Supporting Information

Effect of stress on the molecular structure and mechanical properties of supercontracted spider dragline silks

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Experimental details

**S-FTIR spectroscopy.** The preliminary experiment was performed on Beamline U4 at the National Synchrotron Radiation Laboratory (NSRL), Hefei, China. Most of the data collection was performed at Beamline BL01B1 at Shanghai Synchrotron Radiation Facility (SSRF), China. FTIR spectra were recorded using a Nicolet 6700 FTIR spectrometer with a liquid nitrogen cooled MCT detector coupled with a Nicolet Continuum microscope with a 36× objective at 25 °C. For each measurement, 256 interferograms were co-added and transformed employing a Genzel-Happ apodization function to yield spectra with a nominal resolution of 4 cm⁻¹. Deconvolution of the amide III band (1265 cm⁻¹ for helix, 1224 cm⁻¹ for β-sheet, and 1235 cm⁻¹ for random coil) was carried out using PeakFit 4.12, according to the method reported in our previous study, *i.e.*, a Gaussian model was selected for the band shape, and the bandwidth was automatically adjusted by the software. The orientation of certain moieties in spider dragline silks can be obtained from the angular dependence of the absorbance *A*(ν) at wavenumber ν which corresponds to a vibration of the molecular group under investigation. In the general case, the angular dependence of the absorbance can be determined using the following function.¹⁻⁴

\[
A(ν, Ω)= -\log_{10}\{10^{A_{\text{max}}(ν)}\cos^2(Ω-Ω_0) +10^{A_{\text{min}}(ν)}\cos^2(Ω-Ω_0)\}
\]

where *A*(ν, Ω) is the peak intensity of a certain band, Ω is the polarization angle, Ω₀ is the angle at maximum absorption, *A*_{max} and *A*_{min} are the maximum and minimum absorbance, respectively.

The molecular order parameter (S_{mol}) of the corresponding secondary structural component was calculated as follows.

\[
S_{\text{mol}} = \frac{A_{\text{max}}(ν) - A_{\text{min}}(ν)}{A_{\text{max}}(ν) + 2A_{\text{min}}(ν)}
\]

The theoretical boundary values of S_{mol} are +1 and −0.5, which correspond respectively to perfectly parallel and perfectly perpendicular orientation with respect to the fiber axis.²
**Fig. S1** Amide III bands in unpolarized S-FTIR microspectra of single spider dragline silk. Curve a: original spider dragline silk; curve b: after free supercontraction; curve c: stretched to original length after free supercontraction.

**Fig. S2** S-FTIR microspectra of single original *N. edulis* spider dragline silk at different polarization angles (0–90° in 10° steps).
Fig. S3 Deconvolution results of amide III bands in S-FTIR spectra of single spider dragline silk. (A) After 100% constrained supercontraction; (B) after 90% constrained supercontraction; (C) after 70% constrained supercontraction.

Fig. S4 Amide III bands in polarized S-FTIR microspectra of single spider dragline silk, (A) parallel spectra (0°) and (B) perpendicular spectra (90°). Curve a: original spider dragline silk; curve b: 100% constrained supercontraction.
**Table S1.** Comparison of β-sheet content and order parameter of spider dragline silks and *A. pernyi* silkworm silks acquired by different methods*[^a]*

<table>
<thead>
<tr>
<th>Method</th>
<th>State</th>
<th>β-sheet content (%)</th>
<th>β-sheet order parameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>IR spectroscopy[^5]</td>
<td>Native</td>
<td>17[^a]</td>
<td>n/a</td>
</tr>
<tr>
<td>IR spectroscopy[^6]</td>
<td>Native</td>
<td>45-46[^b]</td>
<td>0.71-0.95[^b]</td>
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<tr>
<td>IR spectroscopy[^7]</td>
<td>Native</td>
<td>48.7[^c]</td>
<td>n/a</td>
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<tr>
<td>IR spectroscopy[^8]</td>
<td>Native</td>
<td>44.9[^c]</td>
<td>n/a</td>
</tr>
<tr>
<td>Raman spectroscopy[^9]</td>
<td>Native</td>
<td>36[^b]; 27[^d]</td>
<td>0.89[^b]; 0.69[^d]</td>
</tr>
<tr>
<td>Raman spectroscopy[^9]</td>
<td>SC</td>
<td>39[^b]; 30[^d]</td>
<td>0.84[^b]; 0.53[^d]</td>
</tr>
<tr>
<td>Raman spectroscopy[^10]</td>
<td>Native</td>
<td>37[^b]</td>
<td>n/a</td>
</tr>
<tr>
<td>Raman spectroscopy[^10]</td>
<td>Native</td>
<td>29[^d]</td>
<td>n/a</td>
</tr>
<tr>
<td>1^3C-CP-MAS NMR[^11]</td>
<td>Native</td>
<td>34[^b]</td>
<td>n/a</td>
</tr>
<tr>
<td>X-ray diffraction[^12]</td>
<td>Native</td>
<td>28[^b]; 31[^c]</td>
<td>0.98[^b]; 0.979[^c]</td>
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<tr>
<td>X-ray diffraction[^13]</td>
<td>SC</td>
<td>n/a</td>
<td>0.885[^b]; 0.859[^c]</td>
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<tr>
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<td>Native</td>
<td>10-15[^b]</td>
<td>0.981[^b]</td>
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<tr>
<td>IR spectroscopy (this study)</td>
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<td>16.1[^a]</td>
<td>0.828[^a]</td>
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<tr>
<td>IR spectroscopy (this study)</td>
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<td>21.2[^a]</td>
<td>0.222[^a]</td>
</tr>
</tbody>
</table>

[^a]: *N. edulis*;[^b]: *N. clavipes*;[^c]: *A. pernyi*;[^d]: *A. diadematus*;[^e]: *A. aurantia.*

**Abbreviation:** SC, supercontraction.

**References**

Small, 2017, 13, 1702266.


