ON THE STRUCTURE OF ARCHETYPAL POLYMER ELECTROLYTE PEO:LiCF$_3$SO$_3$

A. BRODIN[1,2], P. JACOBSSON[3]

UDC 544.6.018.42-16

©2009

[1]**Institute of Physics, Nat. Acad. of Sci. of Ukraine**
(46, Nauky Prosp., Kyiv 03028, Ukraine; e-mail: alex.brodin@gmail.com),

[2]**National Technical University of Ukraine "KPI"**
(37, Peremogy Ave., Kyiv 03056, Ukraine),

[3]**Department of Technical Physics, Chalmers University of Technology**
(Göteborg SE-41296, Sweden)

We report on a systematic micro-Raman and IR spectroscopic investigation of PEO-LiCF$_3$SO$_3$ polymer electrolytes, aimed at revealing the microstructure of ionically conductive amorphous PEO:Li$^+$ complexes. Films (O:Li = 3:1 and 9:1, thickness 2–30 μm) were cast from acetonitrile solutions and further subjected to different heat treatment procedures within the course of investigations. Polarized optical microscopy was used to reveal the morphology of films. At the stoichiometric composition, the highly crystalline films exhibited a rather uniform (although anisotropic) structure which was examined by polarized micro-Raman spectroscopy to establish the relation between the crystalline structure and its spectroscopic signatures. The systems of non-stoichiometric composition (O:Li=9:1) exhibited a non-uniform, multiphase structure. The structural changes on increasing the temperature, when the relative amount of the disordered phase increases to finally form a uniform melt, have been monitored. We show that anion internal vibrational modes, routinely used to quantify different ionic species in the electrolyte, are substantially influenced by the crystalline field of the complexes, so that conventional analysis of the splitting and the band shift of non-degenerate internal modes in terms of different coordinations is no longer applicable. We show that Raman spectroscopy is a more sensitive probe of the polymer conformational order and the cation coordination than IR spectroscopy. We discuss, based on the obtained experimental evidences, to which extent the crystalline structure of the stoichiometric complex is related to the microstructure of the conductive amorphous phase. Comparative analysis of Raman spectroscopic signatures of the crystalline complex, molten phase, and model low molecular weight (M$_w$ $\leq$ 1000 g mol^{-1}) systems allows us to conclude that the structure of amorphous PEO:Li$^+$ complexes is similar (though not identical) to the structure of the crystalline one. The similarity consists in that the polymeric chain "wraps" around a cation in both cases.

1. Introduction

Three decades of research efforts into the field of polymer ionics have resulted in the development of a number of polymer electrolytes suitable for applications and have immensely increased our understanding of the basic physics of these "soft" ionic conductors (for reviews, see [1,2] and references therein). The limiting value of ionic conductivity, as set by liquid electrolytes, has not, however, been reached for solvent free systems. This fact reflects, of course, the basic differences between low molecular weight aprotic solvents and high molecular weight polymers. As for the solvent free systems, a striking observation is that the archetypal compound originally introduced, namely poly(ethylene oxide) (PEO) complexed with a lithium salt, still retains its position both as a model system setting the standard of high ionic conductivity for solid polymer electrolytes and as one of the best ingredients for more sophisticated systems [2].

It has been anticipated already at the beginning of the polymer ionics era that the ability of PEO chains to form helices, "wrapping around" the cations and thus forming channels for ionic transport, may be at the origin of the superior ion conduction properties of these materials [3,4]. For the same reason of high chain flexibility, PEO is an excellent solvent for metal cations. This high flexibility, which means essentially small energy changes associated with internal rotations, allows the chains to easily change the conformational state in response to small perturbations. For instance, elementary steric and electrostatic considerations suggest the all-*trans* (or *ttt*, referring to the bonds in the sequence O-C-C-O) of the lowest-energy conformation of the chain, while the actual conformational state of crystalline PEO is *tgt* (*trans-gauche-trans*), thereby demonstrating how easily the conformation changes under the influence of, in this case, inter-chain dipole-dipole interactions. Hence, it is hardly surprising that an electrostatic interaction with a cation can be a sufficient "perturbation" to induce the chain bending, which thus lends support to the "wrapping" model. A better knowledge of the microstructure is highly desirable, as a seemingly "innocent" difference between intra-chain and inter-

chain cation coordinations implies quite different physics of the ion transport.

As for the experimental determination of the structure of PEO-based polymer electrolytes, it has been most successful concerning non-conductive crystalline stoichiometric phases [5]. Powder X-ray diffractometry of stoichiometric complexes of PEO with a number of alkali metal salts yielded an important conceptual result, namely that, in all these structures, the cations are located within the PEO helices [5]. In one crystalline complex, based on a low molecular polyether and $LiSbF_6$ (O:Li = 6:1), a recent work reported the ionic conductivity only by some order of magnitude lower than in the best high molecular based amorphous complexes [6]. However, it is the structure of the highly conducting disordered phase which is of ultimate interest, and it appears clear that the crystalline structures, while suggesting a clue, may not be directly transferable to the amorphous phase [7]. We have therefore undertaken the present spectroscopic investigation of PEO-based polymer electrolytes, containing $LiCF_3SO_3$ (Li triflate, denoted LiTf below) salt, aimed at revealing the microstructure of ionically conductive PEO:Li$^+$ complexes. We have followed structural changes of the crystalline PEO$_3$:LiTf complex upon melting and combined the obtained spectroscopic information with our previous results on model low-M_w (≤ 1000 g mol^{-1}) systems. Based on these evidences, we discuss, to which extent the crystalline structure of the stoichiometric complex is related to the microstructure of the conductive amorphous phase.

2. Experimental

PEO (M_w = 2.3×10^5 g mol^{-1}, Polymer Source) and $LiCF_3SO_3$ (Aldrich) were dried in vacuum at 50°C and 110°C, respectively, and thereafter dissolved in predetermined amounts in dry acetonitrile (Fluka, H$_2$O<0.01%). Films (O:Li = 3:1, 9:1, thickness 2–30 μm) were cast from the acetonitrile solutions on glass or Si substrates and further subjected to different heat treatment procedures within the course of investigation. Polarized optical microscopy was used to reveal the morphology of the films. At the stoichiometric composition, the highly crystalline films exhibited a rather uniform (although anisotropic) structure which was examined by polarized micro-Raman spectroscopy to establish the relation between the crystalline structure and its spectroscopic signatures. The systems of non-stoichiometric composition exhibited a non-uniform, multiphase structure.

A Dilor LabRam confocal micro-Raman spectrograph equipped with a He-Ne laser, 1800 grooves/mm grating, and a CCD-camera (Wright) and a vacuum chamber/heating stage (Linkam) were used for Raman measurements. The Raman microscope provides the nearly diffraction limited spatial resolution which can be reduced in our implementation to 1μm lateral versus 2μm in-depth. Infrared spectra were recorded using a Bruker VECTOR 22 FT-IR spectrometer. The spectral resolution was typically set to ~1 cm^{-1}. The accuracy of the frequency calibration is estimated to ± 0.5 cm^{-1}.

3. Results and Discussion

3.1. Stoichiometric complex PEO$_3$:LiCF$_3$SO$_3$

The ordered crystalline structure and morphology of the stoichiometric complex presents an important advantage over disordered phases for polarized micro-Raman spectroscopy in that different components of the Raman tensor can be probed independently and a link be established between these spectroscopic signatures and the known structure. Our first objective was thus to prepare homogeneous specimens of PEO$_3$:LiTf (PEO$_3$:LiCF$_3$SO$_3$) with reproducible and well-defined morphology. Initial samples were obtained by drying solution-cast films at 50°C in vacuum. The samples, exhibiting a typical spherulite supermolecular structure, were then subjected to melt re-crystallization in vacuum with different heating/cooling rates in search for the most homogeneous structure, the latter determined by polarized optical microscopy in combination with micro-Raman spectroscopy. IR spectra (not shown) of the films were taken after each step of the preparation procedure, and it is reassuring to note that the spectra of all the samples were virtually indistinguishable, thus proving that, in all cases, we were dealing with the stoichiometric crystalline 3:1 complex and that different treatments resulted only in different supermolecular macrostructures.

In Fig. 1, we present the polarized room temperature Raman spectra of the PEO$_3$:LiTf complex. We emphasize that the sample exhibited a uniform (however non-isotropic) Raman response with no detectable spectral contribution attributable to pure crystalline PEO, i.e. the sample represented a pure crystalline 3:1 complex with well-defined spherulite symmetry and morphology. The traces in Fig. 1 are marked using the conventional Porto notation, where the symbols in sequence $A(BC)D$ refer to the propagation direction (A) and polarization (B) of the exciting light, and

polarization (C) and direction (D) of the scattered field, respectively. The X and Y axes correspond to the radial and tangential directions in a spherulite, respectively.

Before we proceed to discuss the spectra in Fig. 1, some general considerations should be given. The crystallinity of a polymer system is always less than 100% due to the inevitable presence of amorphous interlamellar regions. If, in a micro-Raman experiment, such a system gives a non-isotropic but uniform response across the sample, this means that the length scale of crystallinity variations is less than, while the orientational order scale is greater than, the size of the sampling volume. A measured spectrum then contains two contributions, an isotropic amorphous and an anisotropic crystalline contribution. The anisotropy of the crystalline spectra is related to the local crystal orientation and the structure of the Raman tensor, the latter depending on the crystal symmetry. Thus, information on the local orientation and Raman tensor components can be extracted from anisotropic Raman spectra. In the present contribution we limit, however, the discussion to only basic considerations of the crystal symmetry in relation to vibrational spectra. The crystalline stoichiometric 3:1 PEO:LiTf system is composed of one-dimensional coordination complexes, each one consisting of a polymer chain along with coordinated ions [8]. The crystal symmetry belongs to the space group P2$_1$/a, with the corresponding point group C$_{2h}$. This is a centrosymmetric group, and hence the exclusion principle applies, meaning that the IR-modes are inactive in Raman and vice versa. However, the inversion operation relates different chains in the structure. Hence, the *gerade-ungerade* splitting may diminish for the modes that are not coupled between the chains.

The polarized XX and YY spectra in Fig. 1 are dominated by two bands at $\sim$760 cm^{-1} and $\sim$1050 cm^{-1} originating from a triflate anion. We shall first discuss these spectral features, as they represent a subject of the vast literature devoted to the triflate anion spectroscopy in polymer solutions. For an isolated triflate anion, both bands would correspond to totally symmetric vibrations, so that a splitting and/or frequency shift of the bands are usually interpreted in terms of different coordinations of the anion [9]. According to these assignments, one can distinguish between free anions (752 cm^{-1}, 1032 cm^{-1}), anion-cation pairs (757 cm^{-1}, 1041 cm^{-1}) and more complex ionic species, involving most likely two cations coordinated to a single anion (763 cm^{-1}, 1050 cm^{-1}). An immediate observation from Fig. 1 is that the bands (760 cm^{-1}, 1045 cm^{-1}) cannot be directly
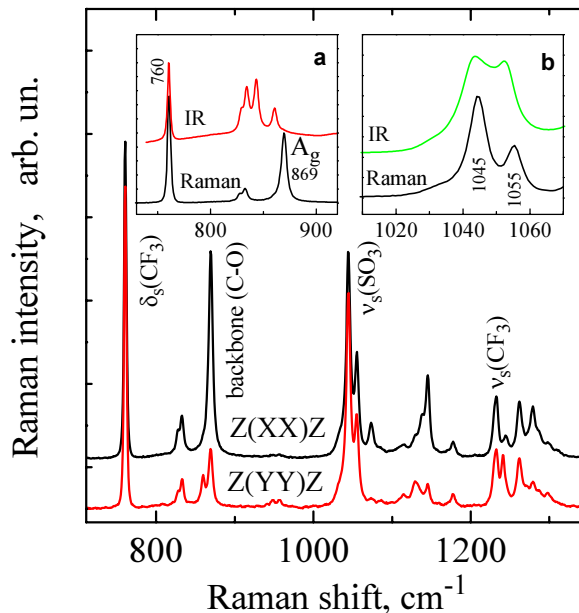

Fig. 1. Room temperature polarized Raman back-scattering spectra of a PEO$_3$:LiCF$_3$SO$_3$ film with well defined supermolecular structure. Inserts *a* and *b* show selected parts of the $Z(XX)Z$ spectrum along with the IR-absorption spectra of the film

associated with any ionic species of the above assignment. However, the structure of the 3:1 complex, and therefore the anion coordination, is known from X-ray diffractometry [8]: all triflate anions occupy equivalent lattice cites and are coordinated to two Li cations, the latter are also coordinated by (enclosed into) the PEO helix. The departure of the bands from the expected frequencies (763 cm^{-1}, 1050 cm^{-1}) shows that the influence of the crystal field in the complex on the vibrational frequencies is comparable in strength to the effect of different coordination numbers. This observation has obvious implications for the interpretation of the spectroscopic information about PEO-salt complexes, particularly in the cases where the presence of ordered phases can be expected. Another important observation is that the 1045-cm^{-1} band is split, with a clear high-frequency component at 1055 cm^{-1}. Attempts to interpret this splitting in terms of different anion environments would be erroneous, as the environment is the same, which is supported by both the diffraction studies [8] and the absence of any splitting of the 760cm^{-1} mode, see Fig. 1. The splitting should thus be due to a coupling of SO$_3$ group vibrations with polymer modes and/or with nearby anions. For instance, a coupling between the transition dipoles of nearby
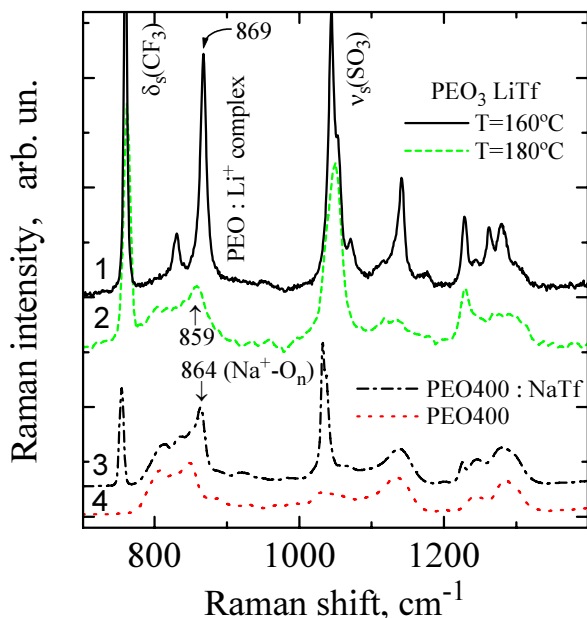
Fig. 2. Traces *1* and *2*: polarized $Z(XX)Z$ Raman spectra of a PEO$_3$:LiCF$_3$SO$_3$ film at temperatures below (trace *1*) and above (trace *2*) the melting point (T_m=179 °C). Traces *3* and *4*: polarized (VV) room temperature Raman spectra of poly(ethylene oxide) dimethyl ether, pure (trace *4*) and complexed with NaCF$_3$SO$_3$ at O:Na=15:1 (trace *3*)

triflate anions would give rise to a correlation field (Davydov) splitting of this vibration into a symmetric / antisymmetric doublet [10]. The two components will then be differently displayed in IR-absorption and Raman scattering. Comparing Raman and IR spectra, see insert *b* in Fig. 1, we observe that both components are present in either spectrum, and that the high-frequency component is more pronounced in the absorbance. The absence of any detectable splitting of the 760-cm^{-1} vibration means that there is no coupling for this mode, in accordance with a much lower transition dipole (absorbance) associated with it.

The most intense polymer mode is observed at 869 cm^{-1} (see Fig. 1). The polarization properties of this mode, along with the fact that it is not IR-active (see insert *a* in Fig. 1), allows us to assign it to an A$_g$ species. A similar, extraordinarily strong Raman band was observed in a number of PEO-Na salt complexes, where it appears at 865 cm^{-1} [4]. Generally, PEO bands with frequencies around 850 cm^{-1} originate from backbone modes, involving mostly the C-O stretch mixed with the CH$_2$ rock [11–13]. These modes are sensitive to the conformational state of the chains, so that a correlation has been established between the conformation of a PEO

molecule and the band frequencies [13,14]. A band at ~850 cm^{-1} is, according to the correlation rule, typical of polymer sequences with *gauche* C-C. The presence of an intense mode at 869 cm^{-1} in the crystalline PEO-Li$^+$ complex, at 865 cm^{-1} in the PEO-Na$^+$ complexes, and at 860 cm^{-1} in crystalline PEO, is then completely consistent with our understanding of the structure of these systems, all exhibiting the *tgt* conformation of O-C-C-O units. The shift of the band frequency from 860 cm^{-1} (PEO) to a higher frequency for PEO:Na$^+$, and to a still higher one for PEO:Li$^+$, can be explained by the polarizing effect of the oxygen-coordinated cations, leading to an increase of the C-O bond force constant. The effect is proportional to the ionic potential e/r [15] and thus stronger for a smaller cation (Li$^+$), as indeed observed. The influence of the crystal field (including the field of the anions) on these frequencies seems of little importance, which follows from the fact that similar Raman bands have been observed in *liquid* complexes of PEO oligomers with Li$^+$ and Na$^+$ ions [16]. Briefly summarizing the relevant results in [16], Li$^+$ and Na$^+$ cations, coordinated *exclusively* to the polymer in the liquid state, give rise to polarized Raman bands at 864 cm^{-1} and 869 cm^{-1} for Na$^+$ and Li$^+$ cations, respectively, i.e. the same frequencies as observed in the corresponding crystalline complexes. The authors of work [16] followed earlier works to term this new band as "metal-oxygen breathing mode", which is somewhat misleading, as the main restoring force of this vibration comes likely from the C-O stretch. Figure 2 (two lower traces) shows the polarized Raman spectra of PEO (M_w=400), pure and complexed with NaTf (O:Na=15:1), both being liquids at room temperature.

The new band at 864 cm^{-1} for PEO:Na$^+$ (depolarization ratio ~0.05) is clearly seen. The following conclusion appears now to be justified: the structural unit giving rise to the new band in *amorphous* PEO:M$^+$, found at 864 cm^{-1} and 869 cm^{-1} for M=Na and Li, respectively, is similar to the structure of the corresponding crystalline complexes in that it should include several monomer units with *gauche* C-C bonds in sequence (to agree with the conformation-frequency correlation rule), with the oxygens coordinating the cation(s) (to account for the band shift). The most likely arrangement of this sort is indeed a turn of the chain wrapping the cation. The apparently high Raman efficiency of the corresponding mode is explained by a coherent in-phase deformation of the several conformationally ordered monomer units in sequence. In the stoichiometric complex, *all* monomer units are conformationally ordered and *all* oxygens

coordinate the cations, accordingly, the band becomes the strongest one of the polymer bands in one of the polarized geometries, see Fig. 1. On increasing the temperature, the crystal and supermolecular structure of PEO$_3$:LiTf does not change until the melting point at 179 °C, and accordingly the Raman spectra stay almost unchanged. However, the further increase to 180 °C brings dramatic changes, see Fig. 2. The mode at 869 cm^{-1}, and therewith the conformational order of the chains (meaning even the short range order), is lost.

3.2. Non-stoichiometric complex PEO$_9$:LiCF$_3$SO$_3$

At this composition, we expect the system be a non-uniform mixture of the crystalline 3:1 complex, crystalline PEO, and an intermediate amorphous phase of varying composition. Accordingly, we expect the Raman spectra sampled from different parts of the specimen to contain contributions from all these phases. Figure 3 shows some representative polarized Raman spectra taken from three different parts of the sample.

Indeed, every one of the spectra can be described as that containing the contributions from crystalline PEO and the crystalline 3:1 complex (these spectra are also presented in Fig. 3 for comparison) in different proportions, ranging from the almost pure stoichiometric complex (trace *1* in Fig. 3) to almost pure PEO (trace *3*). However, this is not a simple additive combination, since the contributions are anisotropic and depend on the relative orientations of crystalline microdomains within the scattering volume, as well as on orientations with respect to the scattering geometry. Some conclusions on the homogeneity of the sample can be drawn from the following observations. As mentioned, the local composition is notably non-uniform and varies on the length scale of $>100\mu$m from salt rich to polymer rich macro-domains, see Fig. 3. In contrast, moving the sampling point by only a few μm (or, alternatively, staying at the same point and changing the spatial resolution of the Raman microscope over 1–4 μm) gave identical spectra. This means that the size of the crystalline microdomains is significantly less than 1 μm, while the local composition is rather uniform over a few μm, including even a certain orientational ordering. Temperature treatment at any temperature above the melting point of PEO ($\sim$60 °C) changed somewhat this morphology, creating minority macrodomains (typical size $\sim$10-30 μm) of almost constant composition. These included even extended amorphous regions. Without the further discussion of the complex morphology of non-stoichiometric complexes and its changes under
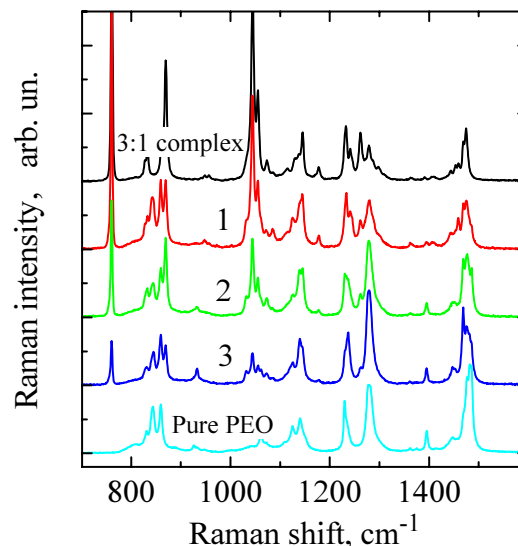

Fig. 3. Room temperature polarized (VV) Raman spectra of a PEO$_9$:LiCF$_3$SO$_3$ film sampled from different regions of the specimen (traces *1–3*) along with spectra of pure PEO and the stoichiometric PEO$_3$:LiCF$_3$SO$_3$ complex

temperature treatment, we note that a part of the systems attributable to the stoichiometric complex shows typical features in Raman spectra, reminiscent of the spectra of the pure complex, see Fig. 3. The most clear spectral "fingerprints" are the triflate anion bands at 760 cm^{-1} and $\sim$1050 cm^{-1}, exhibiting the same frequencies, relative intensities, and the splitting of the high-frequency mode as in the pure complex. Also, both these vibrations have, according to the results of the previous section, almost isotropic Raman tensors, which means that their spectral appearance in a polarized scattering geometry does not depend on the orientation of the crystalline microdomains.

It is known that the ionic conductivity of PEO-LiTf systems is negligibly low at room temperature and starts to rise only at temperatures above the melting point of PEO ($\sim$60 °C), when a part of salt rich crystallites dissolves into the polymer melt. According to the known phase diagram [17], the system remains multiphase up to a composition-dependent temperature, when a homogeneous melt is finally formed. PEO$_9$:LiTf is expected to melt at $\sim$150 °C. The melting temperatures of PEO and PEO$_9$:LiTf determine then the approximate temperature range where the polymer-ion complexes giving rise to the conductivity should be sought.

To separately probe the melt regions by a Raman microprobe, their size should substantially exceed the size of the sampling volume. The latter can be estimated
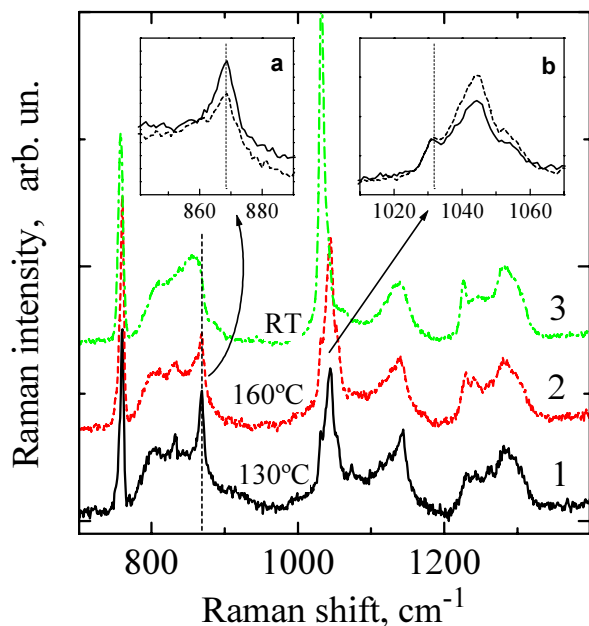
Fig. 4. Polarized (VV) Raman spectra of a $PEO_9:LiCF_3SO_3$ film at two selected temperatures (traces *1* and *2*), and a $PEO_3:LiCF_3SO_3:H_2O$ amorphous film at room temperature (trace *3*)

to $\sim$5–20 μm in our experimental arrangement for measurements at elevated temperatures, i.e. the spatial resolution was significantly reduced in comparison with that in RT measurements. We note that, on this length scale, the samples remained non-uniform until temperatures as high as 120–130 °C, and only then extended uniform melt regions were formed. In Fig. 4, we show the polarized Raman spectra of the same uniform region of the sample at 130 and 160 °C (traces *1* and *2*). We also include (see trace *3*) a room temperature spectrum of a completely uniform amorphous film of the same polymer-salt composition, containing $\sim$15 wt% water (as determined by IR spectroscopy).

Water acts essentially as the crystallization inhibitor. Since it also effectively coordinates cations and ether oxygens (the latter via hydrogen bonding), the polymer-cation complexes get completely destroyed, which is evident from the absence of the corresponding Raman band at 869 cm^{-1}, discussed in the preceding section. Since water itself does not have any Raman bands in the presented spectral region, the spectrum of the water-containing sample (trace *3* in Fig. 4) can be regarded as an ideal case of completely amorphous $PEO_9:LiTf$ without any polymer-cation complexes typical of water-free systems. Comparing this spectrum with spectra *1* and *2* of the PEO-LiTf melt, we note that the latter

demonstrate the existence of polymer-Li^+ complexes, since the mode at 869 cm^{-1} is clearly present (see insert *a* in Fig. 4). The possible presence of microcrystals of the 3:1 phase (which would also give rise to a mode at the same frequency, as discussed above) can probably be ruled out, especially for T=160 °C, where the sample has completely melted, while the 869-cm^{-1} mode is still present. Comparing the intensities of the 869-cm^{-1} mode at the two temperatures, we note that the number of PEO:Li^+ complexes decreases with increasing temperature, in accordance with the accepted models of polymer-cation complexation. Focusing on the SO_3 stretch band (insert *b* in Fig. 4), we note that its intensity (and thereby the salt concentration) is higher for a higher temperature, which should be expected from the phase diagram [17]. A weak spectral feature observed at 1032 cm^{-1} (insert *b* in Fig. 4) can probably be attributed to "free" anions, allowing thereby for the presence of "free" (i.e. polymer-coordinated) cations which, we believe, give rise to the band at 869 cm^{-1}. More detailed quantitative analysis, including the band decomposition into "ion pairs", "aggregates", etc., is probably not warranted, since, as we have shown, the transition dipole and/or mechanical (elastic) coupling between different oscillators, expected for high salt concentrations, may give rise to the band splitting similar to the effect of different coordination numbers. In fact, the band profile in Fig. 4 (insert *b*) bears a certain resemblance with the corresponding split band of the crystalline 3:1 complex (see Fig. 1, insert *b*), discussed in the preceding section. While it hardly seems possible to accept that a true crystalline phase is present in the homogeneous melt (Fig. 4), some short-range ordering of anion-cation complexes may still persist, allowing thus for the correlation field splitting similar to the crystalline case.

4. Conclusions

The formation of polymer-salt complexes in PEO:LiTf polymer electrolytes is accomplished via the conformational ordering of the polymer chains or chain segments, with several ether oxygens in sequence coordinating the cation(s). This arrangement of PEO chains gives rise to distinct spectral features in Raman spectra, which can thus be used to monitor the complex formation. The most sensitive Raman band, found at 864 cm^{-1} for PEO:Na^+ and at 869 cm^{-1} for PEO:Li^+, originates from the in-phase C-O stretch of several monomer units in sequence, each having *gauche* C-C bond and the oxygen coordinating a cation.

This arrangement, found in crystalline stoichiometric complexes of the corresponding compounds, implies that the polymer chain wraps the cations, thus lending support to the wrapping mechanism of cation solvation even in amorphous poly(ethylene oxide)-derived electrolytes. This conclusion does not mean, however, that the structure of crystalline polymer-salt complexes is directly transferable to the amorphous ones, as is often assumed. Exemplifying the possible consequences of such an assumption, we mention a IR-spectroscopic study of a stoichiometric PEO$_3$:LiTf complex [18], where the authors, based on the transferability assumption, reached a conclusion that the structure of the complex (meaning the short-range order) is preserved on melting, while we show, for the stoichiometric complex, that the orientational (short-range) ordering of the polymer needed to form stable complexes, is completely lost in the melt. The mentioned example also indicates that polarized micro-Raman spectroscopy may be a method superior to IR in accessing details of the PEO-ion complexation.

1. M. Armand, Solid State Ionics **69**, 309 (1994).

2. F.M. Gray, *Polymer Electrolytes* (Royal Society of Chemistry, Cambridge, 1997).

3. M. Armand, J. Chabagno, and M. Duclot, in *Extended Abstracts, 2nd International Conference on Solid Electrolytes, St. Andrews, Scotland, 1978.*

4. B. Papke, M. Ratner, and D. Shriver, J. Phys. Chem. Solids **42**, 493 (1981).

5. P. Bruce, Electrochim. Acta **40**, 2077 (1995).

6. Z. Gadjourova, Y.G. Andreev, D.P. Tunstall, and P.G. Bruce, Nature **412**, 520 (2001).

7. P. Johansson and P. Jacobsson, Electrochim. Acta **48**, 2279 (2003).

8. P. Lightfoot and M. Mehta, and P. Bruce, Science **262**, 883 (1993).

9. G. Petersen, P. Jacobsson, and L.M. Torell, Electrochim. Acta **37**, 1495 (1992).

10. R.M. Hexter, J. Chem. Phys. **33**, 1833 (1960).

11. J. Maxfield and I. Shepherd, Polymer **16**, 505 (1975).

12. H. Matsuura and K. Fukuhara, J. Mol. Struct. **126**, 251 (1985).

13. H. Matsuura and K. Fukuhara, J. Polym. Sci. B **24**, 1383 (1986).

14. X. Yang, Z. Su, D. Wu, S. L. Hsu, and H. D. Stidham, Macromolecules **30**, 3796 (1997).

15. M.H. Brooker and M.A. Bredig, J. Chem. Phys. **58**, 5319 (1973).

16. A. Brodin, B. Mattsson, K. Nilsson, L.M. Torell, and J. Hamara, Solid State Ionics **85**, 111 (1996).

17. C.D. Robitaille and D. Fauteux, J. Electrochem. Soc. **133**, 315 (1986).

18. R. Frech, S. Chintapalli, P. Bruce, and C. Vincent, Chem. Commun. 157 (1997).

ДО СТРУКТУРИ КЛАСИЧНОГО ПОЛІМЕРНОГО ЕЛЕКТРОЛІТУ PEO:LiCF$_3$SO$_3$

О. Бродин, П. Якобсон

Р е з ю м е

Повідомлено про систематичне дослідження за допомогою мікрораманівської спектроскопії (КРС) та спектроскопії інфрачервоного поглинання полімерних електролітів PEO-LiCF$_3$SO$_3$, спрямоване на з'ясування мікроструктури іонопровідних аморфних комплексів PEO:Li$^+$. Плівки (O:Li = 3:1 та 9:1, товщина 2 – 30 мкм), отримані з розчинів в ацетонітрілі шляхом випаровування розчинника, піддавалися різноманітним термічним обробкам в процесі досліджень. Морфологію плівок було визначено за допомогою оптичної мікроскопії в поляризованому світлі. Плівки стехіометричного складу були в значній мірі кристалічними з доволі однорідною, проте неізотропною структурою, яку було досліджено за допомогою мікрораманівської спектроскопії поляризованого розсіяння з метою встановлення зв'язку між кристалічною структурою та її спектроскопічними ознаками. Системи нестехіометричного складу (O:Li=9:1) мали неоднорідну, багатофазну структуру. Було досліджено структурні зміни, що відбувалися при підвищенні температури, коли відносна кількість аморфної фази зростала, і система зрештою перетворювалась на однорідний розплав. Показано, що коливальні моди аніона, які, зазвичай, використовуються для кількісного аналізу іонних комплексів, піддаються істотному впливу кристалічного поля, так що традиційний аналіз розщеплення та частотного зміщення невироджених молекулярних мод з метою встановлення типів координаційних зв'язків іонів виявляється непридатним. Показано, що раманівська спектроскопія в значно більшій мірі придатна для визначення конформаційної структури полімеру та катіонної координації, ніж спектроскопія інфрачервоного поглинання. На основі отриманих експериментальних результатів обговорено, в якій мірі кристалічна структура стехіометричного комплексу пов'язана з мікроструктурою іонопровідної аморфної фази. Порівняння та аналіз характерних раманівських спектрів кристалічного комплексу, розплаву, і модельних низькомолекулярних ($M_w \leq 1000$ г моль$^{-1}$) систем дозволяє зробити висновок про те, що структура аморфних комплексів PEO:Li$^+$ подібна (проте неідентична) структурі кристалічного комплексу. Подібність полягає в тому, що в обох випадках полімерний ланцюжок "згортається" навколо катіона.