Supplementary Material (ESI) for Chemical Communications

Quantification of glycine and alanine in β-sheet and helical conformations in spider silk: insight from through-bond carbon-13 homonuclear solid-state NMR

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Supplementary Information

MaSp1

GGAGQGGYGGLGSQGAGRGGLGGQGAGAAAAAA

MaSp2

GPGQQGPGGYGPGQQGPGGYGPGQQGPSGPGSAAAAAAAA

Fig. S1 The consensus primary amino acid sequence of the spider silk proteins MaSp1 and MaSp2.[1, 2] Runs of poly(A) and poly(GA) that from a β-sheet structure are underlined.

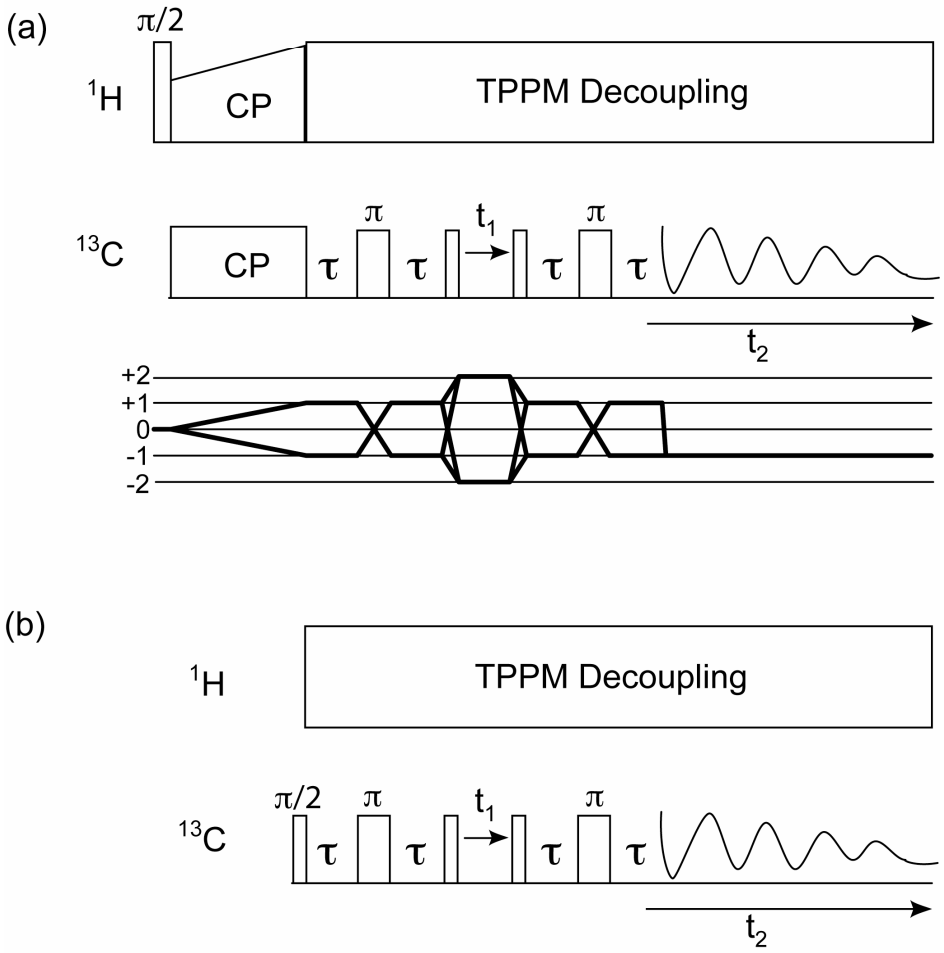

Fig. S2 The NMR pulse sequences used to collect refocused INADEQUATE spectra of *Nephila clavipes* spider dragline silk. INADEQUATE spectra of native samples were collected with (a) CP as previously described.[3] The coherence transfer pathway is presented below the pulse sequence. Typical experimental parameters were a 1 ms CP contact time, τ = 3 ms, 40 kHz MAS, and TPPM ^{1}H decoupling with a 150 kHz radio frequency (rf) field strength. Spectra of water plasticized spider silk were obtained with a (b) refocused INADEQUATE pulse sequence with direct ^{13}C excitation. Typical experimental parameters were $\pi/2$ = 3 μs, τ = 3.5 ms, 20 kHz MAS, and TPPM ^{1}H decoupling with a 100 kHz rf field strength.

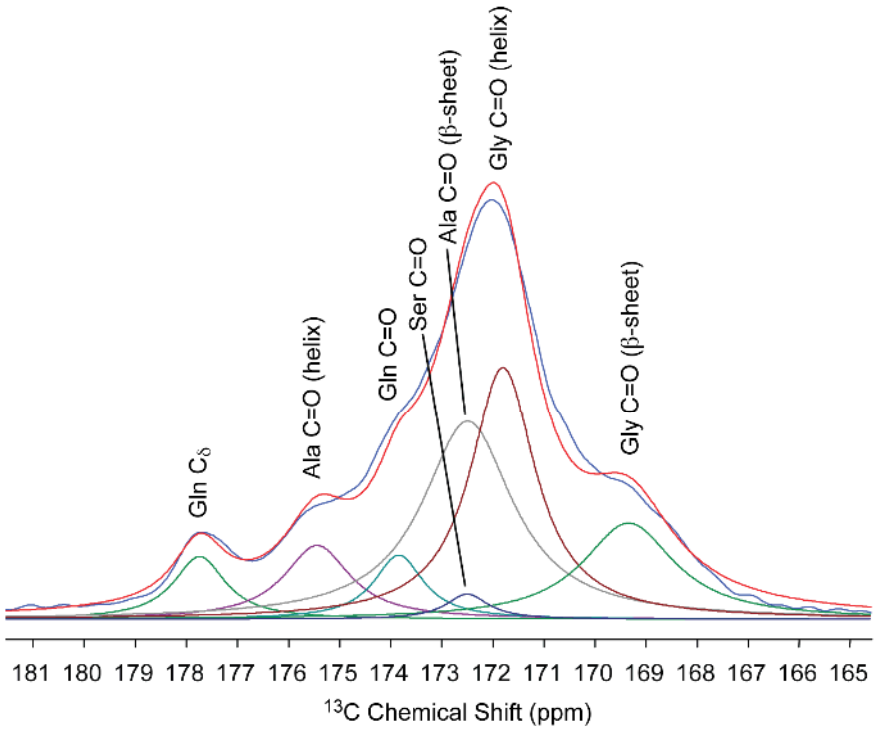

Fig. S3 The carbonyl region of a fully relaxed ^{13}C MAS spectrum of water plasticized *Nephila clavipes* spider dragline silk. The carbonyl resonance was fit to extract the ratio of Gly and Ala in β-sheet and helical structures. The chemical shift and linewidth of each component was extracted from the refocused INADEQUATE spectrum. The fraction of Gly and Ala present in a β-sheet conformation is 28% ± 5% and 82% ± 4%. These two fractions agree well with the fraction of Ala (86%) and Gly (26%) present in poly(A) and poly(GA) motifs from the primary amino acid sequence of the spider silk proteins MaSp1 and MaSp2.[1, 2] The experimental data is shown in blue and the sum of the fitted data in red. The fitting routine was performed with the DMFIT software package.[4]

References

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