

ON THE STRUCTURE OF ARCHETYPAL POLYMER
ELECTROLYTE PEO:LiCF₃SO₃

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S u m m a r y

We report on a systematic micro-Raman and IR spectroscopic investigation of PEO-LiCF₃SO₃ 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analysis of the splitting and the band shift of non-degenerate internal modes in terms of different coordinations is no longer applicable.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 ($M_w \leq 1000 \text{ g mol}^{-1}$) 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.