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Supporting Information

Precise Correlation of Macroscopic Mechanical Properties and Microscopic Structures of Animal Silks —— Using *Antheraea pernyi* Silkworm Silk as An Example

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EXPERIMENTAL DETAILS

Mechanical Testing. The mechanical properties of *A. pernyi* silks were tested with an Instron 5565 mechanical testing instrument (at 25 ℃ and 45% relative humidity; gauge length: 10 mm; cross-head speed: 15 mm min^{-1}) with a load cell of 2.5 N. To obtain the cross-sectional area of the samples, the silks were embedded in epoxy resin, and then the whole silk-embedded epoxy resin was fractured perpendicular to the fiber axis using a custom-built fracture tool. The fracture cross-sections of *A. pernyi* silks were sputtered with gold for 10 s, and then observed with a Tescan 5136MM SEM at 20 kV. The area was calculated using Atlas 2.9.9.9 software, provided with the SEM equipment.

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 the National Centre for Protein Science Shanghai in the 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 Continuμm microscope with a 36× objective at 25 ℃. 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 α-helix, 1222 cm^{-1} for β-sheet, and 1242 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 *A. pernyi* 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.

$$A(\nu, \Omega) = -\log_{10}\{10^{-A\mathrm{max}(\nu)}\cos^2(\Omega-\Omega_0) + 10^{-A\mathrm{min}(\nu)}\cos^2(\Omega-\Omega_0)\}$$

where $A(\nu, \Omega)$ is the peak intensity of a certain band, Ω is the polarization angle, Ω_0 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.

$$S^{mol}= \frac{Amax(\nu)-Amin(\nu)}{Amax(\nu)+2Amin(\nu)}$$

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.

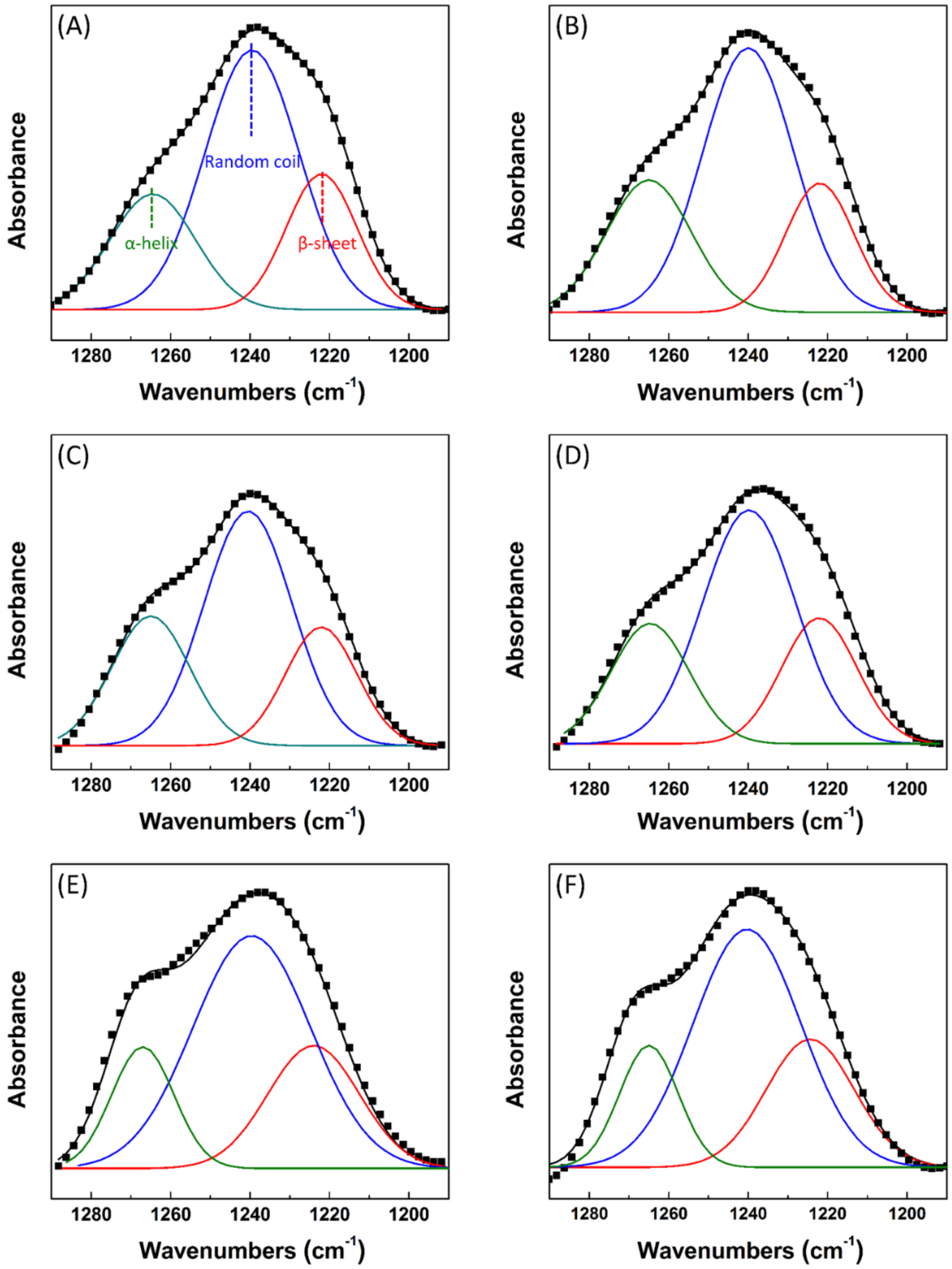

Fig. S1 Deconvolution results of amide III band of *A. pernyi* silks. (A) naturally spun silk, (B) reeled at 8 mm/s, (C) reeled at 15 mm/s, (D) reeled at 30 mm/s, (E) reeled at 50 mm/s, and (F) reeled at 75 mm/s.

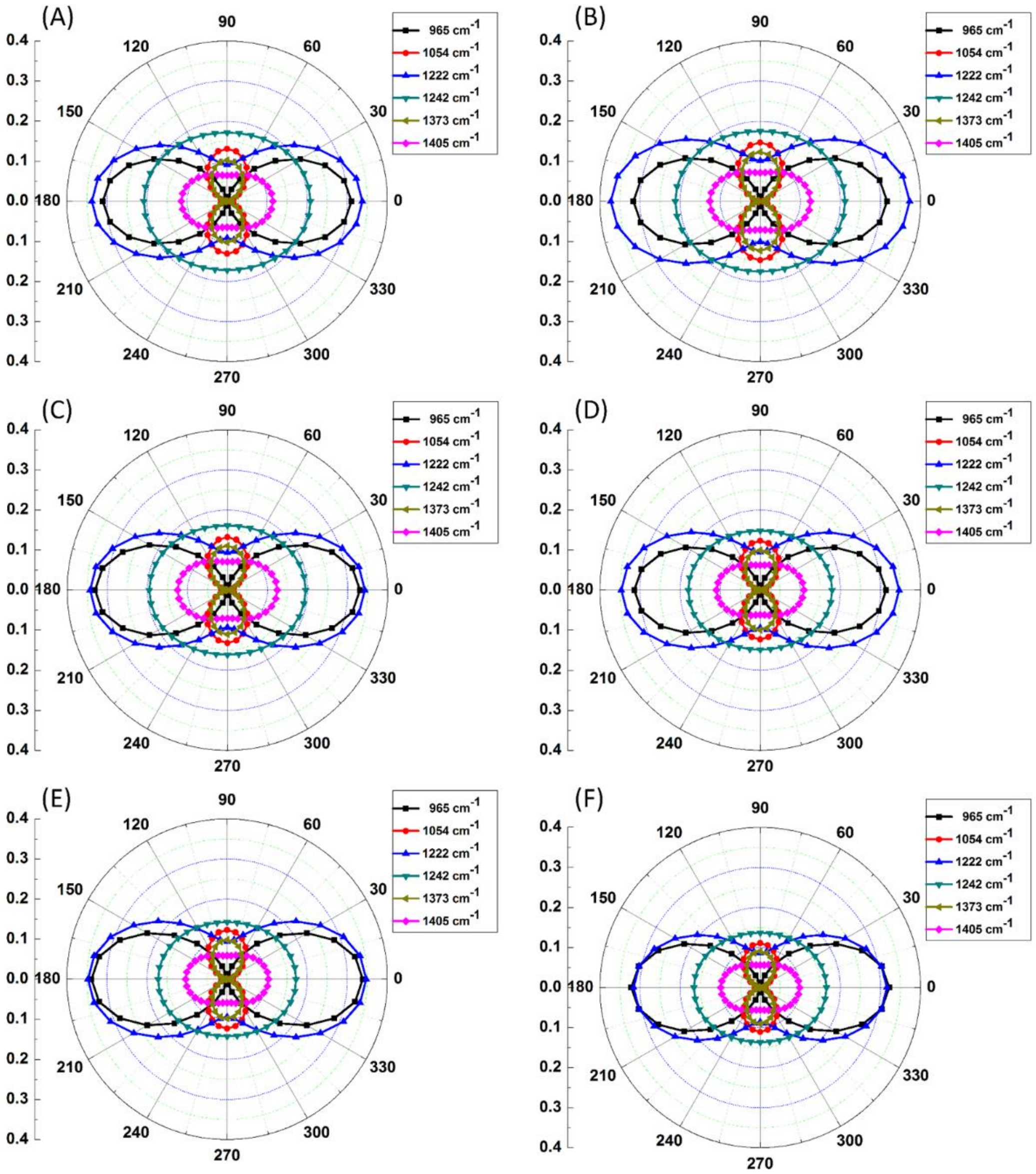

Fig. S2 Polar plot of the absorbance of the characteristic peaks in S-FTIR microspectra in the 1500-800 cm^{-1} region of single *A. pernyi* silks. (A) naturally spun silk, (B) reeled at 8 mm/s, (C) reeled at 15 mm/s, (D) reeled at 30 mm/s, (E) reeled at 50 mm/s, and (F) reeled at 75 mm/s.

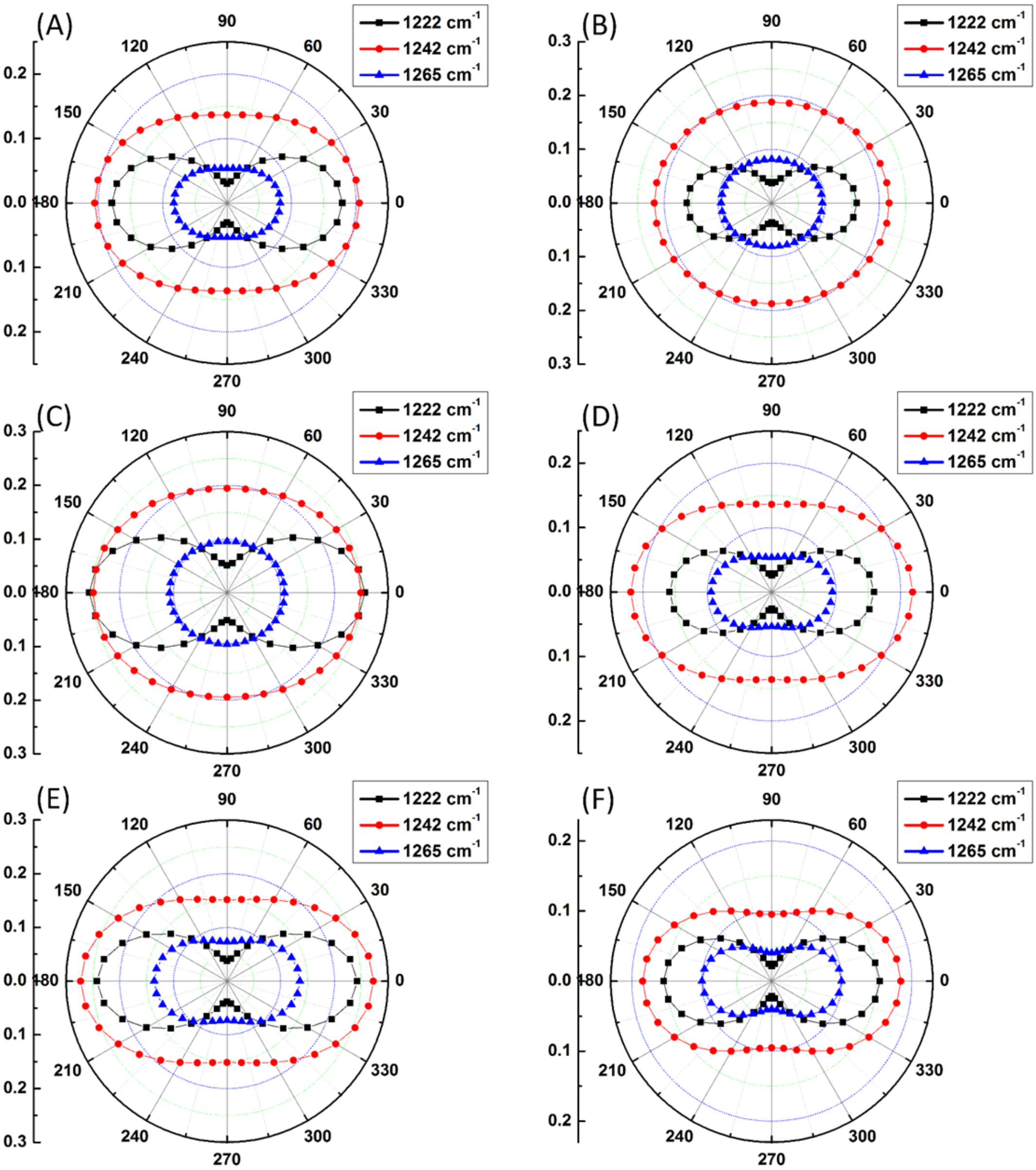

Fig. S3 Polar plot of the relative intensity of different component from the deconvolution of amide III band in S-FTIR microspectra of *A. pernyi* silks. (A) naturally spun silk, (B) reeled at 8 mm/s, (C) reeled at 15 mm/s, (D) reeled at 30 mm/s, (E) reeled at 50 mm/s, and (F) reeled at 75 mm/s.

Table S1 Mechanical properties of the forcibly reeled *A. pernyi* silks with different reeling rates

Samples	Modulus (GPa)	Breaking strain (%)	Breaking stress (MPa)	Breaking energy (MJ/m^{-3})
8 mm/s	10.4 ± 0.3	38.1 ± 1.4	386 ± 9	105 ± 4
15 mm/s	12.4 ± 0.8	31.0 ± 1.7	528 ± 14	132 ±12
30 mm/s	16.3 ± 1.4	24.9 ± 1.3	633 ± 8	108 ± 6
50 mm/s	23.7 ± 0.9	15.4 ± 1.8	671 ± 12	82 ± 8
75 mm/s	24.2 ± 0.7	10.3 ± 2.3	714 ± 14	49 ± 7

Table S2 The content of secondary structures in naturally spun and forcibly reeled *A. pernyi* silks with different reeling rates.

Samples	α-helix (%)	β-sheet (%)	Random coil (%)
Naturally spun	22.6±1.1	22.0±1.6	55.4±2.4
8 mm/s	25.0±1.7	20.4±1.3	54.6±1.8
15 mm/s	25.5±1.4	21.4±1.8	53.0±2.2
30 mm/s	22.9±1.6	23.1±1.1	53.9±1.2
50 mm/s	18.7±1.3	24.2±2.0	57.1±2.1
75 mm/s	17.2±1.8	25.8±1.9	57.0±1.9