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Infrared Spectroscopic Study of the Phases and Phase Transitions in Poly(ethylene oxide) and Poly(ethylene oxide)−Lithium Trifluoromethanesulfonate Complexes

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ABSTRACT: The infrared vibrational spectra of high molecular weight poly(ethylene oxide) and complexes of poly(ethylene oxide) with lithium trifluoromethanesulfonate at two different salt concentrations have been measured from 25 to 150 °C. Bands observed in the polymer−salt complexes can be assigned to either the pure crystalline poly(ethylene oxide) phase or a 3:1 polymer−salt compound. The temperature-dependent spectrum is interpreted in terms of the published phase diagram. Cation−anion association is observed at all temperatures. The degree of ionic association in the amorphous region appears to be higher than that observed in the crystalline compound.

1. Introduction

Polymer electrolytes have been extensively investigated after the discovery that reasonably high ionic conductivity can be achieved in solid state polymers complexed with inorganic salts.[1] Various studies have focused on understanding the fundamental processes underlying ionic conductivity, ionic association, and morphology in polymer−salt complexes,[2−6] due to potential applications such as solid state batteries, fuel cells, electrochromic displays, and chemical sensors. Lithium-ion conducting systems are of particular interest because of high potentials and the high energy density available in a lithium-based electrochemical system. Salt complexes based on poly(ethylene oxide), PEO, have received the most attention as possible candidates for solid polymer electrolytes.[7,8] Although electrochemical cells using these electrolytes are near commercialization, there are still major drawbacks that limit the applicability of these systems. A deeper understanding of various factors that control the conduction mechanism in polymer electrolytes is therefore of vital importance in order to optimize the performance of devices based on these materials.

High molecular weight poly(ethylene oxide) is a helical polymer with amorphous regions and crystalline regions which can be described by the space group $P2_1/a$ ($C_{2h}{}^5$)[9]. Many PEO−salt complexes also consist of amorphous and crystalline regions. According to thermal (DSC) measurements and NMR relaxation studies of these complexes, the degree of crystallinity decreases with increasing temperature due to melting of crystalline regions.[10−12] One of the more widely studied polymer−salt complexes is PEO complexed with lithium trifluoromethanesulfonate (triflate), $LiCF_3SO_3$. The phase diagram of the PEO−$LiCF_3SO_3$ system reveals that pure PEO melts around 60 °C and the $(PEO)_9$−$LiCF_3SO_3$ complex melts around 140 °C.[13,14] Below 60 °C, the complex consists of a mixture of three phases: a crystalline phase of pure PEO, and a crystalline, stoichiometric compound, both embedded in a minority amorphous phase.[15] The stoichiometric compound is reported to have the composition $(PEO)_3$−$LiCF_3SO_3$ and a monoclinic unit cell with space group $P2_1/a$ ($C_{2h}{}^5$).[16] This compound will be abbreviated as $(PEO)_3$LiTf in this paper. According to recent X-ray diffraction and vibrational spectroscopic studies, the local structure of high molecular weight PEO is modified upon complexation with metal salts.[17,18]

Above 60 °C, the complex consists of a mixture of an amorphous, elastomeric phase containing coordinated LiTf and the crystalline compound $(PEO)_3$LiTf. With increasing temperature, the relative amount of the crystalline compound decreases and the amount of the LiTf-containing amorphous phase increases. Finally, at temperatures above 140 °C the whole complex consists of the amorphous phase containing dissolved LiTf.[13] It is believed that (i) the amorphous phase is responsible for the ionic conduction in PEO−salt complexes, (ii) both crystalline PEO and the salt-rich complexes inhibit ionic conductivity, and (iii) ionic transport is closely coupled to local segmental motion of the polymer chain.[8,11,15] While these chains perform large amplitude motions, the lithium ion appears to maintain its coordination with the ether oxygens of the polymer backbone. A reasonable model for the microscopic mobility mechanism in polymer−salt complex electrolytes would involve the cations moving by breaking one or more metal−oxygen bonds and then replacing these bonds by links to a different oxygen, while the anions move freely through the fluctuating free volume of the structure.[10] In order to properly understand the ionic conductivity mechanism in these materials, ion−ion and ion−polymer interactions must be studied in detail. Vibrational spectroscopic studies indicate that an increase in the number of uncharged ion pairs in PEO and poly(propylene oxide) (PPO)-based electrolytes containing monovalent ions is accompanied by a decrease in ionic conductivity.[19,20] There are several different types of charge carriers which are expected to participate in the conduction process: (i) "free" ions which are weakly solvated in PEO and have relatively high mobilities, (ii) cations which interact strongly with PEO and thus have low mobility, and (iii) charged aggregates (small clusters) with moderate to low mobilities.

Since the cations are coordinated by the ether oxygens of the polymer backbone, these interactions may influence the local structure of the polymer backbone. Although there is a dramatic change in ionic conductivity of PEO-based polymer−salt complexes across the

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crystalline/amorphous phase transition, to our knowledge a vibrational spectroscopic study focused on the change of the local structure of the polymer–salt complex across this phase transition has not been reported. Such a study is of vital importance in understanding the transport properties of polymer–salt complexes utilized as solid polymer electrolytes. Among various physical and spectroscopic techniques used to investigate these systems, infrared spectroscopy provides a convenient and powerful method for probing both ion–polymer interactions and ionic association. This is a particularly useful technique for studying lithium triflate complexes, since the intramolecular vibrations of the triflate anion are especially sensitive to ionic association effects.

For the $(PEO)_xLiTf$ system in the temperature range 100–140 °C, the highest conductivities are found for compositions with x between 9 and 20. Because of its superior mechanical stability at these temperatures, the optimum composition for use as an electrolyte membrane is considered to be $(PEO)_9LiTf$, which has a conductivity of 1.5×10^{-4} S cm^{-1} at 120 °C.[12,21] Early work by Hooper et al. on the performance of polymer electrolyte cells has shown that at 100 °C, the $(PEO)_9LiTf$ solid polymer electrolyte has an electrochemical stability window of 3.8 V.[21] The influence of temperature on the stability window of the polymer electrolyte is significant, since the stability window is considerably reduced as the temperature is increased, falling from 3.8 V at 100 °C to 3.3 V at 140 °C and 1.9 V at 170 °C. This temperature effect deserves particular attention when the $(PEO)_xLiTf$ electrolyte is assessed for practical applications. Insight into the temperature-dependent changes in ion–polymer interactions and ionic association in the $(PEO)_9LiTf$ complex may be obtained by studying the temperature dependence of the IR bands. In this paper we report the results of a FTIR study of $(PEO)_9LiTf$ films prepared in the same manner as for solid polymer electrolyte cells. $(PEO)_5LiTf$ and pure PEO films have been included in this work to aid in the assignment of bands.

2. Experimental Section

Poly(ethylene oxide) (PEO) of average molecular weight 4×10^6 and lithium triflate, $LiCF_3SO_3$, of 99% purity obtained from Aldrich Chemicals were used without further purification. The $(PEO)_9LiTf$ and $(PEO)_5LiTf$ complexes were prepared by dissolving the required amounts of the polymer and the vacuum-dried $LiCF_3SO_3$ salt in anhydrous acetonitrile. After continuous stirring for 24 h at room temperature, the solution was allowed to stand at room temperature for a further 24 h to facilitate degassing.[21] The gelatinous polymer solution was then cast on a Teflon support. Subsequent solvent evaporation led to bubble free and pin hole free uniform films of 20–30 μm thickness. Pure PEO films were prepared by the same method without mixing the salt. The films were finally dried overnight in vacuum at 120 °C.

For FTIR studies, an unstretched, thin polymer film was placed in between two AgBr windows in an IR cell. A type K thermocouple in contact with the polymer film measured the temperature of the film. Temperature-dependent mesurements were done at 5 deg increments with a 15 min equilibration time allowed after each 5 deg increase of temperature. Spectra were recorded on a Digilab FTS-40 FTIR spectrometer in the transmission mode in the range 400–4000 cm^{-1} with a resolution of 2 cm^{-1}.

3. Results and Discussion

A. Temperature-Dependent Spectra of Pure Poly(ethylene oxide). The temperature dependence of the pure PEO bands in the 700–1500 cm^{-1} region is shown in Figure 1 from 25 to 100 °C. The frequencies at 25 °C are in agreement with the band positions reported in the literature based on the 7_2 helix conformation.[22-24] These frequencies and assignments are summarized in Table 1. The intensities of almost all bands gradually decrease with increasing temperature up to 60 °C, the crystalline/amorphous phase transition temperature, but no significant frequency shifts are seen. Bands at 1361, 1280, 1244, 1236, 1061, 963, and 844 cm^{-1} disappear above 60 °C and are attributed to modes in the crystalline phase of PEO following the assignments of Yoshihara et al.[22] Although Yoshihara et al.[22] and Matsui et al.[25] report a strong feature at 1103 cm^{-1}, no such band was observed in this study. Rather, this feature probably occurs as a broadening on the low-frequency side of the 1113 cm^{-1} band and is quite similar to the results reported in the study by Shimomura et al.[23] In addition, strong bands at 1343, 1150, and 1113 cm^{-1} which are also assigned to the crystalline phase have shoulders at 1350, 1142, and 1110 cm^{-1}, respectively, which give rise to broad bands at these frequencies in the amorphous phase. Li and Hsu observed that the intensity of a doublet at 1360 and 1343 cm^{-1} decreased with decreasing crystallinity in a PEO/poly(methyl methacrylate) blend,[26] and this decrease appeared to be correlated with a corresponding intensity increase of a band at 1349 cm^{-1}. This observation supports the assignment of the 1350 cm^{-1} band to the amorphous phase. A careful examination of the spectra shows that at 25 °C there are also very weak bands present at 1325, 1294, 1250, 1040, 993, and 856 cm^{-1}, which increase in intensity with increasing temperature and become broad bands observed in the amorphous phase. These observations suggest the

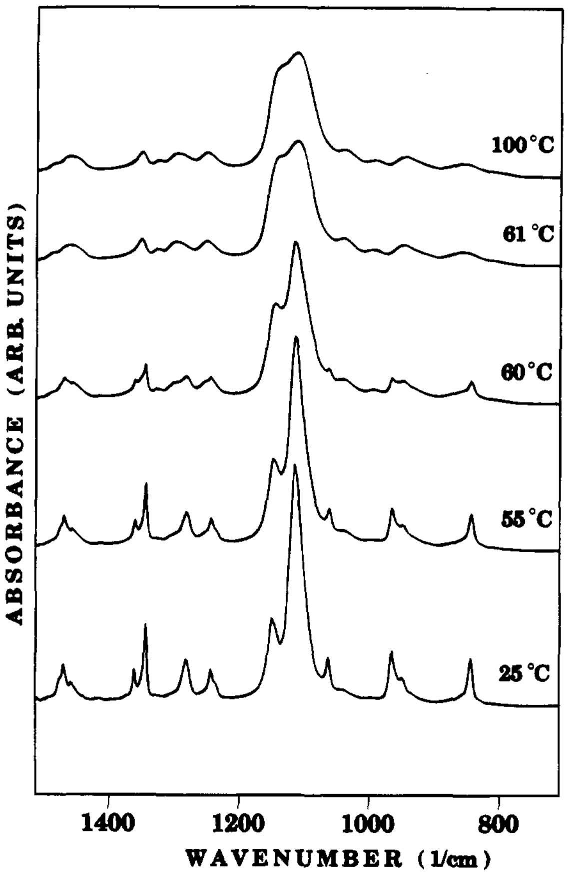

Figure 1. Infrared spectra of PEO from 25 to 100 °C in the spectral region between 1400 and 800 cm^{-1}.

Table 1. Selected Frequencies (cm^{-1}) and Assignments of Infrared Active Bands of PEO in the Amorphous Phase (A) at 100 °C, the Crystalline Phase (X) at 25 °C, and the Polymer–Salt Complex (PEO)$_9$LiTf at 25 °C[a]

PEO (A)	PEO (X)	(PEO)$_9$LiTf	assignment
		1367 (C)	
	1361	1361 (P)	$w_s(CH_2) + \nu(CC)$
1350			
		1353 (C)	
	1343	1343 (P)	$w_{as}(CH_2)$
		1340 (C)	
1325			
		1309 (C)	
		1298 (C)	$\nu_{as}(SO_3)$
1294			
		1288 (C)	$\nu_{as}(SO_3)$
	1280	1280 (P)	$t_{as}(CH_2) + t_s(CH_2)$
		1263 (C)	$\nu_{as}(SO_3)$
1250			
	1244	1244 (P)	$t_{as}(CH_2)$
	1236		$t_{as}(CH_2) - t_s(CH_2)$
		1233 (C)	$\nu_s(CF_3)$
		1179 (C)	
		1160 (C)	$\nu_{as}(CF_3)$
	1150	1150 (P)	$\nu(CC) - \nu_{as}(COC)$
	1144	1144 (C, P)	$\nu(CC) - \nu_{as}(COC)$
1142			
		1138 (C)	
	1113		$\nu_s(COC)$ or $\nu_{as}(COC)$
1110	1111	1111 (P)	$\nu_s(COC)$ or $\nu_{as}(COC)$
		1092 (C)	
		1082 (C)	
	1061	1061 (P)	$\nu_{as}(COC) + r_s(CH_2)$
		1045 (C)	$\nu_s(SO_3)$
1040			
993			
		969 (C)	
	963	964 (P)	$r_{as}(CH_2)$
		952 (C)	
948	949		$r_s(CH_2) - \nu_{as}(COC)$
		940 (C)	
	934		
		927 (C)	
		860 (C)	
856	857		
	844	844 (P)	$r_{as}(CH_2)$
		833 (C)	
	828	828 (P)	
		760 (C)	$\delta_s(CF_3)$

[a] The phase assigned to each mode in the (PEO)$_9$LiTf complex is indicated in parentheses after the frequency, where P is pure crystalline PEO and C is the compound (PEO)$_3$LiTf. The notation follows Yoshihara et al.[20] with ν = stretching, δ = bending, t = twisting, w = wagging, and r = rocking. The subscripts s and as (symmetric and antisymmetric, respectively) denote the symmetry of modes with respect to the 2-fold axis, and the sign signifies the phase relations of coupled coordinates.

presence of a small amount of the amorphous phase below the phase transition temperature. Similar observations have been made earlier by Yoshihara et al.[22]

There are several spectral regions in which the vibrational multiplet structure of the crystalline phase collapses into broad spectral features associated with the amorphous phase with increasing temperature, although this appears to occur without any significant frequency shifts in the crystalline PEO modes. This behavior is most apparent in the CH_2 wagging region and the CH_2 rocking region. From a spectroscopic point of view the transition from the crystalline phase into the amorphous phase can be best understood as the simple growth of the amorphous phase at the expense of the crystalline phase. It should be noted that in the amorphous phase there was no change observed in the relative intensities of the PEO bands from 60 to 120 °C. The frequency data discussed in this section are summarized in Table 1.

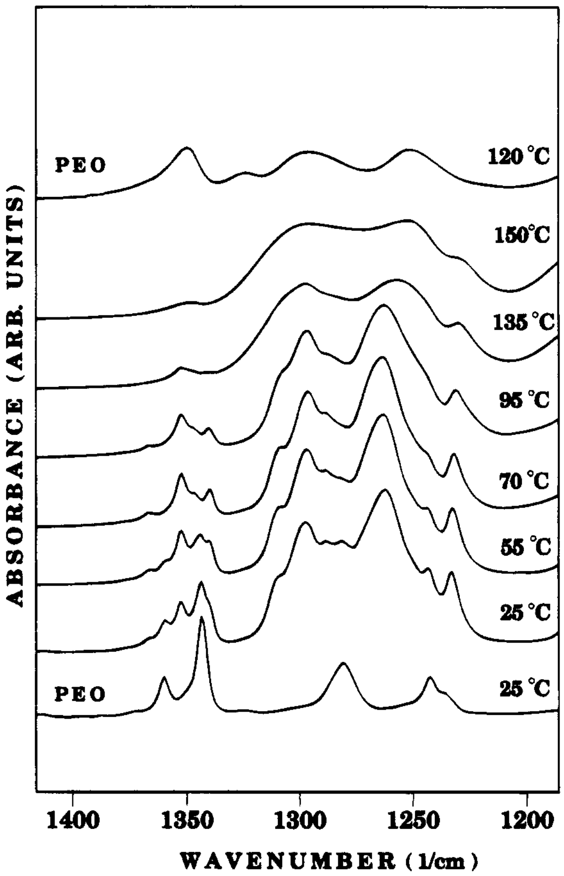

Figure 2. Infrared spectra of (PEO)$_9$LiTf complex from 25 to 120 °C in the spectral region between 1400 and 1200 cm^{-1} with a comparison of the PEO spectra at 25 and 120 °C.

B. Temperature-Dependent Spectra of the (PEO)$_9$LiTf Complex. FTIR spectra in the mid-IR region from 1400 to 1200 cm^{-1} of a thin film of (PEO)$_9$LiTf polymer–salt complex at various temperatures from 25 to 150 °C are shown in Figure 2 along with the spectra of PEO for comparison. The major temperature dependence of the main features in the IR spectrum can be understood in terms of the reported phse diagram, although ionic association effects on the polymer–salt complex also play a role.[27] At an overall composition of (PEO)$_9$LiTf below 60 °C there are two solid phases present: crystalline PEO and the (PEO)$_3$LiTf compound. The spectral features observed in the temperature interval from room temperature to 60°C can be assigned to one of these two phases. Upon heating above 60 °C, the crystalline PEO transforms into its amorphous phase while the salt-rich compound (PEO)$_3$LiTf gradually dissolves in the amorphous phase until it disappears completely at the liquidus around 140 °C. Significant changes in the spectral bands assigned to crystalline PEO are observed in the vicinity of the phase transition temperature of 60 °C. In the two phase region between 60 and 140 °C, the complex consists of the (PEO)$_3$LiTf compound and amorphous PEO into which some LiTf has dissolved. In this region the bands gradually broaden and band center intensities decrease with increasing temperature until about 140 °C, above which the entire spectrum appears as broad, weak spectral features generally characteristic of an amorphous phase. The observed increase in ionic conductivity with temperature above 60 °C is generally attributed to the growth of the amorphous phase containing dissolved LiTf. The temperature dependence of the conductivity in this region is, in fact, governed by the thermally activated rate of ion exchange between the crystalline and amorphous phases.[10]

It is possible to assign different IR bands in the polymer−salt complex to the vibrational modes of the different phases present. At 25 °C there is a faint shoulder at 1367 cm^{-1} and a peak at 1353 cm^{-1} shown in Figure 2, which gradually decrease in intensity as the temperature is increased from 25 to 135 °C. Both of these are CH_2 wagging modes which are associated with $(PEO)_3LiTf$. The peaks at 1361 and 1343 cm^{-1}, which disappear above 60 °C, occur as analogous modes in crystalline PEO. The feature at 1340 cm^{-1}, which appears as a shoulder below 60 °C and becomes more visible as a peak above this temperature, also originates in the $(PEO)_3LiTf$ phase. A very faint feature at 1347 cm^{-1} starts to appear above 60 °C but disappears gradually with increasing temperature. Above 140 °C, where the complex appears to consist entirely of a single amorphous phase, only a broad spectral feature around 1350 cm^{-1} remains. This is also observed in pure PEO above 60 °C. In the temperature interval from 70 to 120 °C, where the polymer−salt complex is useful as a solid polymer electrolyte, only the 1353 and 1340 cm^{-1} bands associated with the crystalline compound $(PEO)_3LiTf$ are dominant. There is a shoulder at 1309 cm^{-1} at 25 °C which gradually disappears above 60 °C and seems to be associated with the presence of the crystalline compound. The band at 1280 cm^{-1}, observed in pure PEO at 25 °C, is seen in the poymer−salt complex only as a very faint structure below 60 °C, which disappears completely above 60 °C. The intensity of the band at 1244 cm^{-1} rapidly decreases from 25 to 70 °C, although it persists to 95 °C. As pure PEO at 25 °C exhibits a CH_2 twisting mode at 1244 cm^{-1}, this band is identified with the crystalline PEO phase in the complex. The CH_2 twisting band at 1236 cm^{-1} in pure PEO is masked by the CF_3 symmetric stretch at 1233 cm^{-1} in the complex.

The temperature dependence of relative peak intensities in this spectral region behaves as expected. Intensities of peaks associated with crystalline PEO gradually decrease with increasing temperature up to 60 °C and disappear completely, while intensities of peaks associated with the compound remain essentially constant up to 60 °C and then decrease with increasing temperature until the transition into the amorphous phase at 140 °C.

The assignment of bands is also aided by considering the concentration dependence of the lithium triflate salt. An increase in the relative intensity of a particular band in a complex which is richer in LiTf and hence the $(PEO)_3LiTf$ compound confirms that the band can be assigned to the compound. For this purpose a second complex with the composition $(PEO)_5LiTf$ was prepared and spectra, shown in Figure 3, at 25 and 175 °C are compared with those of the $(PEO)_9LiTf$ complex at 25 and 150 °C. The higher temperature was necessary for the former complex to ensure the transition into the amorphous phase. Although the relative band intensities of the two spectra are similar for both complexes in the amorphous phase, there are significant differences in the spectra of the crystalline phases at 25 °C.

A number of bands originating in the intramolecular motions of the triflate anion are observed in the spectral region from 1100 to 1300 cm^{-1} in Figures 2−4. The symmetry of the triflate ion, assumed to be C_{3v} in the isolated state, generally will be lowered when coordinated to a cation, causing the doubly degenerate antisymmetric stretching mode $\nu_{as}(SO_3)$ to split into two components which are observed in Figures 2 and 3 as two strong peaks at 1298 and 1263 cm^{-1} at 25 °C. The higher frequency component appears to remain unshifted in frequency up to 150 °C; however the lower frequency peak shifts to 1265 cm^{-1} at 60 °C as the band splitting $\Delta\nu_{as}(SO_3)$ appears to decrease slightly over this temperature range. As the temperature is raised above 60 °C, $\Delta\nu_{as}(SO_3)$ then increases with temperature within the two-phase region below the liquidus and continues to increase into the amorphous region up to 150 °C. These two component bands become very broad spectral features in the amorphous phase above 140 °C. These data are summarized in Table 2. There is a weak band at 1288 cm^{-1}, which is seen even at 135 °C. This frequency is somewhat too high to be comfortably assigned to the "free" triflate anion and is consequently attributed to the $\nu_{as}(SO_3)$ mode of the triflate ion in a state of aggregation which differs from the ionic association responsible for the two bands at 1298 and 1262 cm^{-1}. The relative intensities of the three bands which are associated with the $\nu_{as}(SO_3)$ vibrations increase slightly from 25 to 60 °C and then decrease gradually with temperature. The maximum intensity appears to occur at the pure PEO phase transition temperature of 60 °C. In Figure 3 there is a rather striking salt concentration dependence of the intensities of these bands. At 25 °C the intensity of the 1298 cm^{-1} feature appears to decrease while the intensities of the 1285 and 1262 cm^{-1} bands appear to increase markedly from the $(PEO)_9LiTf$ complex to the $(PEO)_5LiTf$ complex.

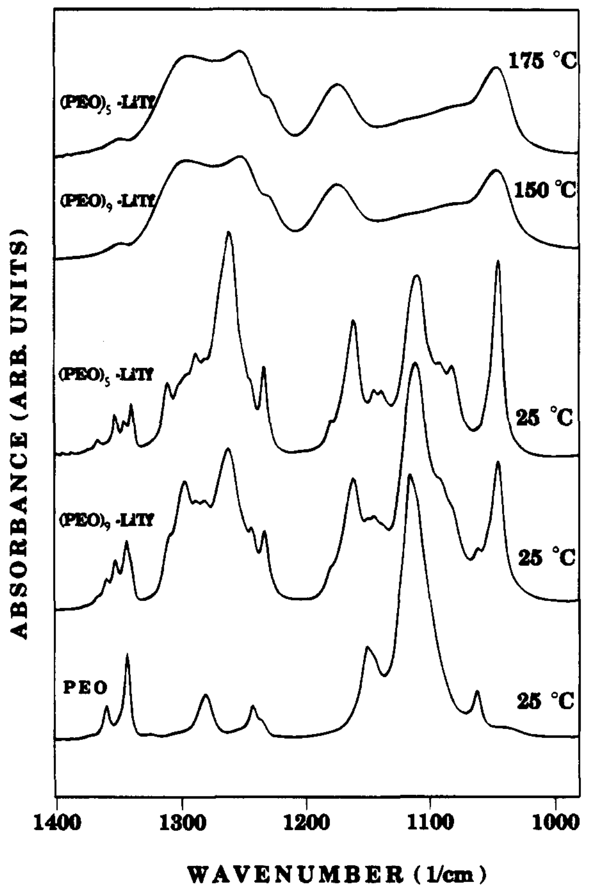

Figure 3. Comparison of the infrared spectra of the $(PEO)_9LiTf$ complex and the $(PEO)_5LiTf$ complex at several temperatures in the spectral region between 1400 and 1000 cm^{-1}.

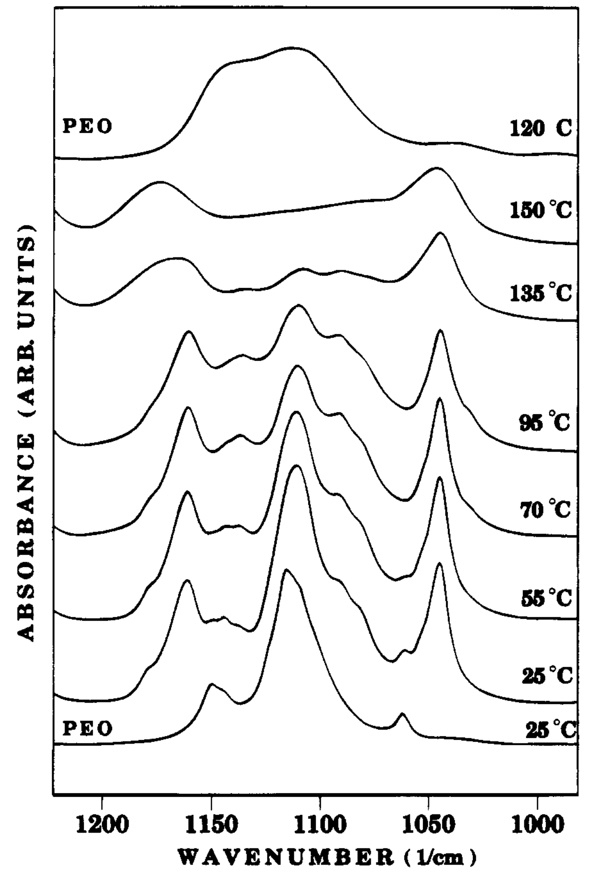

Figure 4. Infrared spectra of the $(PEO)_9LiTf$ complex from 25 to 120 °C in the spectral region between 1200 and 1000 cm^{-1} with a comparison of the PEO spectra at 25 and 120 °C.

Table 2. Temperature Dependence of the $\nu_{as}(SO_3)$, $\nu_s(CF_3)$, and $\nu_{as}(CF_3)$ Band Frequencies (cm^{-1}) in $(PEO)_9LiTf$

mode	25 °C	60 °C	135 °C	150 °C
$\nu_{as}(SO_3)$	1262	1265	1257	1250
$\nu_{as}(SO_3)$	1296	1296	1296	1296
$\nu_s(CF_3)$	1233	1233	1228	1227
$\nu_{as}(CF_3)$	1160	1160	1160	1174

The $\nu_s(CF_3)$ and $\nu_{as}(CF_3)$ bands of the coordinated triflate ions are observed at 25 °C at 1233 (Figure 2) and 1160 cm^{-1} (Figure 4), respectively, and do not change up to 60 °C. Above this temperature the frequency of the $\nu_s(CF_3)$ mode gradually decreases with increasing temperature and the band becomes a broad spectral feature at 1227 cm^{-1} at 150 °C. The intensity of this band also appears to go through a maximum at 60 °C, similar to the behavior of the $\nu_{as}(SO_3)$ bands. The 1160 cm^{-1} band, however, remains unchanged up to 135 °C and becomes a broad band at 1174 cm^{-1} at 150 °C, where the complex is in its amorphous state, as shown in Figure 4. These data are also summarized in Table 2.

In Figures 3 and 4, the polymer–salt complex shows a faint shoulder at 1179 cm^{-1}, which gradually disappears with increasing temperature and is assigned to the compound. Two overlapping peaks at 1150 and 1144 cm^{-1} in pure PEO appear as two faint structures in the complex at 25 °C. The 1150 cm^{-1} peak which disappears above 60 °C originates from the crystalline PEO phase. The 1144 cm^{-1} band, however, persists above 60 °C as a faint feature and may be due to the presence of a small amount of amorphous PEO even below 60 °C, as described earlier. A band at 1147 cm^{-1} was assigned to a mixture of C–C and C–O stretching motion by Yoshihara et al.[22] Another weak band at 1138 cm^{-1} is observable only in the complex, at first increasing in intensity above 60 °C and then gradually disappearing by 140 °C.

The most significant change in this spectral region occurs in the strong band at 1111 cm^{-1}, which can be assigned either as an E_1 $\nu_s(COC)$ mode or an A_2 $\nu_{as}(COC)$ mode. Instead of the two overlapping bands at 1113 and 1111 cm^{-1} seen in PEO, there is only one intense band at 1111 cm^{-1} in the complex. This band dominates the absorption spectrum of the complex below 60 °C, but gradually becomes a broad feature as the temperature approaches 140 °C. This feature vanishes completely when the complex transforms into its amorphous phase above 140 °C. The amorphous phase of pure PEO at 120 °C, however, has a strong absorption band in this region. The frequency of the 1111 cm^{-1} band is unchanged up to 60 °C, but decreases to 1107 cm^{-1} at 135 °C. As can be seen in the spectra of Figures 1 and 4, the temperature-dependent behavior of the polymer–salt complex is dramatically different from that of pure PEO in this region. It is also interesting to note the salt-concentration dependence of the 1111 cm^{-1} band. According to Figure 3, the relative intensity of this band in the $(PEO)_9LiTf$ complex is higher than in the $(PEO)_5LiTf$ complex, in contrast to the behavior of the bands associated with the triflate ions, e.g. 1263, 1233, 1160, and 1045 cm^{-1}. This suggests that the absorption coefficient of this particular vibration in the complex is decreased relative to that in the uncomplexed PEO. Two other weak bands appear at 1092 and 1082 cm^{-1} in the complex and persist up to 135 °C, but disappear above this temperature. The band at 1061 cm^{-1} which disappears above 60 °C is associated with crystalline PEO. The SO_3 symmetric stretching mode of the triflate ion at 1045 cm^{-1} does not undergo a measurable frequency shift over the entire temperature range from 25 to 150 °C, but does become considerably broader at higher temperatures. The intensities of the strong triflate ion bands at 1160 and 1045 cm^{-1} as well as the intensities of the shoulders assigned to the compound appear to go through a maximum at 60 °C, in contrast to the slowly decreasing intensity of bands associated with PEO.

Figure 5 depicts the spectral region in which modes due to CH_2 rocking vibrations coupled with C–O stretching motions occur. The frequencies of these modes are particularly sensitive to the interaction of the cation and the polymer backbone.[24] The 964 cm^{-1} band disappears above 60 °C and is attributed to crystalline PEO whereas the 969 and 952 cm^{-1} bands, which disappear only above 140 °C, are due to the PEO_3LiTf compound in the complex. In the IR spectrum of pure PEO there are additional bands at 949 and 934 cm^{-1}, which are not seen in the spectrum of the complex. Although the 949 cm^{-1} band appears to vanish upon complexation, it may occur as a low-frequency shoulder on the strong broad band which grows in at 952 cm^{-1}. The faint feature at 934 cm^{-1} in pure PEO is not observed in the complex at 25 °C. Figure 6 depicts the salt-concentration dependence of the bands in this region and clearly shows that the band at 969 and 952 and the shoulder at 940 cm^{-1} originate in the compound, as evidenced by their intensity increase from the 9:1 complex to the 5:1 complex. The weak band at 927 cm^{-1} occurs in both the 5:1 and 9:1 complexes, although it appears to show a slight intensity decrease in the

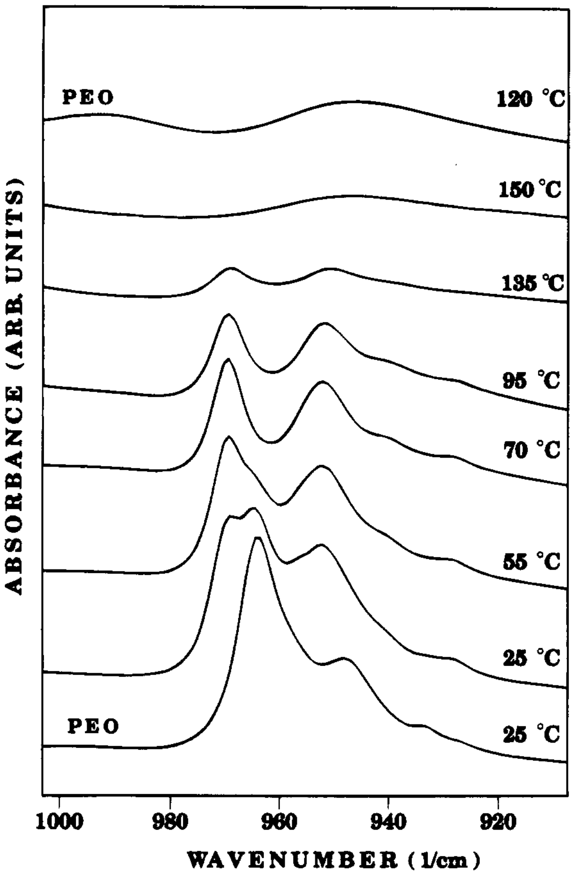

Figure 5. Infrared spectra of the $(PEO)_9$LiTf complex from 25 to 120 °C in the spectral region between 1000 and 920 cm^{-1} with a comparison of the PEO spectra at 25 and 120 °C.

$(PEO)_5$LiTf complex and might result from the 934 cm^{-1} PEO band. In both salt complexes a very weak shoulder is observed at 956 cm^{-1}, which disappears above 60 °C. However, these weak features at 927 and 956 cm^{-1} are difficult to assign with any degree of confidence.

The modes in the region from 820 to 880 cm^{-1} also consist of a mixture of CH_2 rocking vibrations coupled with C−O stretching motions and are also sensitive to the interaction of the cation and polymer backbone. As shown in Figure 7, pure PEO has a strong IR absorption band at 844 cm^{-1} and two very faint structures at 857 and 828 cm^{-1} at 25 °C. Upon complexation, two other bands appear at 860 and 833 cm^{-1} and are assigned to the $(PEO)_3$LiTf compound. This assignment is consistent with the salt-concentration dependence of these two bands, as illustrated in Figure 6. The temperature-dependent behavior of the 844 cm^{-1} band is unusual. Although this band is dominant in the pure PEO sample, it is also seen in the complex at temperatures well above the PEO transition at 60 °C. With increasing temperature the intensity of the band rapidly decreases from 25 to 55 °C and then gradually decreases into the completely amorphous phase. In contrast, the intensities of the two compound bands at 860 and 833 cm^{-1} go through a maximum at 60 °C and then gradually decrease. As can be noted from Figure 6, the intensity of the 844 cm^{-1} peak decreases with salt concentration; however this band is observed at temperatures as high as 135 °C in Figure 7. Therefore it seems plausible that this band contains contributions from both the compound and the pure PEO phase.

The band which appears at 760 cm^{-1} upon complexation is the $\delta_s(CF_3)$ mode of an ionically associated triflate ion. A closer inspection of the temperature dependence of this band (not shown) reveals that the frequency and intensity of this band remain essentially unchanged from 25 to 60 °C. The band then shifts to lower frequency with decreasing intensity from 60 to 140 °C. A second, less intense feature at 766 cm^{-1} starts to emerge from the background at about 120 °C and grows in intensity with increasing temperature. At 150 °C both bands appear to merge in a single very broad band centered at roughly 763 cm^{-1}, although this feature probably consists of the original two bands which can no longer be resolved due to the increase in bandwidth of each component.

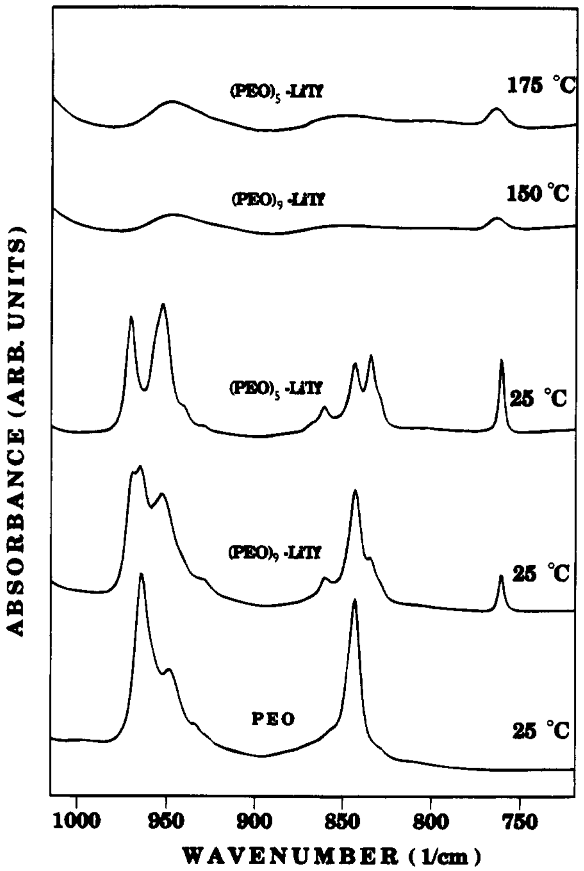

Figure 6. Comparison of the infrared spectra of the $(PEO)_9$LiTf complex and the $(PEO)_5$LiTf complex at several temperatures in the spectral region between 1000 and 750 cm^{-1}.

4. Conclusions

A comparison of the spectra of the $(PEO)_9$LiTf complex, the $(PEO)_5$LiTf complex, and the pure PEO polymer establishes that the spectrum of the complexes can be viewed as the superposition of the spectra of the pure crystalline phase of PEO and the compound $(PEO)_3$LiTf. The local conformational change in the polyether backbone induced by complexation with a cation is extensively discussed elsewhere,[28] where it is shown that the coordination of the cation by the ether oxygen atoms stabilizes the polymer in a conformation which is energetically unfavorable in the noncomplexed state. Polymer vibrations which are particularly sensitive to conformation will then be shifted in frequency, as is seen in the comparisons of pure PEO with the complexes in a number of spectral regions.

As noted earlier, the temperature dependence of the spectra of the complexes is consistent with the phase diagram. However the details of local structural changes with increasing temperature are important. In this

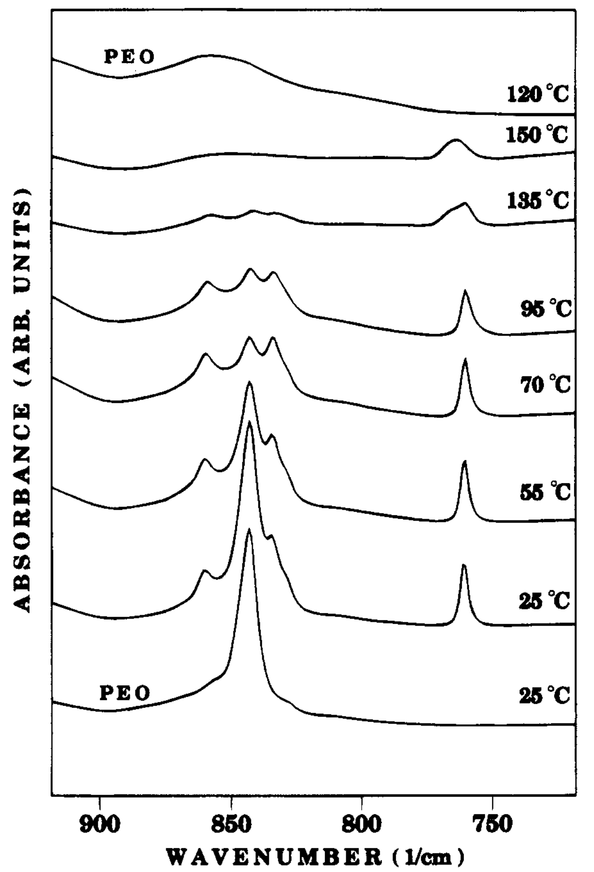

Figure 7. Infrared spectra of the $(PEO)_9LiTf$ complex from 25 to 120 °C in the spectral region between 900 and 750 cm^{-1} with a comparison of the PEO spectra at 25 and 120 °C.

respect, the region between 1050 and 1150 cm^{-1} of PEO as shown in Figure 3 is particularly significant. Bands in this region have been assigned to C−O−C stretching vibrations and are quite sensitive to cations interacting with the ether oxygen atoms of the polymer backbone. In this figure, the relative intensities of the PEO and $(PEO)_9LiTf$ spectra at 25 °C have been scaled by a multiplicative factor to be comparable, focusing on the 1113 cm^{-1} mode which is the most intense in this spectral region. The other spectra have been scaled by this factor so as to preserve relative intensities and allow a direct comparison. Although at 25 °C there are modest differences between the pure PEO spectrum and the PEO bands in the spectrum of the complexes, the differences in behavior at higher temperatures are rather striking. As pure PEO passes into the amorphous phase, the bands at 1150 and 1111 cm^{-1} broaden but do not appreciably shift in frequency, as is seen in Figure 1. This is in contrast to the behavior of the complex noted in Figure 4. At 135 °C there is still some structure due to the C−O−C stretching vibrations, but at 150 °C there is only a smeared out absorption in the region between the $\nu_{as}(CF_3)$ mode at 1174 cm^{-1} and the $\nu_s(SO_3)$ mode at 1045 cm^{-1}. This comparison suggests that even in the amorphous phase at higher temperatures there is a significant interaction of the polymer chain oxygen atoms with ionic species. But what kind of ionic species are present?

Several IR bands provide information about the nature of the ionic association in in the polymer−salt complex, based on previous studies of PEO systems complexed with triflate salts.[29,30] At 25 °C the two bands at 1298 and 1263 cm^{-1} (Figure 2) which are assigned to the split components of the $\nu_{as}(SO_3)$ mode necessarily result from a breaking of the double degeneracy present in the isolated triflate anion. However the band at 1045 cm^{-1} provides a more detailed picture of the associated species. Bands at frequencies somewhat lower than this have been observed in numerous studies of ionic association in polyether−lithium triflate complexes. Torell et al.[31] reported a band at 1042 cm^{-1} in a study of LiTf in PEO 400 and assigned this band to the $\nu_s(SO_3)$ mode of ion pairs, based on the cation-dependent shift. Measurements of short chain length glyme−lithium triflate complexes give comparable results, e.g. a band at 1043 cm^{-1} in the PEO diglyme complex[32] and a band at 1043 cm^{-1} in the PEO triglyme complex.[33] Extensive studies of the ionic association of lithium triflate in a number of solvents conclude that the frequency of the cation−anion pair band is 1042−1043 cm^{-1} and not 1045 cm^{-1}. Particularly relevant is a study of LiTf in PPO 400 and PPO 4000, in which the frequency of $\nu_s(SO_3)$ for the ion pair band was found to be 1042 and 1041 cm^{-1}, respectively.[34] Furthermore, the assignment of the 1045 cm^{-1} band to a simple cation−anion pair would be inconsistent with the X-ray diffraction study of the $(PEO)_3LiTf$ compound by Lightfoot et al.[16] Their results show that two oxygen atoms of the triflate ion are each coordinated to a different lithium ion ("bridging bidentate structure", $[Li_2Tf]^+$). We recently calculated the structures and normal vibrations of the triflate ion and its ion pairs and aggregates using a 3-21+G* basis set.[35] In that calculation the lithium triflate bidentate bridging structure, which is the structure arrived at in the X-ray study, was found to occur at a frequency higher than that of the lithium triflate monodentate ion pair after correction for solvent effects.

Consequently, we conclude that the band at 1045 cm^{-1} observed in the $(PEO)_9LiTf$ and $(PEO)_5LiTf$ complexes originates in the triflate ion in the 3:1 compound. Specifically, each triflate ion vibrates essentially as a $[Li_2Tf]^+$ species in the compound, although each lithium ion in the $[Li_2Tf]^+$ species is in reality coordinated to two oxygens, one each from adjacent triflate ions, as well as being coordinated to three ether oxygen atoms in the polyether backbone.

In the interval from 60 to 110 °C a very weak band is observed at 1030 cm^{-1}, which is too low to be assigned to $\nu_s(SO_3)$ of noncoordinated or "free" triflate ions, whose frequency is expected at about 1033 cm^{-1}.[36] The "free" ion $\nu_{as}(SO_3)$ mode is expected at about 1272 cm^{-1}, on the basis of studies of tetrabutylammonium triflate dissolved in various solvents.[33] However, the only mode observed in this region is at 1288 cm^{-1}, which is too high to be assigned as a "free" ion. The failure to observe "free" triflate ion bands is expected in the two phase region below 60 °C, however it is a bit surprising that in the complexes above 60 °C there are also no "free" ion bands seen. Therefore the conclusion is that there are no "free" triflate ions present in either complex at any temperature considered in this study.

The frequency of the CF_3 symmetric deformation mode, $\delta_s(CF_3)$, is also a sensitive measure of the vibrational potential energy environment[33] and in some cases is a better measure of the degree and nature of ionic association than the $\nu_s(SO_3)$ mode.[36,37] In the interval from 25 to 135 °C there is a band at 760 cm^{-1} which is significantly higher than the "free" ion band observed between 752 and 754 cm^{-1}. It is particularly interesting that in the 135 °C spectrum in Figure 7, a second band can be seen growing in at roughly 766 cm^{-1}.

The higher frequency of this band argues that in the amorphous phase either there is a more highly associated lithium triflate species than the [Li$_2$Tf]$^+$ species found in the (PEO)$_3$LiTf compound or the structure of the dominant [Li$_2$Tf]$^+$ species is significantly different in the amorphous phase than in the compound. Similar behavior is seen in the ν_{as}(CF$_3$) mode at 1160 cm^{-1} in Figure 4. The band is relatively unchanged with increasing temperature until 135 °C, where a second band grows in at 1174 cm^{-1}. The new band is quite broad and is dominant at all higher temperatures. Identical behavior is observed for these bands in the (PEO)$_5$LiTf complex, where the transition into the amorphous phase occurs around 165 °C.

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