

## Characterization of Sulfonated Polysulfone Polymers by EELS

Chen Wang<sup>1</sup>, Stephen J. Paddison<sup>2</sup>, John R. Dunlap<sup>3</sup>, and Gerd Duscher<sup>4</sup>

<sup>1</sup> Division of Applied Research and Technology, National Institute for Occupational Safety and Health, Cincinnati, OH, 45226, USA

<sup>2</sup> Department of Chemical and Biomolecular Engineering, University of Tennessee, Knoxville, TN 37996, USA

<sup>3</sup> Advanced Microscopy and Imaging Center, University of Tennessee, Knoxville, TN 37996, USA

<sup>4</sup> Department of Materials Science and Engineering, University of Tennessee, Knoxville, TN, 37996, USA

A novel class of polysulfone ionomers have recently been synthesized and proposed as candidate electrolyte membrane materials for fuel cells.[1] These materials show superior proton conductivity and thermal stability due to their unique backbone structures consisting of sulfonated aromatic rings and sulfone units ( $-\text{SO}_2-$ ). The local hydration and proton conductivity are closely related to the degree of backbone sulfonation and the spacing of the sulfone units. Electron energy-loss spectroscopy (EELS) has been undertaken to understand the conformational changes in the backbone of various perfluorosulfonic acid (PFSA) ionomers.[2] The combination of spectroscopy and simulation has successfully revealed the conformational dependence of the EEL spectra for PFSA ionomers. In the present work, the specific features in the low-loss and core-loss spectra of light elements (*e.g.*, C and S) were investigated to understand the backbone chemistry of polysulfone ionomers.

We have performed EELS with a 200 kV Zeiss Libra 200 TEM/STEM equipped with a monochromator to investigate the spectral characteristics of three types of sulfur-containing aromatic polymers: poly-(1,4-phenylene ether-ether-sulfone) (PEES); poly-(phenylene sulfide) (PPS) and sulfonated poly-(phenylene sulfone) (sPSO<sub>2</sub>), as seen in Fig.1. Both low-loss EEL spectra and the energy-loss near-edge structure (ELNES) have been acquired with a high energy resolution of 0.15 eV. The thin sections of the samples were prepared by cryo-microtome and examined in the cryo environment to minimize sample damage due to electron beam exposure.

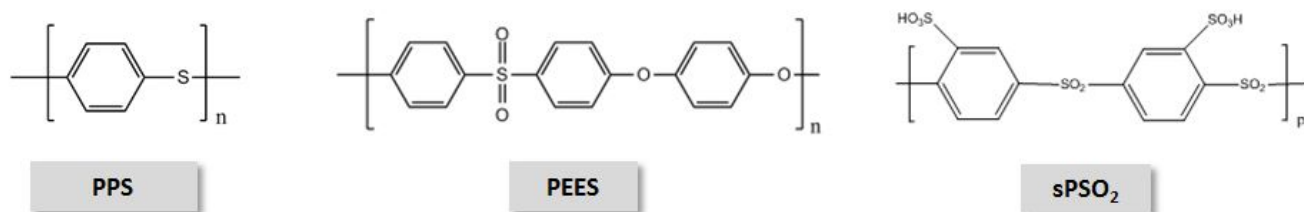
The spectral dependence of the different aromatic backbone structures were investigated by low-loss spectra, C K-edges and S-L<sub>2,3</sub> edges as shown in Fig. 2. The spectra show distinct features in the low-loss region and the onset of the C K-edges for PEES, PPS, and sPSO<sub>2</sub>. The addition of sulfonic acid groups ( $-\text{SO}_3\text{H}$ ) or ether linkages ( $-\text{O}-$ ) in backbones can both alter the intensities and shapes of  $\pi$  peaks in C K-edges and near edge structures. A strong singlet peak in the S-L<sub>2,3</sub> ELNES was observed in sPSO<sub>2</sub> ionomers, which can be used to characterize the sulfonate groups directly attached to the aromatic backbones. The fine structures of the S-L<sub>2,3</sub> ELNES of PPS and PEES were also identified and possessed features similar to the previously reported X-ray absorption spectra of sodium sulfate.[3]

### References:

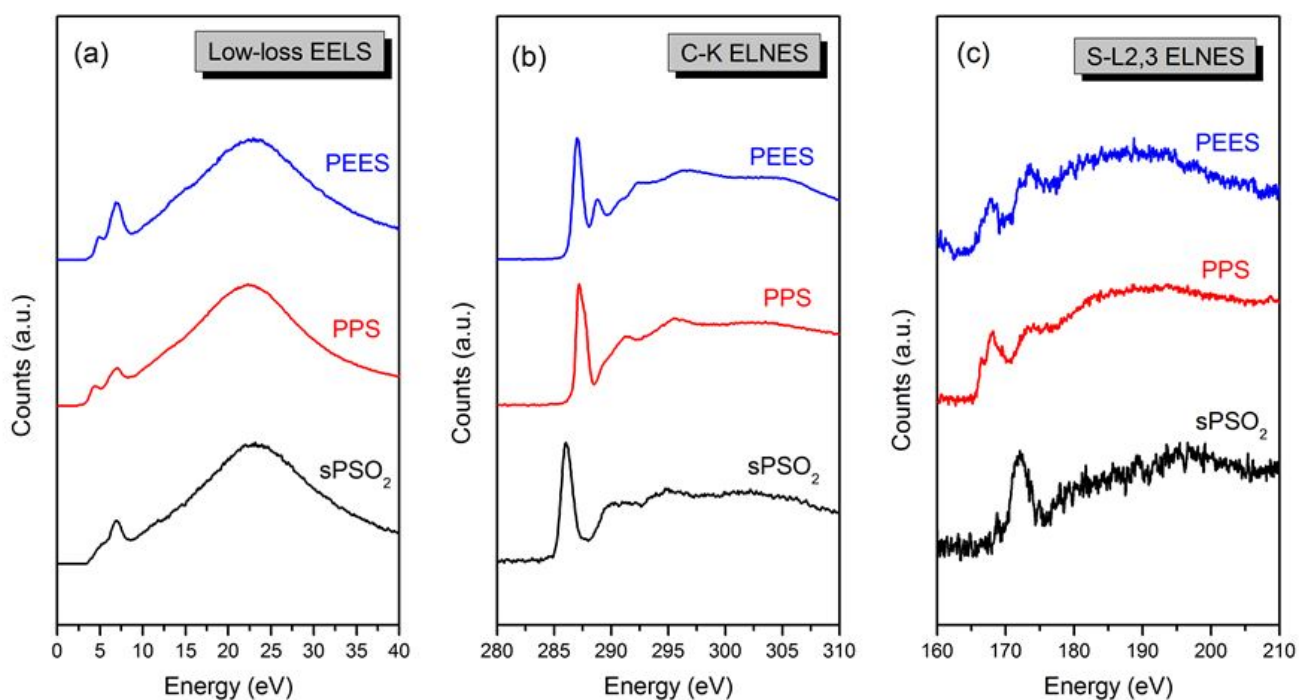
[1] M. Schuster *et al.*, *Macromolecules*, **42** (2009), 3129-3137.

[2] C. Wang *et al.*, *RSC Adv.*, **5** (2015), 2368-2373.

[3] F. Jalilvand, *Chem. Soc. Rev.*, **35** (2006), 1256–1268.



**Figure 1.** Chemical structures of repeat units of poly-(1,4-phenylene ether-ether-sulfone) (PEES); poly-(phenylene sulfide) (PPS) and sulfonated poly-(phenylene sulfone) (sPSO<sub>2</sub>).



**Figure 2.** Measured EEL spectra of PEES, PPS, and sPSO<sub>2</sub>: (a) low-loss (0–40 eV) after the removal of zero-loss (logarithmic function) and plural scattering (Fourier-log deconvolution); (b) C-K ELNES (280–310 eV) and (c) S-L<sub>2,3</sub> ELNES (160–210 eV) after background subtractions (power-law function) and single scattered removal (Fourier-ratio deconvolution).