β-Sheet Nanocrystalline Domains Formed from Phosphorylated Serine-Rich Motifs in Caddisfly Larval Silk: A Solid State NMR and XRD Study

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Supporting Information

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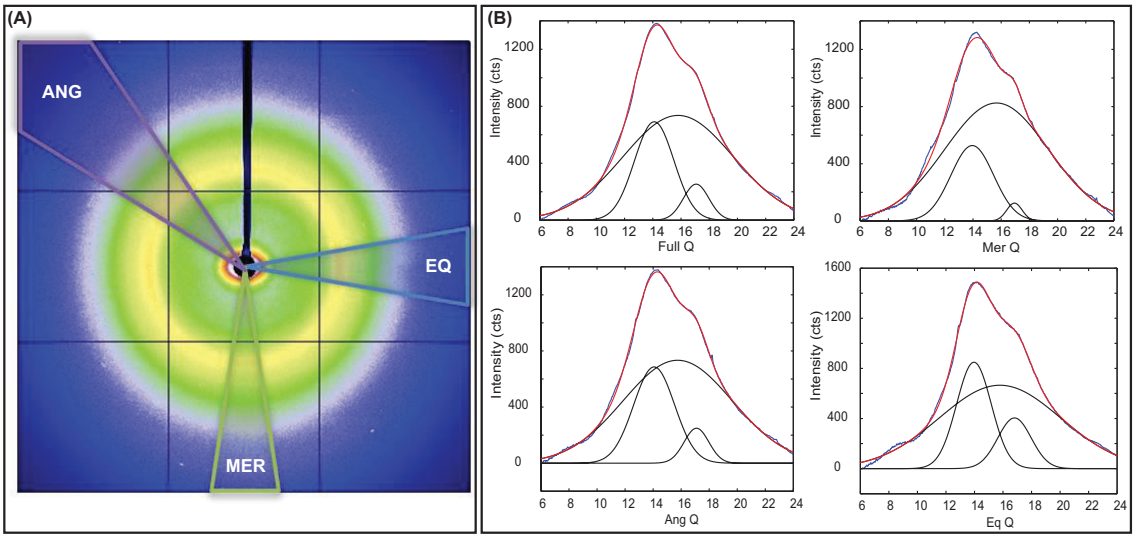

Figure 1: A: 2D wide angle X-ray diffraction pattern of caddisfly silk, with equatorial, meridian and 45 degree angle regions highlighted. B: Q integration plots of the full 2D diffraction pattern, and of the three highlighted regions. The peak positions were fixed 14.0, 15.8 and 16.8 in Q-space, and a Gaussian fitting protocol was used to fit each data set. It is clear that the peaks located at 14.0 and 16.8 Q-space, associated with distances of 4.5 and 3.7 inverse angstroms, respectively, are observed in increased intensity in the equatorial region. The differences in peak area in the three regions were used to estimate percent crystallinity at $\sim$7-8%.

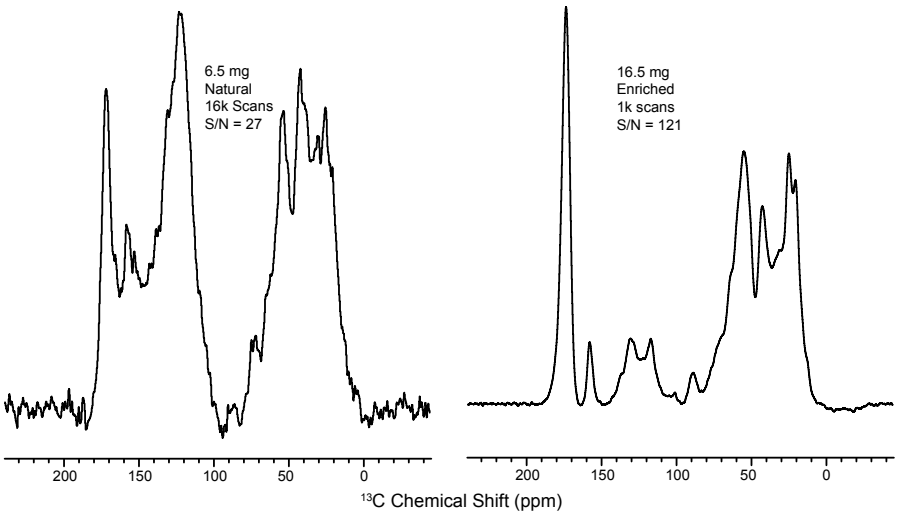

Figure 2: ^{1}H-^{13}C CP-MAS of naturally-abundant caddisfly silk (left) and ^{13}C, ^{15}N isotopically enriched caddisfly silk (right). The signal-to-noise ratios were estimated for each spectrum. By adjusting for differences in sample weight and number of scan averages, the percent enrichment was estimated at 6-8%. The large broad peak near 130 ppm in the natural spectrum is due to background from the rotor.

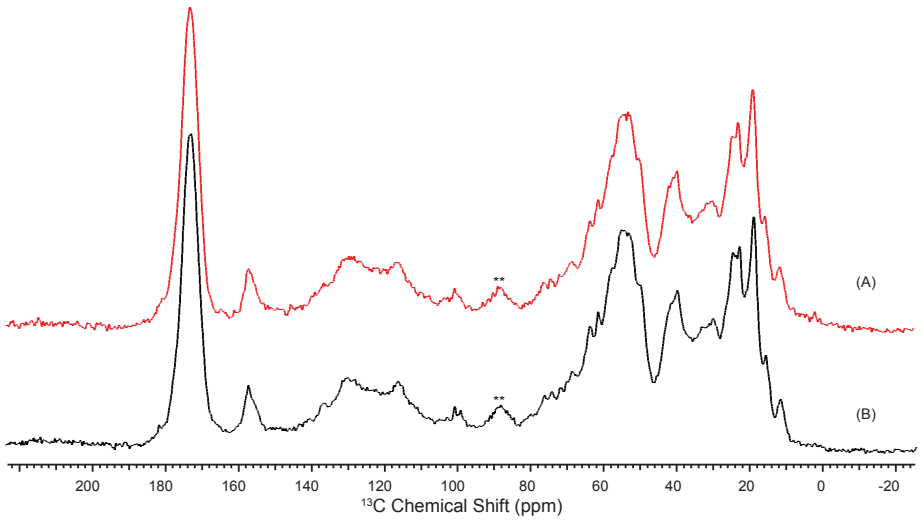

Figure 3: ^{1}H-^{13}C CP-MAS NMR spectra of isotopically-enriched hydrated caddisfly silk before drying the silk under nitrogen gas (A), and after re-hydrating the same sample (B). Spectra were taken with a Varian 400 MHz Wide-Bore spectrometer using a 3.2 mm solid state probe configured in HCN triple resonance mode under 8.5 kHz MAS. Carbonyl spinning side bands are indicated with a double asterisk. Experimental conditions were identical: 4096 transients, 5 second recycle delay, 1 ms CP contact time, and 100 kHz TPPM proton decoupling during acquisiton. 25 Hz exponential line broadening was applied to each spectra before Fourier Transformation. The spectra are identical (within experimental error), indicating that drying and re-hydrating the silk has no significant effect on the structural nature of the silk.

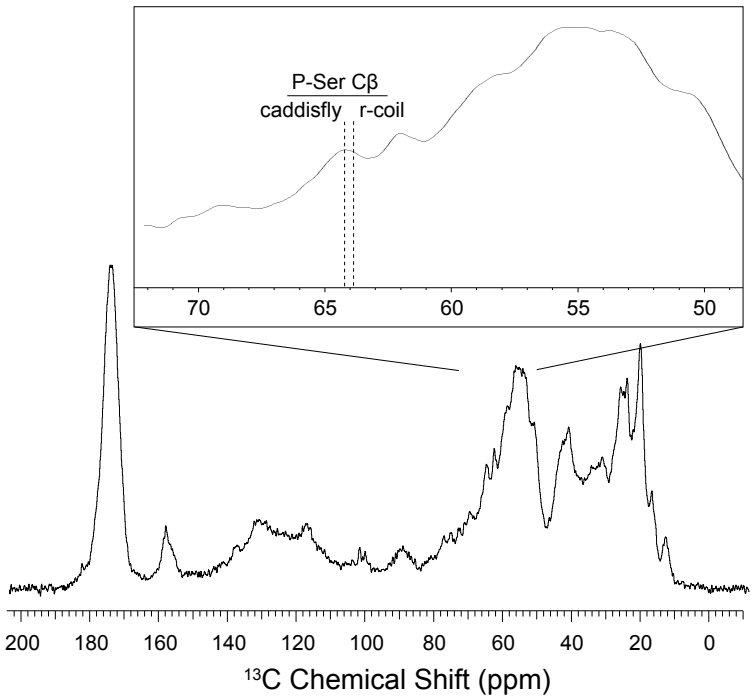

Figure 4: ^{1}H-^{13}C CP-MAS NMR spectra of isotopically-enriched hydrated caddisfly silk. The region near the phosphoserine resonance is expanded to illustrate that the p-Ser Cβ resonance of caddisfly silk is shifted downfield with respect to a random coil chemical shift.