

Supplementary Information

Spectroscopic Characterization of Sulfonate Charge Density in Ion-Containing Polymers

Sarah B. Smedley^{1†}, Tawanda J. Zimudzi^{1†}, Ying Chang², Chulsung, Bae², Michael A. Hickner^{1*}

¹Department of Material Science and Engineering, The Pennsylvania State University,
University Park, PA 16802, United States

²Department of Chemistry and Chemical Biology, New York State Center for Polymer
Synthesis, Rensselaer Polytechnic Institute, NY, 12180, United States

[†]These authors contributed equally to this work

*Corresponding author E-mail: hickner@matse.psu.edu Tel: (814) 867-1847

Spectral fitting of OD region for polysulfonated sulfone samples

The non-Codon effect results in an increase of the transition dipole strength with decreasing frequency. The areas of the fitted peaks were corrected for the frequency dependence of the transition dipole moment by determining the transition dipole (μ) at each wavenumber using eq1,

$$\frac{\mu}{\mu_g} = 31.27 - (1.0 \times 10^{-2}) \omega \quad (1)$$

where μ_g and ω represent the gas phase transition dipole and the frequency of the vibration, respectively. In linear IR spectroscopy, absorbance depends on μ . To obtain the correct frequency dependent absorbance values using the newly acquired transition dipoles, eq 2 was used, and the area of the new curve was calculated.

$$A_{corrected} = \frac{A_{fit}}{\mu} \quad (2)$$

As described in the manuscript text, the OD region ($2700 - 2400 \text{ cm}^{-1}$) was fit using three Gaussian peaks; One peak corresponding to bulk-like water, was held constant for all samples and was centered at 2509 cm^{-1} with a constrained FWHM of 170 cm^{-1} while the headgroup-associated and intermediate water peaks varied by sample. The peak positions and FWHM for headgroup-associated and intermediate water were determined by fitting the lowest RH samples with three peaks; headgroup and intermediate water with undetermined peak characteristics and the third peak being bulk water with peak position of 2509 cm^{-1} and FWHM of 170 cm^{-1} , as stated previously. The peak shape (peak position and FWHM) of the head-group associated water was held constant throughout the remainder of the fitting at each RH. The intermediate peak position was held constant but the FWHM was allowed to vary. Once fit, the areas were corrected for non-Condon effects. Figure S1 below shows OD region deconvolutions of the samples S1, S2, S5 and S6 at different hydrations.

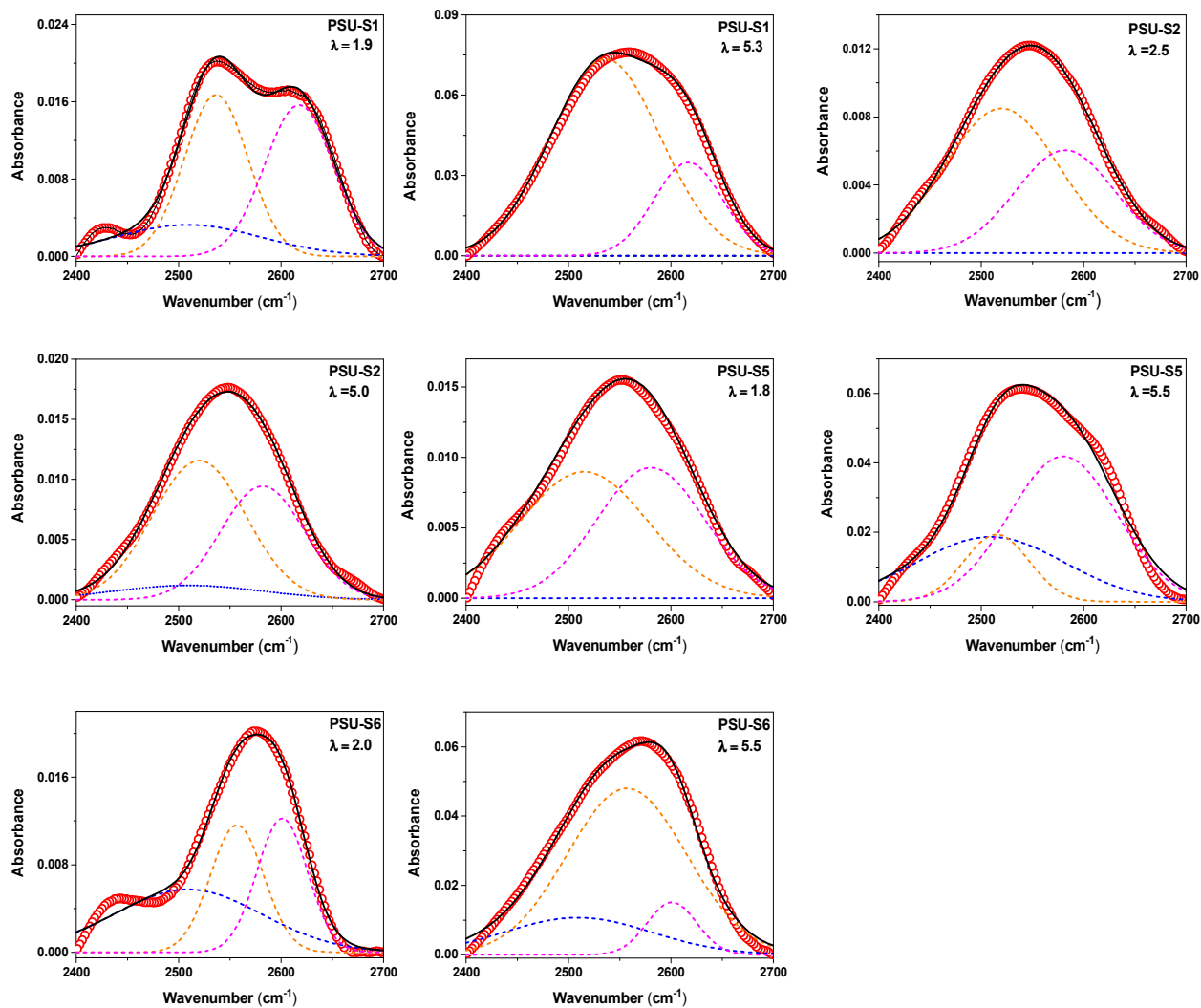


Figure S1. The OD stretch deconvolution of PSU-S1 at $\lambda = 1.9$ and 5.3 , PSU-S2 at $\lambda = 2.5$ and 5.0 , PSU-S5 at $\lambda = 1.8$ and 5.5 and PSU-S6 a $\lambda = 2.0$ and 5.5 .