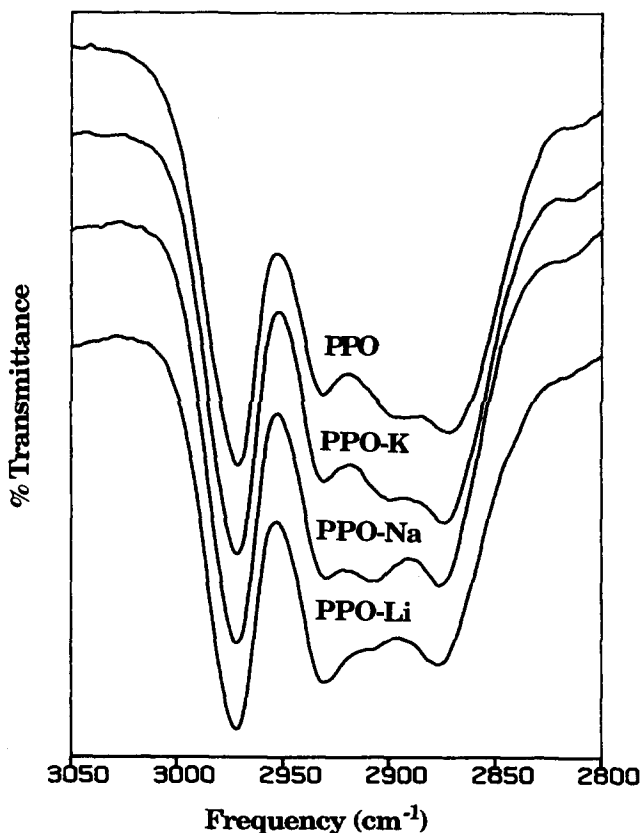


Figure 2 Thin-film infrared transmission spectra of uncomplexed PPO and the highest concentration PPO-MSCN complexes over the region 2800–3050 cm^{-1}

imply that the interactions which are responsible for the high frequency shifts of the bands arising from C-H symmetric stretching are very weak when PPO is complexed with KSCN, but become stronger when PPO is complexed with NaSCN. Similarly, these interactions are even stronger when PPO is complexed with LiSCN. The increasing degree of interaction observed in the vibrational spectra correlates well with the decreasing size of the cation and the corresponding increase in charge density. These observations, considered together with other data to be described in later sections, suggest that the interactions affect the dynamics of the polymer backbone. This conclusion will be discussed more thoroughly in the summary section.

MID I.R. REGION

In the earlier study of complexes of PPO and NaSCN¹⁴, many bands in the mid-infrared spectral region displayed significant changes upon complexation with NaSCN. Figure 3 presents infrared spectra of uncomplexed PPO and the highest concentration PPO-MSCN complexes over the region 700–1600 cm^{-1} . Upon formation of a polymer-salt complex, most bands in this region exhibit slight shifts to higher frequency and small changes in relative intensity. Nearly every band in the mid-infrared spectral region of PPO which was sensitive to complexation with NaSCN also demonstrates marked cation dependence upon complexation with LiSCN or KSCN.

Two broad features in the mid-infrared spectral region also exhibit marked cation dependence in response to complexation. The first is the broad band centred at $\approx 1300 \text{ cm}^{-1}$, which displays small frequency shifts upon substitution of one cation for another and increases in intensity in the order $\text{Li} > \text{Na} > \text{K}$. The second is a broad feature between 800 and 880 cm^{-1} which is composed of a number of component bands that seem to show slight frequency shifts and differences in relative intensity dependent upon the cation in the PPO-MSCN complex. Bands in the region between 800 and 880 cm^{-1} have been assigned to deformation vibrations of the CH , CH_2 and CH_3 groups²³, strengthening the suggestion that different cations show distinct effects on the dynamics of the polymer backbone.

One very interesting feature which shows substantial changes upon complexation with all metal salts studied, but no distinct cation dependence, is the broad band which lies between 1050 and 1200 cm^{-1} in the infrared spectrum of uncomplexed PPO. Polarized Raman spectra reveal that this broad feature consists of at least three discernible bands, which have been assigned to polymer backbone vibrations consisting of combinations of C-C and C-O stretching motions²³. In the polarized Raman spectra, the three component bands which make up this feature show almost no frequency shifts upon complexation, but do display very small variations in relative intensities. However, the infrared spectra exhibit a remarkable splitting of this feature upon increasing concentration of complexed salt, which can be seen in Figure 3. This 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 surprising in the light of the splitting displayed in the infrared spectra. However, the failure to observe

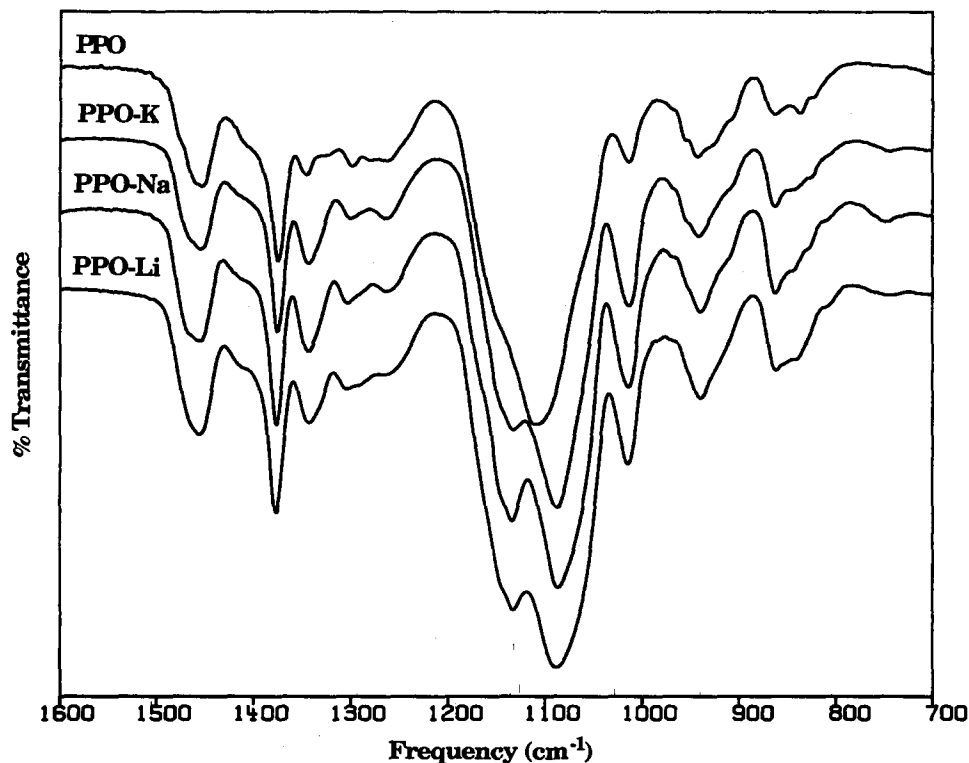


Figure 3 Thin-film infrared transmission spectra of uncomplexed PPO and the highest concentration PPO-MSCN complexes over the region 700-1600 cm^{-1}

frequency shifts in the Raman spectra is consistent with the suggestion that the observed splitting in the infrared spectra results from the narrowing of one or more of the component bands making up this feature.

LOW FREQUENCY REGION

In the earlier study of complexes of PPO and NaSCN¹⁴, this region of the vibrational spectra was shown to contain a number of polymer bands which are very sensitive to complexation. In addition, new bands were observed which were introduced upon complexation, and grew in intensity with increasing concentration of complexed NaSCN. In the present work, the low frequency spectra of each polymer-salt complex show similar changes with a striking cation dependence.

Figure 4 presents the parallel polarized Raman spectra of uncomplexed PPO, the 5:1 PPO-NaSCN complex and the 8:1 PPO-KSCN complex over the region 100-650 cm^{-1} . The polymer band centred at $\approx 504 \text{ cm}^{-1}$ in the spectrum of uncomplexed PPO displays an apparent growth in intensity on its high frequency side in the spectrum of the 5:1 PPO-NaSCN complex. This new feature, centred at 524 cm^{-1} , is 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. In the spectra of the PPO-KSCN complexes, this band is less intense and shifted to slightly lower frequency, making it unresolvable in the parallel polarized Raman spectra, but easily discernible in the perpendicularly polarized Raman spectra.

In the parallel polarized Raman spectrum of uncomplexed PPO, the region between 150 and 350 cm^{-1} is

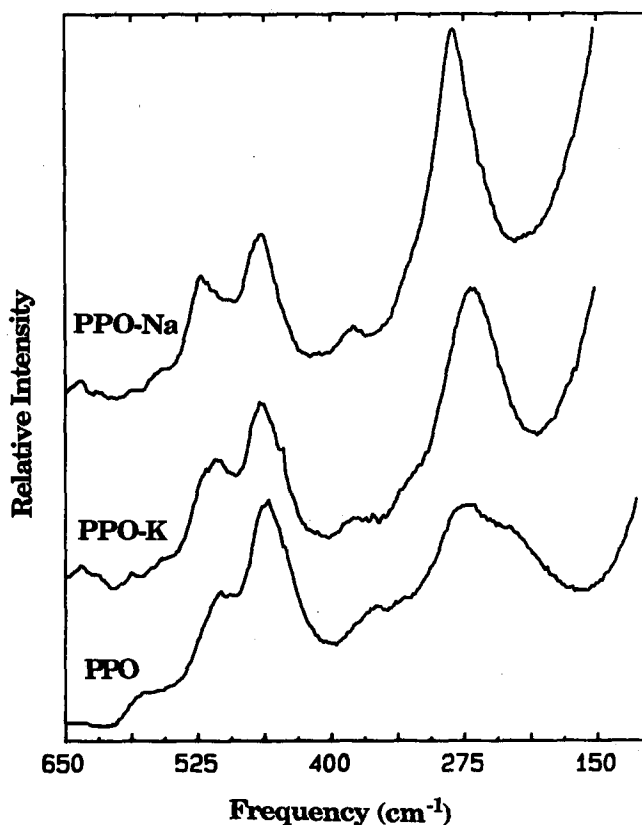


Figure 4 Parallel polarized Raman scattering spectra of uncomplexed PPO, the 8:1 PPO-KSCN complex and the 5:1 PPO-NaSCN complex over the region 100-600 cm^{-1}

dominated by a very broad band centred at $\approx 255 \text{ cm}^{-1}$ with a high frequency shoulder at 282 cm^{-1} . With increasing concentration of complexed salt, the entire feature appears to narrow and display a corresponding

increase in intensity. Deconvolution analysis suggests that the apparent narrowing of the entire feature results from the growth in intensity of a broad band in the centre of the even broader original feature.

The bandwidth and frequency of this new feature display a striking cation dependence. In spectra of the PPO-KSCN complexes, the resulting feature is broader than the corresponding feature observed in spectra of the PPO-NaSCN complexes. The band centre frequency of this feature is 268 cm^{-1} in the 8:1 PPO-KSCN complex and 286 cm^{-1} in the 5:1 PPO-NaSCN complex. This band displays concentration-dependent shifts in the spectra of both complexes. In spectra of the 40:1 PPO-NaSCN complex, this feature appears at 282 cm^{-1} and shifts to higher frequency with increasing concentration of complexed NaSCN. The upper two curves in Figure 5 describe the frequency shifts displayed by this band in spectra of the PPO-NaSCN and PPO-KSCN complexes.

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 in far-infrared transmission spectra. Metal-oxygen stretching motions would be expected to give rise to fairly strong infrared bands as a result of the rather large dipole moment derivative associated with such a mode. Although bands appearing between 200 and 300 cm^{-1} have not been assigned in the vibrational spectra of PPO²³, bands in this frequency range have been assigned to a combination of C-C-O and C-O-C bending motions coupled with torsions along the polymer

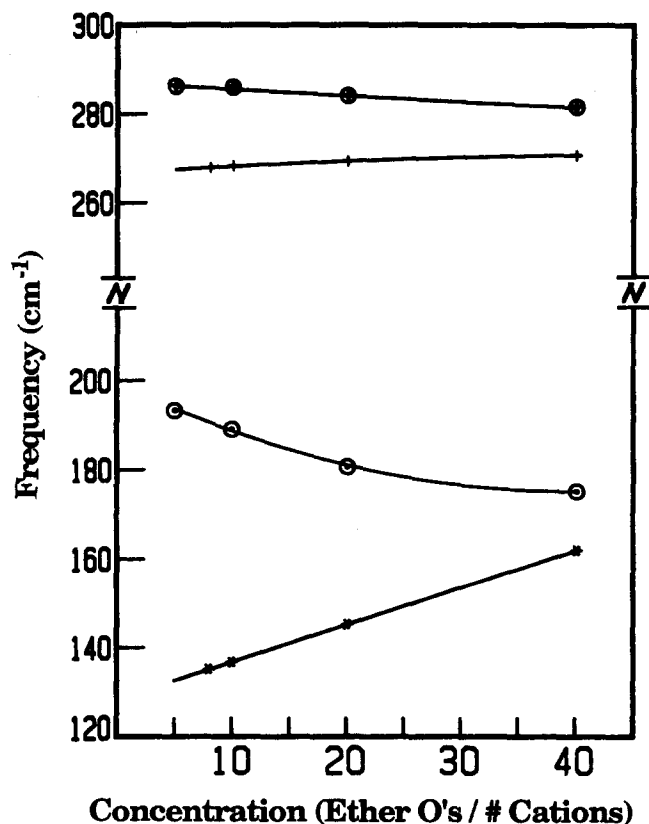


Figure 5 Frequencies exhibited by the low frequency Raman band in PPO-NaSCN (\oplus) and PPO-KSCN ($+$) complexes. In addition, frequencies of the metal-oxygen stretching band are presented for the PPO-NaSCN (\odot) and PPO-KSCN ($*$) complexes

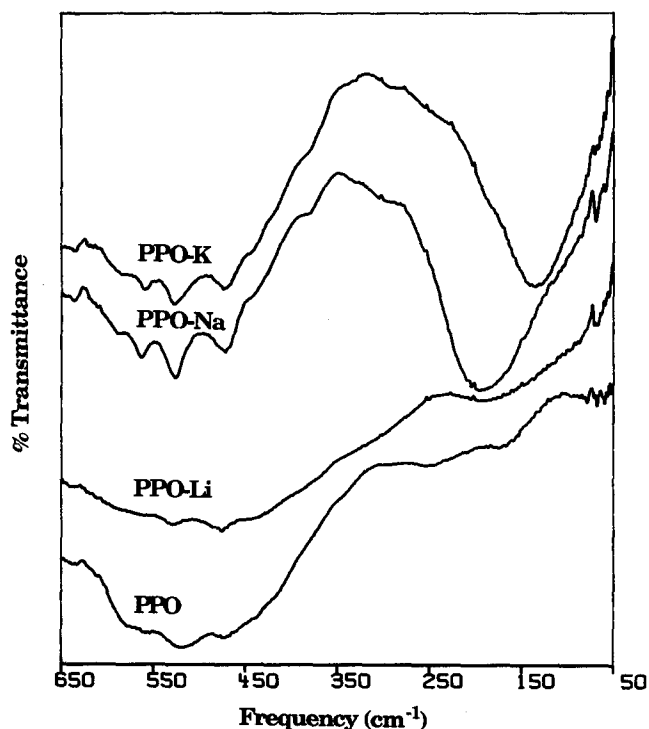


Figure 6 Far-infrared transmission spectra of uncomplexed PPO and the highest concentration PPO-MSCN complexes over the region $50\text{--}650\text{ cm}^{-1}$

backbone for PEO^{24,25}; an analogous assignment seems reasonable for PPO.

Figure 6 presents far-infrared transmission spectra of uncomplexed PPO, and the highest concentration of each PPO-MSCN complex over the region between 50 and 650 cm^{-1} . The far-infrared spectrum of PPO contains a broad, rather poorly resolved feature between 350 and 625 cm^{-1} and two bands at 175 and 252 cm^{-1} . Upon complexation with a metal salt, a band which may be assigned as arising from metal-oxygen stretching grows into the spectra and becomes more intense with increasing concentration of complexed salt. As would be expected, the breadth and position of this band are both very sensitive to the cation in the PPO-MSCN complex. The breadth of the band increases in the order $\text{Li} > \text{Na} > \text{K}$. The actual breadth of the lithium-oxygen stretching band is impossible to determine, but its effect on the spectra begins at 250 cm^{-1} and extends well into the middle of the broad feature at 475 cm^{-1} .

The frequency of maximum absorption for the metal-oxygen stretching band increases in the order $\text{Li} > \text{Na} > \text{K}$, where once again the position of the lithium-oxygen stretching band is unresolvable, but certainly at a much higher frequency than the others. This trend in the band positions would be expected based upon the relative masses of the cations involved.

It is interesting that the position of the metal-oxygen stretching band is also highly concentration dependent. The lower two curves in Figure 5 portray the concentration dependence of the position of this band in spectra of the PPO-NaSCN and PPO-KSCN complexes. Upon increasing concentration of complexed salt, the sodium-oxygen stretching band shifts to higher frequency, and the potassium-oxygen stretching band shifts to lower frequency.

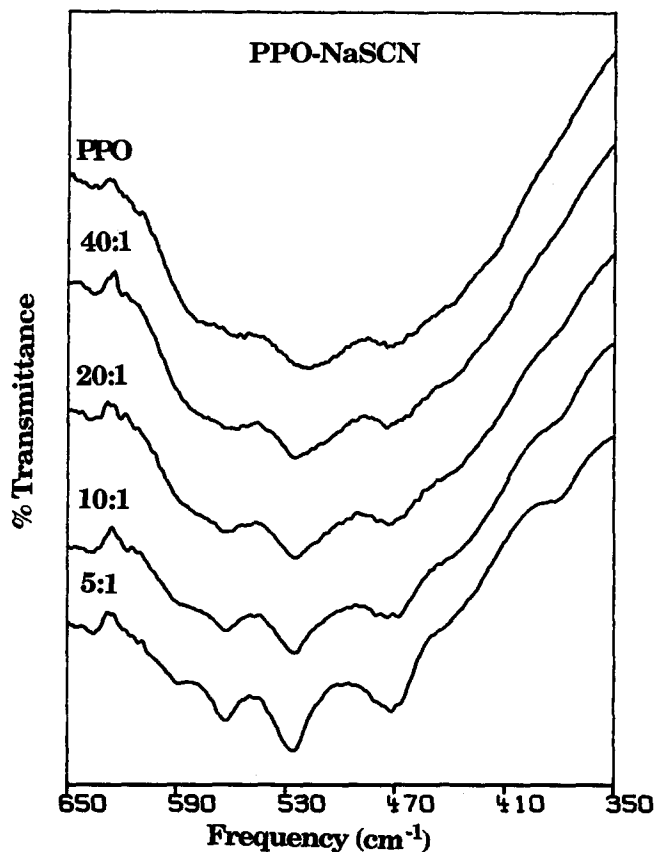


Figure 7 Far-infrared transmission spectra of uncomplexed PPO and the 40:1, 20:1, 10:1 and 5:1 PPO-NaSCN complexes over the region 350-650 cm^{-1}

Figure 7 depicts another interesting trend which occurs upon formation of a polymer-salt complex. Concentration dependent infrared spectra of the PPO-MSCN complexes reveal that the broad feature between 350 and 625 cm^{-1} becomes increasingly structured. This trend is not easily observable in spectra of the PPO-LiSCN complexes, since the lithium-oxygen stretching band is superimposed on this region of the spectra. The increasing degree of structure displayed in this region of the spectra does not seem to result from frequency shifts, but it appears as if a number of the component bands have narrowed. This is very similar to the splitting observed in the C-O stretching band in the mid-infrared spectral region. In the earlier concentration-dependent study of PPO-NaSCN complexes¹⁴, it was suggested that splitting of the C-O stretching band between 1050 and 1200 cm^{-1} could result from increased local homogeneity introduced upon complexation. These observations support such a suggestion.

THIOCYANATE ANION INTERNAL VIBRATIONS

Internal vibrational degrees of freedom of the thiocyanate anion give rise to three modes, ν_1 , ν_2 and ν_3 , which have also been labelled ν_{CN} , δ_{SCN^-} , and ν_{SC} in group frequency terminology, representing the internal coordinate most displaced by the normal mode of vibration. Three bands corresponding to these modes are observed in the vibrational spectra of the PPO-MSCN complexes.

The ν_1 band of the thiocyanate anion is simultaneously observed in both infrared and Raman spectra between 2000 and 2100 cm^{-1} . Figure 8 compares the infrared

transmission spectra of the highest concentration of each PPO-MSCN complex over the region 1950-2150 cm^{-1} . Band centre frequencies for ν_1 follow the trend $\text{Li} > \text{Na} > \text{K}$ and are 2071 cm^{-1} in the 5:1 PPO-LiSCN complex, 2059 cm^{-1} in the 5:1 PPO-NaSCN complex and 2056 cm^{-1} in the 8:1 PPO-KSCN complex. As can be seen in Figure 8, the bandwidths also increase in the order $\text{Li} > \text{Na} > \text{K}$. This band displays marked asymmetry in the spectrum of the 5:1 PPO-LiSCN complex. Although Raman spectra were recorded for only the PPO-NaSCN and PPO-KSCN complexes, the frequencies (8:1 PPO-KSCN, 2058 cm^{-1} ; 5:1 PPO-NaSCN, 2061 cm^{-1}) and bandshapes of the corresponding features were almost identical.

The ν_2 band of the thiocyanate anion is observed as a relatively intense feature between 745 and 755 cm^{-1} in parallel polarized Raman spectra of the PPO-KSCN and PPO-NaSCN complexes. This band is observed to be completely polarized, displaying no intensity in perpendicularly polarized Raman spectra. Band centre frequencies for this feature in spectra of the 8:1 PPO-KSCN and 5:1 PPO-NaSCN complexes are 750 and 751 cm^{-1} , respectively. The bandwidth of this feature displays no discernible concentration dependence. The infrared spectra shown in Figure 3 contain a corresponding feature which is very weak and observed at slightly lower frequency. Band centre frequencies for this feature in the infrared spectra are 745 cm^{-1} for the 8:1 PPO-KSCN complex, 748 cm^{-1} for the 5:1 PPO-NaSCN complex, and 744 cm^{-1} for the 5:1 PPO-LiSCN complex.

The ν_3 band of the thiocyanate anion is weakly observed in the parallel polarized Raman spectra shown

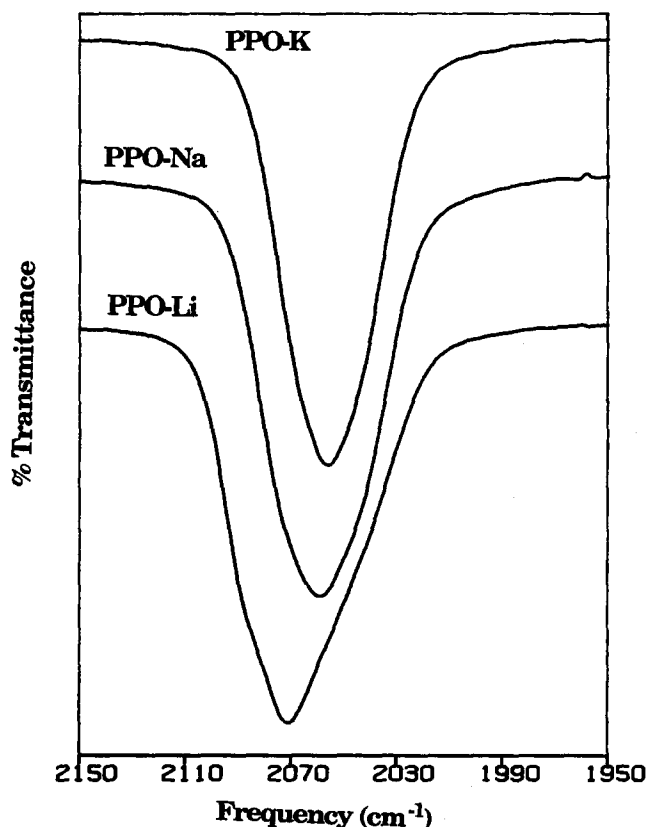


Figure 8 Thin-film infrared transmission spectra of the highest concentration PPO-MSCN complexes over the region 1950-2150 cm^{-1}

in Figure 4, but exhibits relatively strong scattering intensity in perpendicularly polarized Raman spectra, allowing its straightforward assignment. Band centre frequencies for this feature in spectra of the 8:1 PPO–KSCN and 5:1 PPO–NaSCN complexes are 521 and 524 cm^{-1} , respectively. A number of authors have probed the structure of alkali metal thiocyanate salts solvated in media of low permittivity^{26–31}. Characteristic vibrational frequencies for free thiocyanate anions (ν_1 , 2053; ν_3 , 735; ν_2 , 465 cm^{-1}), contact ion pairs and dimers have been reported³⁰. 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 ν_1 and ν_3 , while coordination at the sulphur end of the anion increases ν_1 , but decreases ν_2 and ν_3 ^{28,30,32}.

Since ν_1 and ν_3 were observed at frequencies consistently higher than those of the free thiocyanate anion, it seems fairly clear that the only thiocyanate anion species which was spectroscopically detected in the PPO–MSCN complexes is the $\text{M}^+ \cdot \text{NCS}^-$ ion pair coordinated at the nitrogen end of the anion. In addition, ν_1 displays relatively large cation-dependent frequency shifts, implying substantial cation–anion interaction, as would be expected in a contact ion pair. There is no unambiguous evidence of bands arising from the free anion, dimer or more highly associated species; however, the marked asymmetry of ν_1 in the infrared spectra of PPO–LiSCN complexes hints that the situation is somewhat more complex.

SUMMARY

The guiding idea behind this work was to characterize the nature of interactions between the complexed salts and their polymer host. In this study, vibrational spectroscopy was used to follow changes in the vibrational dynamics of PPO, which are introduced upon complexation with LiSCN, NaSCN and KSCN. The PPO bands which were affected by complexation were carefully studied over a wide range of concentration of complexed salt. Particular attention was paid to the changes which displayed a noticeable cation dependence. In addition, the polyatomic thiocyanate anion possesses internal vibrational modes, giving rise to bands which were used to probe the environment and structure of the complexed salts.

It is clear that increasing polymer–salt complexation involves more than just a higher degree of interaction between the metal cations and the ether oxygen atoms, since these interactions appear to affect the polymer dynamics and, to some extent, the structure. On the basis of cation charge density, it would be expected that the strength of the interactions of the cations with oxygen atoms constituting a portion of the polymer backbone would increase in the order $\text{Li} > \text{Na} > \text{K}$. Spectra of the C–H stretching region reveal that the effect of the cation on these bands increases in the same manner. Since C–H stretching vibrations are sensitive to changes in the conformation and dynamics of the polymer backbone, this observation suggests that an increasing degree of complexation increasingly affects the backbone structure and dynamics. The cation-dependent frequency shifts and

intensity changes observed for bands assigned to deformation vibrations of the CH, CH₂ and CH₃ groups further support this suggestion.

Further insight into the nature of these changes in structure and dynamics is obtained from consideration of other spectral features. At higher concentrations of complexed salt, the appearance of band splittings, as in the case of the intense infrared active band between 1050 and 1200 cm^{-1} , or the growth of structure on broad spectral features between 350 and 625 cm^{-1} suggests that the breadth of the distribution of potential energy environments underlying the component bands significantly decreases. Alternatively, this trend might be described as an increase in the local homogeneity of the polymer–salt complex with increasing concentration of complexed salt¹⁴. One might further speculate that the increase in local homogeneity results from interactions of a particular metal cation with the oxygen atoms of several adjacent monomer units in a polymer chain. These interactions decrease the number of local conformations available to that segment of the chain, which in turn decreases the heterogeneity of the local potential energy environment.

Note that the splitting of the intense infrared band observed between 1050 and 1200 cm^{-1} is independent of the cation in the thiocyanate salt. This is surprising since this band has been assigned to combinations of C–C and C–O stretching motions of the polymer backbone. It would be expected that those motions which have a large C–O component would be strong absorbers in the infrared; therefore, this intense infrared band should arise from vibrations containing a large C–O stretching contribution. Since complexation is viewed as occurring through metal–oxygen interactions, as evidenced by corresponding bands in the far infrared spectra, it would seem likely that the interaction responsible for the observed splitting would be cation dependent. However, this does not appear to be the case in the polymer–salt systems discussed in this paper.

Vibrational spectra of the thiocyanate anion in the PPO–MSCN complexes indicate that the thiocyanate anion is ion paired with the alkali metal cation at the nitrogen end of the anion. The ν_1 band of the thiocyanate anion displays relatively large cation-dependent frequency shifts, implying substantial cation–anion interaction, as would be expected in a contact ion pair. Bands arising from the thiocyanate internal vibrations are observed as single, fairly symmetric features in spectra of the PPO–NaSCN and PPO–KSCN complexes, indicating that ion pairs are the only form of the thiocyanate anion spectroscopically detected in these polymer–salt systems. However, ν_1 of the thiocyanate anion displays marked asymmetry in spectra of concentrated PPO–LiSCN complexes, implying that the situation is more complex.

Finally, bands which are assigned as arising from metal–oxygen stretching motions have been observed in far infrared transmission spectra of the PPO–MSCN complexes. Since the metal cations are apparently involved in contact ion pairing with the thiocyanate anions, bands which are assigned to metal–oxygen stretching were studied for possible counterion effects. Far infrared spectra of PPO–LiBF₄ and PPO–NaCF₃SO₃ complexes show bands corresponding to those found in the spectra of the PPO–LiSCN and PPO–NaSCN complexes, respectively; no substantial counterion effect was observed. This observation further supports the

assignment of these bands as arising from metal-oxygen stretching motions.

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