Effects of temperature and dissolved $LiClO_4$ on the viscoelastic and dynamic properties of poly(ethylene oxide), (PEO) melts

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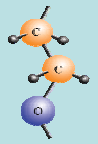
Abstract

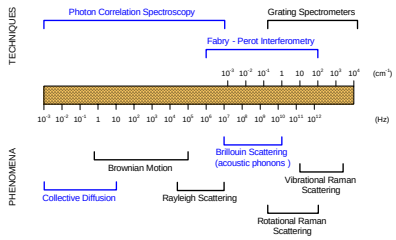
The physical properties of poly(ethylene oxide) (PEO) melts and PEO/$LiClO_4$ complexes are of major importance for understanding the mechanism and dynamics of lithium-ion transport in polymer electrolytes. We used a fiber-optic coupled triple-pass Fabry-Perot interferometer to study the Brillouin light scattering spectra of PEO melts and PEO melt/$LiClO_4$ solutions for various salt concentrations and in the temperature range from the melting point up to 140°C. We report the measured Brillouin line-shifts and line-widths. A relaxation process was identified in the gigahertz frequency range and was studied in detail. The "mapping" of the relaxation in the frequency–temperature–concentration parameter space yields important information about the local segment dynamics of the polymer chain, which has a direct effect on the transport of the charge carriers in the polymer electrolyte.



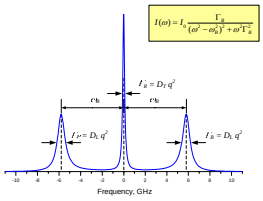
Poly(ethylene oxide) (PEO)

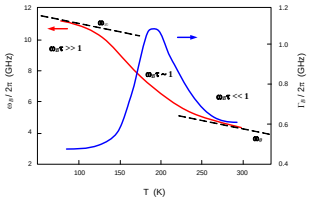
Laser Light Scattering

- Photon correlation spectroscopy and Fabry-Perot interferometry cover a combined dynamic range of 15 decades in frequency allowing experimental observation of processes occurring on very broad range of characteristic time and length scales.
- Brillouin light scattering probes the important gigahertz range were many visco-elastic liquids, including polymer melts, exhibit relaxations commonly referred to as "structural relaxations".

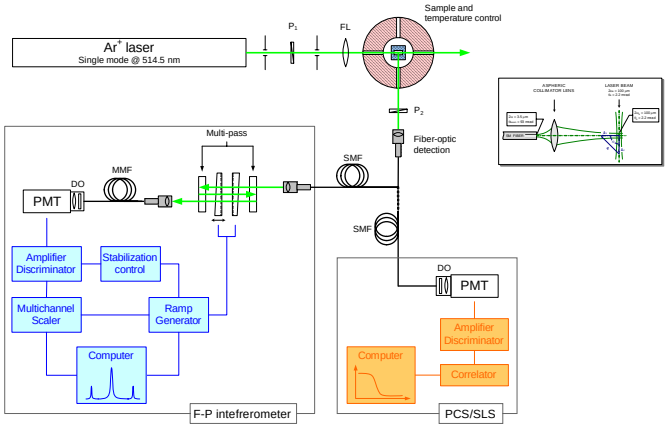


Brillouin Scattering



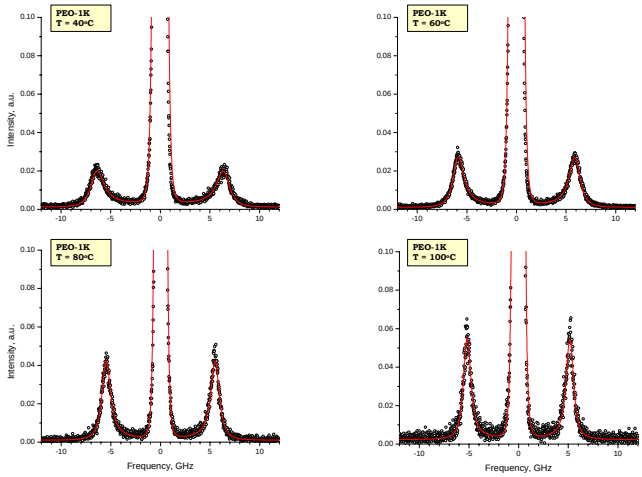


Experimental setup

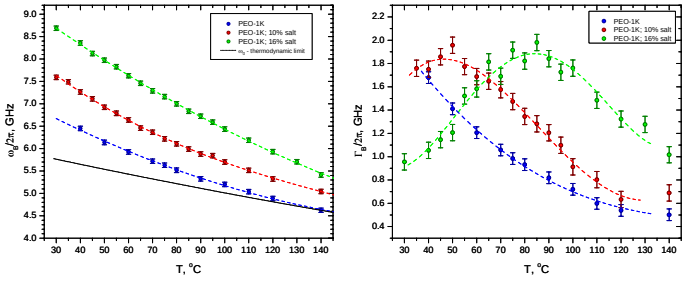


- Single-mode fiber detection
  - Gaussian beam scattering geometry with very small line broadening
  - compact, rigid collection optics facilitates easy and robust optical alignment
- Temperature controlled sample from 30°C to 140°C with stability better than ±0.05°C
- Triple-pass Fabry-Perot interferometer with electronic drift control, typical finesse ~65-70

Brillouin spectra



Brillouin shift and linewidth



Conclusions

Brillouin light scattering provides important information about the elastic and dynamic properties of the polymer electrolytes. In particular, the structural relaxation processes in the gigahertz frequency range can be investigated in detail. We studied the structural relaxation in the PEO melt/$LiClO_4$ system as a function of temperature and lithium perchlorate concentration. Upon increasing the $LiClO_4$ concentration, the relaxation shifts to higher temperatures. The longitudinal elastic modulus increases while the maximum loss shifts to higher temperature. The average relaxation time at the peak of the absorption is about 140-150 ps and it is roughly unchanged with salt concentration.

References:

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[4] **R. Bogoslovov *et al.***, Rev. Sci. Instr. 75(10), 3216 (2004)

Acknowledgements:

Technical assistance – A. Sanchez, W. O'Donnell, J. Kilburg

Special thanks to David Shelton and G. D. Patterson

Financial support – DOE (BES), Bigelow Foundation