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Temperature-Dependent Raman Spectroscopy of Lithium Triflate−PEO Complexes: Phase Equilibrium and Component Interactions

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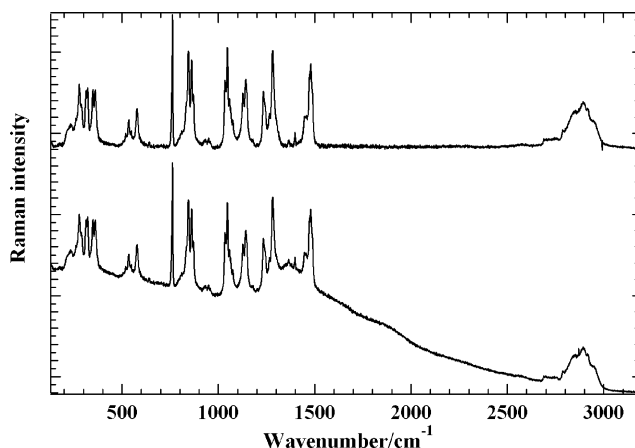
Poly(ethylene oxide) and complexes of lithium trifluorosulfonate−poly(ethylene oxide) (LiTf−PEO) with $4 \leq$ O/Li ≤ 18 have been studied by Raman spectroscopy from room temperature up to 160 °C. The Raman spectrum of the $(PEO)_3LiTf$ defined compound has been deduced from the experimental data. Subtraction of the Raman spectrum due to $(PEO)_3LiTf$ in each sample allowed us to determine for the first time the composition and the $Li^+−Tf^-$ and $Li^+−PEO$ interactions in the part of the polymer not crystallized as $(PEO)_3LiTf$. It is shown that the local interactions between cation and anion or between cation and PEO chain persist even in the melted state, up to near the liquidus temperature. In particular, the $Li^+−PEO$ interactions decrease significantly just below the liquidus temperature with a simultaneous strong increase in the ion pair concentration.

Introduction

Solid polymer electrolytes have been extensively studied due to their ionic conduction properties and their potential application in lithium batteries, solar cells, and electrochromic systems.[1] Lithium salt−poly(ethylene oxide) (PEO) complexes have attracted much attention, in spite of the need to heat them near 60 °C to get a sufficient ionic conductivity. Ionic conduction occurs in the amorphous parts of the polymer, and it depends on the salt concentration and dissociation. Vibrational spectroscopies,[2,3] IR and Raman, have proved to be efficient tools to determine these characteristics, especially for lithium triflate (LiCF$_3$SO$_3$, hereafter denoted LiTf)−PEO complexes. Internal modes of the triflate anion (Tf$^-$) CF$_3$SO$_3^-$ have been particularly studied with a special attention to the SO$_3$ symmetric stretching mode near 1050 cm^{-1} and the CF$_3$ symmetric deformation[4] near 760 cm^{-1} since these two modes show bands depending on the Li$^+$−Tf$^-$ association. Another region of interest is located near 860 cm^{-1}, where a band appears in the Li salt−PEO complexes and which is associated with ether oxygen breathing about a Li$^+$ ion solvated by the macromolecular chain[5] or with CH$_2$ rocking influenced by the Li$^+$ solvation.[6] It has to be noticed that most studies were conducted at room temperature, while PEO-based electrolytes have good electrical properties above the PEO melting temperature of 60 °C. One noticeable exception is the IR study by Frech et al.[7,8] performed at high temperature, who concluded an amorphous phase existed in addition to the pure PEO and compound PEO$_3$LiTf was defined with a O/Li ratio of 3, as expected from the phase diagram.[9]

Our objective in this study was to provide a more systematic view of the structure of PEO−LiTf complexes as a function of temperature and composition, as it can be observed by Raman spectroscopy. For this purpose, we have determined the Raman spectrum of PEO and of PEO−LiTf complexes with O/Li ranging from 4 to 18 between room temperature and 160 °C. We have used as excitation light a near-infrared source, thus minimizing the problems associated with fluorescence. We have
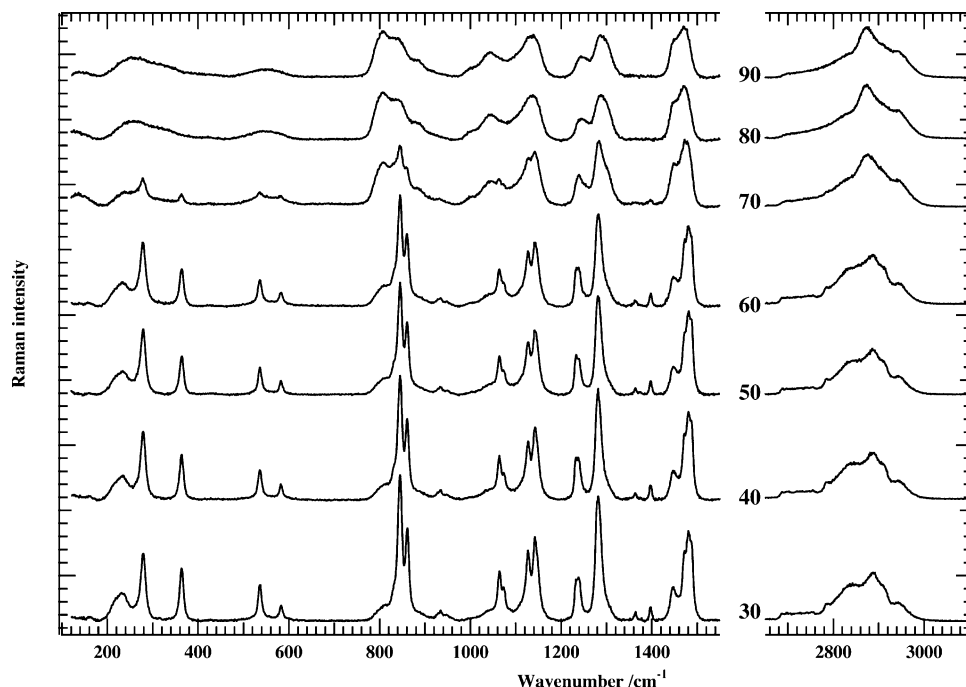
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Figure 1. Raman spectrum of $(PEO)_{11}LiTf$ at 30 °C as acquired (bottom) and after fluorescent background and borosilicate glass spectra removal (top).

determined the Raman spectrum of the $(PEO)_3LiTf$ defined compound and used it to determine the Raman spectrum of the fraction of the complex not belonging to this compound, with a particular view to the interactions of Li$^+$ with Tf$^-$ and with the polymeric chain.

Experimental Section

LiCF$_3$SO$_3$ was purchased from Acros, dried in vacuum at 120 °C, and stored in a glovebox in argon atmosphere with less than 3 ppm O$_2$ and H$_2$O. High molecular weight PEO ($M_w = 5 \times 10^6$ g mol^{-1}) was purchased from Aldrich and used as-received. Mixtures were prepared in a glovebox by dissolving the appropriate amounts of PEO and LiTf in acetonitrile. The resulting solution was stirred overnight and cast on a Teflon plate. Solvent evaporation was carried out in a glovebox for 12 h at room temperature. Films were then dried in vacuum at 80 °C for 48 h and stored in a glovebox in argon. For Raman measurements, films were placed between two glass plates sealed with Torr-seal glue.

Figure 2. Raman spectra of PEO at various temperatures (indicated near each spectrum in °C).

Raman spectra were collected with a Renishaw InVia spectrometer. The light source was a 785 nm laser diode and the Raman photons were collected on a Peltier-cooled CCD detector. The Rayleigh line was suppressed by two dielectric filters. A micro-Raman configuration was used. The laser beam was focused at the surface of the sample as a line of about 20 μm in length and 2 μm in width. For temperature measurements, a laboratory-designed cell was used.[10]

Even with the use of a near-IR excitation, which reduces the fluorescent background, and due to the presence of broad bands associated with borosilicate glass, a strong background was observed (Figure 1). The background was removed using a laboratory-made software by a cubic spline interpolation between hand-selected points. We checked that this method allowed the correct subtraction of the borosilicate glass spectrum. Difference spectra were then obtained with Igor Pro software. The region of 1600−2600 cm^{-1}, which shows only very large bands possibly due to second-order effects, has been omitted.

Results

Raman Spectrum of Pure PEO. The Raman spectra obtained on pure PEO at various temperatures are shown in Figure 2. Very strong changes are observed above 60 °C, which is the melting temperature of PEO. Bands below 600 cm^{-1}, which imply long-range ordering, almost disappear. Bands between 800 and 1500 cm^{-1}, representative of more localized phonons, enlarge, and many doublets cannot anymore be separated by eye. The C−H stretching region near 3000 cm^{-1} also shows a decrease in the number of individual components. The appearance of a strong feature near 2730 cm^{-1} seems to indicate that in amorphous PEO many C−H bonds become equivalent with a bond strength lower than that observed in the crystal. Fusion is still incomplete at 70 °C: small narrow bands still appear at low wavenumbers. It is complete at 80 °C.

Determination of the Raman Spectrum of (PEO)₃LiTf Compound. The sample with O/Li = 4 is, according to the phase diagram,[9] composed of 3/4 (PEO)₃LiTf and 1/4 pure PEO.

Raman spectra were collected every 10 °C up to 160 °C (Figure 3). At each temperature, the Raman spectrum of pure PEO obtained at the same temperature was subtracted after hand-adjustment of the intensity. Bands belonging only to the PEO spectrum disappear or enlarge markedly above 60 °C. We used the shoulder at 365 cm^{-1} and the two bands at 535 and 1395 cm^{-1} as fingerprints to scale the PEO spectrum (Figure 4). The difference spectra obtained from five spectra of (PEO)₃LiTf between 30 and 60 °C were very similar (Figure 5). The same procedure, i.e., subtraction of the PEO spectra, was applied to the sample with O/Li = 6. Again, the difference spectra obtained between 30 and 60 °C were identical and also highly similar to that obtained with the O/Li = 4 sample (Figure 5). This difference spectrum is characteristic of the (PEO)₃LiTf compound. Figure 5 also shows the mean distance between individual spectra and their mean, which can be used as a fingerprint of the dispersion of the data. This distance, calculated at each wavenumber by

$$d(\bar{\nu}) = \sqrt{\frac{\sum (a_i(\bar{\nu}) - \bar{a}(\bar{\nu}))^2}{N}} \qquad (1)$$

where $a_i(\bar{\nu})$ is the intensity of spectrum i at wavenumber $\bar{\nu}$, $\bar{a}(\bar{\nu})$ the intensity of the mean spectrum at the same wavenumber, and N the number of averaged spectra, is always lower than 7%. Figure 6 shows the Raman spectra of PEO at 30 °C, (PEO)₃LiTf determined as described above, and 1 M LiTf in water. In this last case, LiTf is likely fully dissociated, and the observed bands are the internal modes of Tf$^-$. These bands are observed almost unchanged in the (PEO)₃LiTf spectrum, which confirms structural data.[11] The major changes are observed in the 1030−1080 cm^{-1} range, corresponding to the symmetric stretching of the SO₃ subunit. These changes are discussed later.

Determination of the Various Phases Raman Spectra. PEO−LiTf complexes are multiphase systems. Their Raman spectrum is therefore the superimposition of the Raman spectra of the various phases. Relevant informations about each phase can thus be obtained if we are able to separate the various
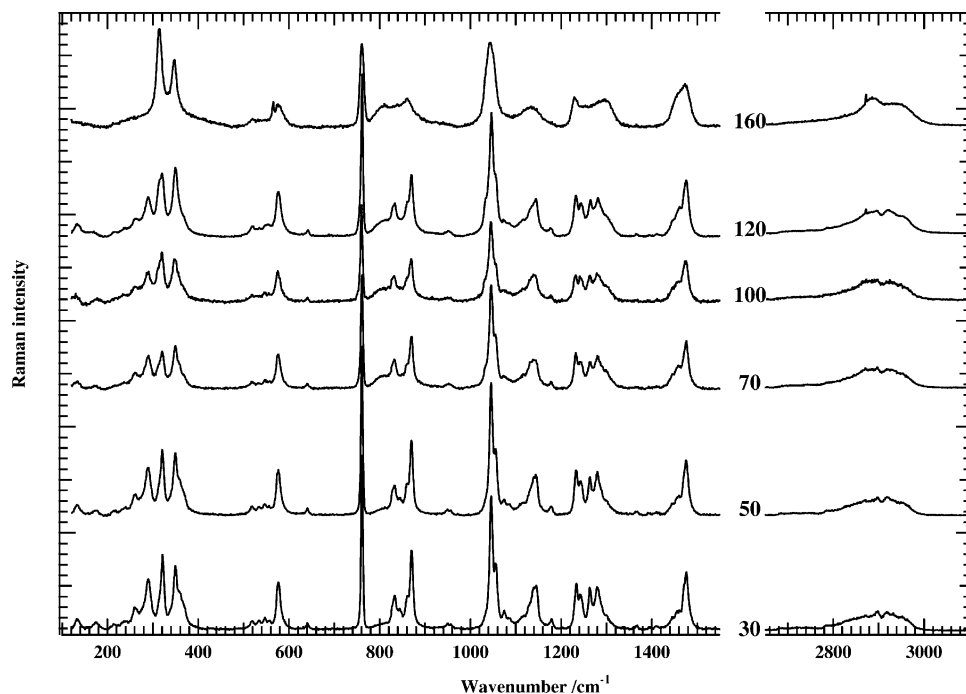
Figure 3. Raman spectra of PEO−LiTf with O/Li = 4 at various temperatures, indicated in °C near each spectrum.
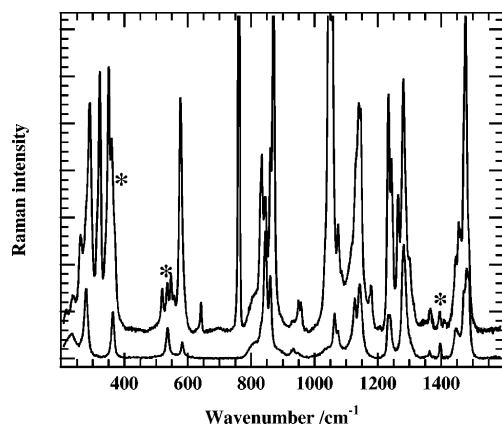
Figure 4. Raman spectrum of PEO−LiTf complex with O/Li = 6 (top) and of PEO (bottom) at 40 °C. Asterisks indicate bands which were used to scale the PEO spectrum before subtracting it.

contributions to the experimental Raman spectrum. Below 60 °C and for O/Li = 4 and 6, we have shown that the Raman spectrum is the sum of that of PEO and a spectrum that we attribute to (PEO)$_3$LiTf. Above the liquidus temperature, and for all samples, there is only one liquid phase. For other temperatures and compositions, we expect the sample to be composed of (PEO)$_3$LiTf, PEO, and at least one other phase, either solid (below 60 °C) or liquid. Since we know the Raman spectrum of (PEO)$_3$LiTf, which does not change much with temperature, and the Raman spectrum of PEO as a function of temperature, the goal is to remove these spectra from the experimental ones. This was achieved by manually scaling the spectrum to be removed so that bands specific to this spectrum disappear while no part of the remaining spectrum becomes negative. A typical example is shown in Figure 7 for O/Li = 18 at 80 °C. Spectra obtained by subtracting the (PEO)$_3$LiTf spectrum from the experimental one are shown. The ×1-labeled spectrum is that obtained with the finally retained (PEO)$_3$LiTf fraction. Other spectra show the result of subtracting more (×1.1 and ×1.2) or less (×0.9 and ×0.8) (PEO)$_3$LiTf. If we subtract too much (PEO)$_3$LiTf spectrum, negative bands appear (indi-

cated by arrows in Figure 7). On the contrary, an underestimation of the (PEO)$_3$LiTf content is indicated by the presence of specific bands (indicated by asterisks) and shoulders. The determination of the limit value is thus rather stringent.

After having subtracted the correctly scaled (PEO)$_3$LiTf spectrum, calibration and subtraction of the PEO spectrum are quite easy because of the very different bands of each component.

Sample Structure for *T* > 60 °C and O/Li > 6. We have shown that, for O/Li = 4 and 6, and below the melting temperature of PEO, Raman spectra could be decomposed into pure PEO spectrum and (PEO)$_3$LiTf spectrum. This is not any more the case for *T* > 60 °C, in agreement with the phase diagram. Above 60 °C, PEO melts and (PEO)$_3$LiTf starts to melt, thus releasing PEO and salt into the liquid phase. Since electrical conduction takes place in this melted phase, it is important to know its LiTf content. It was determined as follows. The Raman spectrum of melted PEO is mostly composed of wide bands, especially below 800 cm^{-1}. Narrow bands in the experimental spectrum are thus those of Tf$^−$ and (PEO)$_3$LiTf compound. Once the spectrum of (PEO)$_3$LiTf is properly scaled, the ratio of the intensity of one Tf$^−$ band in the scaled (PEO)$_3$LiTf spectrum and in the initial spectrum gives the fraction of LiTf remaining in the (PEO)$_3$LiTf compound. For this purpose, the narrow and isolated band at 756 cm^{-1} was chosen.

Below 60 °C, the PEO fraction not present in the (PEO)$_3$LiTf compound is equal to $(a - 3)/a$, where a is the O/Li ratio of the sample. If x is the fraction of LiTf in the (PEO)$_3$LiTf compound, the PEO fraction not involved in the (PEO)$_3$LiTf compound above 60 °C becomes $(a - 3x)/a$. The mass fraction of LiTf, m_{LiTf}, in the liquid phase can then be determined according to

$$m_{LiTf} = \frac{(1 - x)M_{LiTf}}{(1 - x)M_{LiTf} + (a - 3x)M_{EO}} \quad (2)$$

where M_{LiTf} and M_{EO} are the molecular weights of the salt (156 g) and of an ether oxide subunit (44 g).

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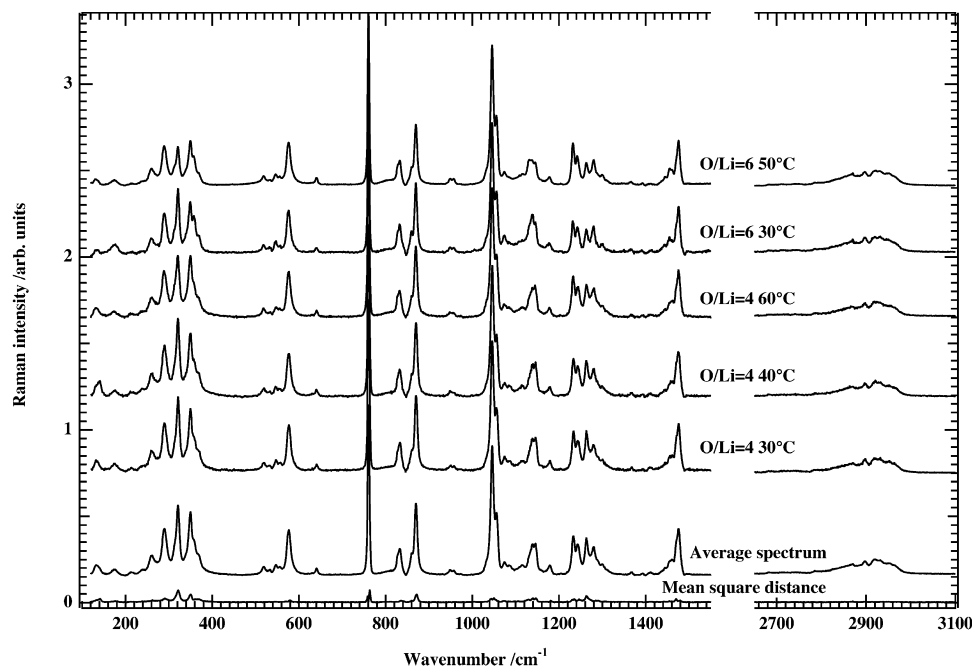
Figure 5. Raman spectrum of (PEO)₃LiTf obtained by subtracting the appropriate amount of PEO spectrum from the experimental data. The five top spectra are individual difference spectra. The specrum labeled average is the mean of all difference spectra obtained from samples with O/Li = 4 and 6 at temperatures between 30 and 60 °C. The bottom line is the mean square distance between average and individual difference spectra (see text).
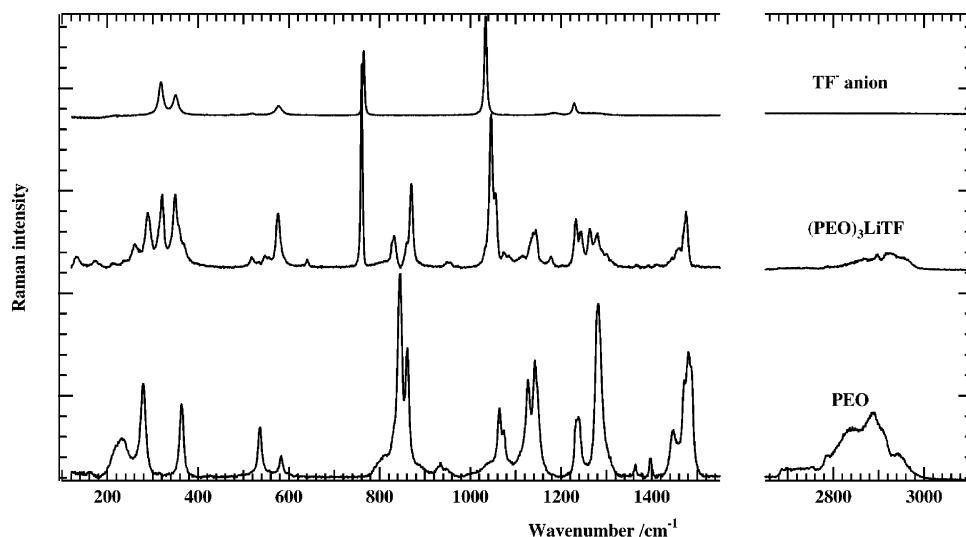

Figure 6. Raman spectrum of PEO at 30 °C, (PEO)₃LiTf determined from difference spectra of (PEO)₄LiTf and PEO at temperatures between 30 and 60 °C and averaged, and Tf⁻ from a 1 M solution of LiTf in water at room temperature.

m_{LiTf} has been calculated over 60 °C for the samples with O/Li = 3 and 6, and at all temperatures for O/Li = 11, 15, and 18 and reported in the phase diagram of Vallée et al.[9] (Figure 8). There is a good correlation between the values calculated from the Raman spectra and the phase diagram, except for O/Li = 4 for which values are systematically overestimated. Below 60 °C, for O/Li = 11 and over, the experimental points lie roughly below the eutectic point. It means that the part of the sample which has not crystallized as (PEO)₃LiTf has the eutectic composition.

**Li⁺−Tf⁻ Association.** Interactions of Tf⁻ with Li⁺ in polymers have been widely studied both experimentally and theoretically through the symmetric stretching bands located in the 1030−1060 cm⁻¹ region. Free anions are characterized by a band at 1035 cm⁻¹. The Raman spectrum of LiTf in water fits well with these data: a single band is observed at 1034 cm⁻¹

(Figure 6). For the (PEO)₃LiTf compound, three bands appear at 1033, 1045, and 1056 cm⁻¹, with relative intensities of 0.03, 0.72, and 0.25, respectively (Figure 9a). For the samples with O/Li > 6 and below 70 °C, subtraction of the Raman spectrum of (PEO)₃LiTf and of pure PEO gives spectra very close to that of (PEO)₃LiTf. Figure 9a shows a typical example for O/Li = 15, while Figure 9b shows for two temperatures the different subtraction steps. Above 70 °C, the two major bands located at 1045 and 1055 cm⁻¹ are progressively replaced by bands at 1032 and 1040 cm⁻¹ (Figure 9).

Figure 10 shows the relative intensities of the bands at 1032, 1040, 1045, 1050, and 1056 cm⁻¹ as a function of temperature for two samples: O/Li = 18 and O/Li = 6. For temperatures below the liquidus temperature, the 1045 cm⁻¹ band dominates, with an important contribution of the 1032 cm⁻¹ band. Above the liquidus temperature, there is a strong change with the

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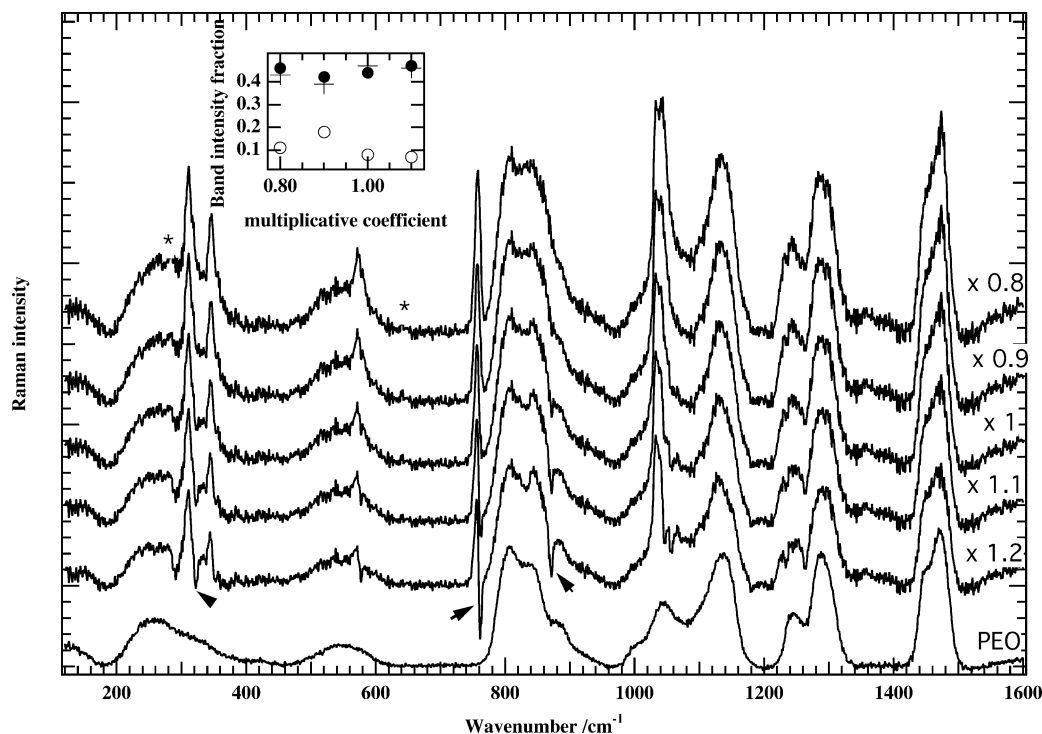
Figure 7. Subtraction of the (PEO)$_3$LiTf spectrum from experimental spectra. Sample with O/Li = 18 at 80 °C. The (PEO)$_3$LiTf spectrum is scaled by hand and then subtracted from the experimental spectrum. In this figure, the finally retained difference spectrum is that labeled ×1. For the other spectra, the (PEO)$_3$LiTf spectrum was first multiplied by the factor indicated and then subtracted. When the (PEO)$_3$LiTf fraction is overestimated (spectra ×1.1 and ×1.2), negative spots appear (arrows). If the (PEO)$_3$LiTf fraction is underestimated, some of its bands start to appear (asterisks). The spectrum of PEO is shown to demonstrate that its accurate subtraction is rather easy. Insert: decomposition of the 1030−1060 cm^{-1} region as a function of the multiplicative coefficient applied to the (PEO)$_3$LiTf spectrum. Symbols are those of Figure 10.
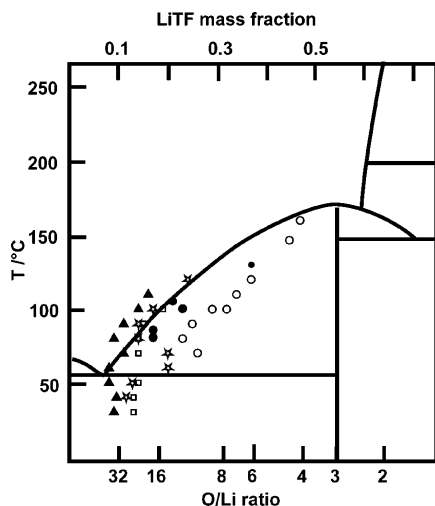
Figure 8. Calculated LiTf mass fractions in the PEO phase (liquid phase above 60 °C) reported in the phase diagram from ref 9. Samples with O/Li = 4 (open circles), O/Li = 6 (close circles), O/Li = 11 (stars), O/Li= 15 (squares), and O/Li = 18 (triangles).

disappearance of the 1045 and 1056 cm^{-1} bands and the appearance or increase of a 1050 cm^{-1} band. Simultaneously, the band at 1040 cm^{-1} becomes more important.

The accuracy of the technique has been checked using data shown in Figure 7. The inset of Figure 7 shows the results obtained when the fraction of (PEO)$_3$LiTf spectrum is overestimated or underestimated. In fact, the decomposition in the 1030−1060 cm^{-1} region is quite independent of quite large misestimations of the (PEO)$_3$LiTf content in the sample.

Li$^+$−PEO Association. The solvation of lithium cations by the ether oxygen of the PEO chain has been viewed through a band appearing near 870 cm^{-1} and attributed by both theoretical and experimental[5] results to the vibration of ether oxygens solvating the Li$^+$ cation. The ratio of this band to the band at 756 cm^{-1} corresponding to δ-CF$_3$ can be used to determine the fraction of Li$^+$ ions solvated by the polymer chains[12] by comparing it to that obtained for PEO$_3$LiTf (0.68), assuming that all Li$^+$ ions are solvated by the PEO chains in PEO$_3$LiTf. We have applied this method to the spectra obtained after subtraction of the (PEO)$_3$LiTf spectrum. The fraction of "free" Li$^+$ ions, i.e., not solvated by the polymer chain, is shown in Figure 11. For O/Li = 4, this ratio could not be determined for $T < 120$ °C because of insufficient remaining spectrum. It can be observed that the free Li$^+$ fraction solvated by PEO increases abruptly near the liquidus temperature for a given composition. Above the liquidus temperature, the interactions, as measured by the band at 870 cm^{-1}, vanish.

Discussion

The usual description of PEO−LiTf complexes structure is a three-components one, crystals of (PEO)$_3$LiTf mixed with pure PEO and an amorphous phase. Our results are consistent with this picture for a part only. The Raman spectrum of (PEO)$_3$LiTf has been determined. It is present in proportions consistent with the phase diagram of Figure 8 at all salt contents and all temperatures and disappears at the liquidus temperature. This calculated spectrum is consistent for the 700−900 cm^{-1} region with that published by Frech et al.[8] In the 100−1100 cm^{-1} region, the spectrum published by Rhodes and Frech[2] is rather different, with a single band at 1050 cm^{-1} that they attribute to Tf$^-$ linked to two Li$^+$, in agreement with the structural data. Our result is however consistent with that of Caruso et al.,[13] with bands at 1032 (shoulder), 1045 (major), and 1056 (minor) cm^{-1}. It can be noticed that we used a near-IR excitation (785
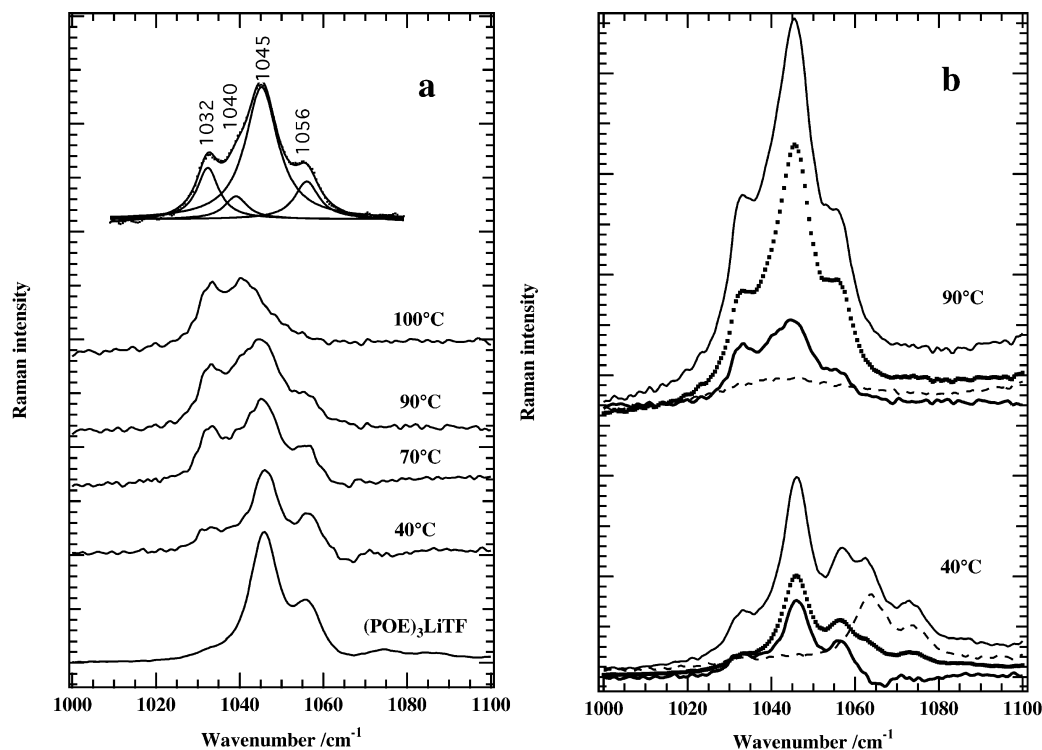
Figure 9. (a) Raman spectra characteristic of Tf⁻ in PEO−LiTf complex with O/Li = 15 at various temperatures in the SO_3 symmetric stretching region. These spectra were obtained by subtracting first the spectrum of $(PEO)_3LiTf$ calculated as indicated in the text and second the spectrum of pure PEO at the same temperature. The Raman spectrum of $(PEO)_3LiTf$ is provided for comparison. Top: decomposition of the 90 °C spectrum into four bands. (b) Example of spectral subtractions at two different temperatures: thin full line, experimental spectrum; dots, scaled $(PEO)_3LiTf$ spectrum; broken line, scaled PEO spectrum; thick full line, final difference spectrum.

nm) and Caruso et al. a red excitation (633 nm) while Rhodes et al. used a green excitation which implied a fluorescence bleaching step at 100 mW laser power. It is possible that this bleaching step has locally allowed the polymer melting and quenching. In accordance with this interpretation, we have observed such a band at 1050 cm⁻¹ at high temperature (Figure 10).

The observation of two intense bands in the SO_3 symmetric stretching region in the Raman spectrum of $(PEO)_3LiTf$ is not consistent with the generally accepted picture of bands depending on the association with cations. The crystal structure indicates that all triflate anions have the same environment, with two of the oxygens linked to a Li⁺ cation and one free. A better explanation could be found in the symmetry properties of the crystal. Even with a triflate anion described in the C_{3v} symmetry, one expects two bands in the crystal originating from the symmetric stretching mode of the isolated molecule. Another possibility, which preserves the molecular nature of the vibration, is to take into account the departure from C_{3v} symmetry for the triflate ion in the crystal. The real symmetry is C_1, with two S−O distances very close,[11] consistent with two strong bands. For temperatures higher than 60 °C, the bands which become predominant at 1032 and 1040 cm⁻¹ can be explained in terms of ion association, the band at 1032 cm⁻¹ corresponding to free anions and that at 1040 cm⁻¹ to ion pairs. The sharp increase of the 1040 cm⁻¹ band near the liquidus temperature suggests that the local symmetry is very close to that of the crystal as long as there remains an important fraction of solid, even in melted regions.

Below 60 °C, the part of the polymer not involved in $(PEO)_3LiTf$ was assumed to be pure PEO for the samples with O/Li = 4 and 6. For the samples with a higher O/Li ratio, the remaining sample is better described by a mixture of lithium

triflate and PEO, in which interactions between Li⁺ and Tf⁻, and between Li⁺ and the PEO chain are very similar to those observed in $(PEO)_3LiTf$. This is clearly observed in the 1030−1060 and in the 850−870 cm⁻¹ regions. The overall composition is close to that of the eutectic. It can be supposed that the remaining liquid with the eutectic composition crystallizes rapidly, thus inhibiting the growth of real $(PEO)_3LiTf$ crystals, but that the local structure is similar that of $(PEO)_3LiTf$. More surprisingly, above 60 °C, the same interactions remain up to temperatures close to the liquidus temperatures. This indicates a high stability of these local interactions.

Finally, there has been no evidence of an important amorphous phase in the solid fraction of the samples. Because of the polymer chain length, disordered domains must exist between crystallites which permit accommodation of crystallographic misfits. We suggest that these regions have a local structure very close to that observed in the crystals, thus preventing one from observe them as very different regions by spectroscopic techniques. In the absence of dynamic disorder, such as in the liquid state, the static disorder of these regions is probably insufficient to modify strongly the Raman spectrum. This interpretation is in accordance with the study of Frech et al.,[8] who observed no significant shift in the frequency of the CH_2 rocking bands upon melting of the $(PEO)_3LiTf$ complex.
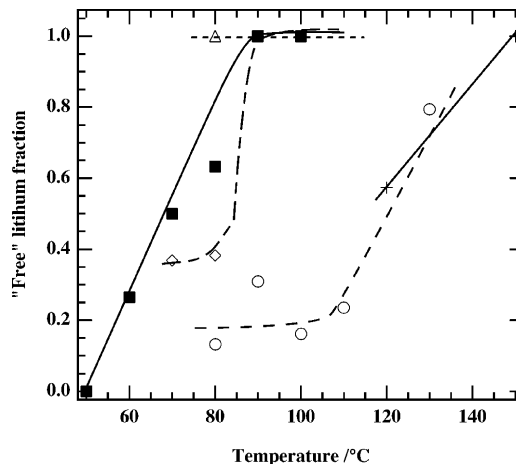
Conclusion

Raman spectra of PEO−LiTf complexes have been obtained as a function of temperature with a 785 nm excitation. The complete Raman spectrum of PEO is provided for the first time up to complete fusion. The Raman spectrum of the $(PEO)_3LiTf$ defined compound has been calculated. Below 60 °C, and for O/Li = 4 and 6, samples are composed of pure PEO and

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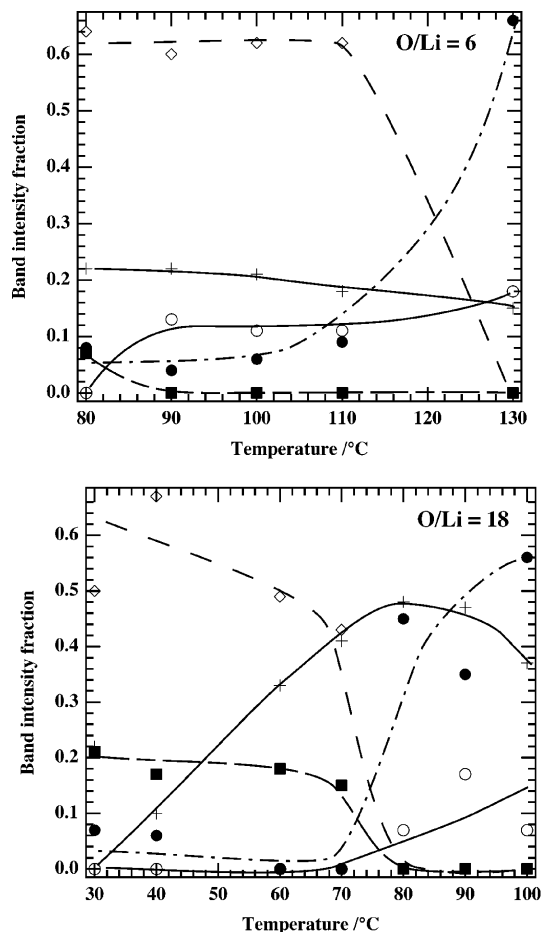
Figure 10. Relative intensities of the bands in the SO_3 symmetric stretching region for O/Li = 6 (top) and O/Li = 18 (bottom). Symbols: 1032 cm^{-1} (+), 1040 cm^{-1} (filled circles), 1045 cm^{-1} (diamonds), 1050 cm^{-1} (open circles), and 1056 cm^{-1} (filled squares). Lines are guides for the eyes.

Figure 11. "Free" lithium ion fraction outside (PEO)$_3$LiTf as a function of temperature: triangles, O/Li = 18; diamonds, O/Li = 15; squares, O/Li = 11; circles, O/Li = 6; +, O/Li = 4. Lines are guides for the eyes.

at the liquidus temperature. At the same time, the number of ion pairs increases sharply. This suggests that salt and PEO backbone become quite independent at this temperature.

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(PEO)$_3$LiTf. For higher O/Li ratios, it is composed of (PEO)$_3$LiTf and a mixture of PEO and LiTf having the composition of the eutectic. The Li$^+$−PEO chain and Li$^+$−Tf$^-$ interactions are very similar to those observed in (PEO)$_3$LiTf. Surprisingly, these interactions remain the same above 60 °C up to temperatures close to the liquidus temperature where important changes are observed. In particular, the Li$^+$−PEO chain interaction, as measured by the band at 870 cm^{-1}, vanish