Moderate conformational transition promotes the formation of a self-reinforced highly oriented silk fibroin network structure

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Other Supplementary Material for this manuscript includes the following:

- Movie S1. The mechanical training process of SFMs under the polarized light.

Movie S1. The mechanical training process of SFMs under the polarized light.

Description: The two ends of the rectangle SFMs was fixed on the self-made mechanical training device under two orthogonality polarizers. At first, SFMs is dull under the polarized light. Then, the birefringence fringes were appeared and gradual strengthened as the mechanical time increased. Meanwhile, the color of SFMs changed during this process, with changing from white to yellow, to purple-red and further to blue.

- Abbreviations

Abbreviation	Full name
HOMNS	Highly oriented molecular network structure
WS-SFFs	Wet-spun silk fibroin fibers

SFMs	Silk fibroin materials
MD	Molecular dynamic
MT	Mechanical training
FA	Formic acid
PEG	Polyethylene glycol
SFFs	Silk fibroin fibers
TR-FTIR	Time-resolved Fourier transform infrared spectroscopy
RESP	Restrained electrostatic potential
VMD	Visual Molecular Dynamics
ET-MT-SFMs	SFMs produced by mechanical training in ethanol solution
PEG-MT-SFMs	SFMs produced by mechanical training in PEG solution
ET-WS-SFFs	SFFs produced by wet spinning in ethanol solution
PEG-WS-SFFs	SFFs produced by wet spinning in PEG solution
WAXS	Wide-angle X-ray scattering
SAXS	Small-angle X-ray scattering
polyAG	single Ac-$(AG)_6$-NHMe peptide chain

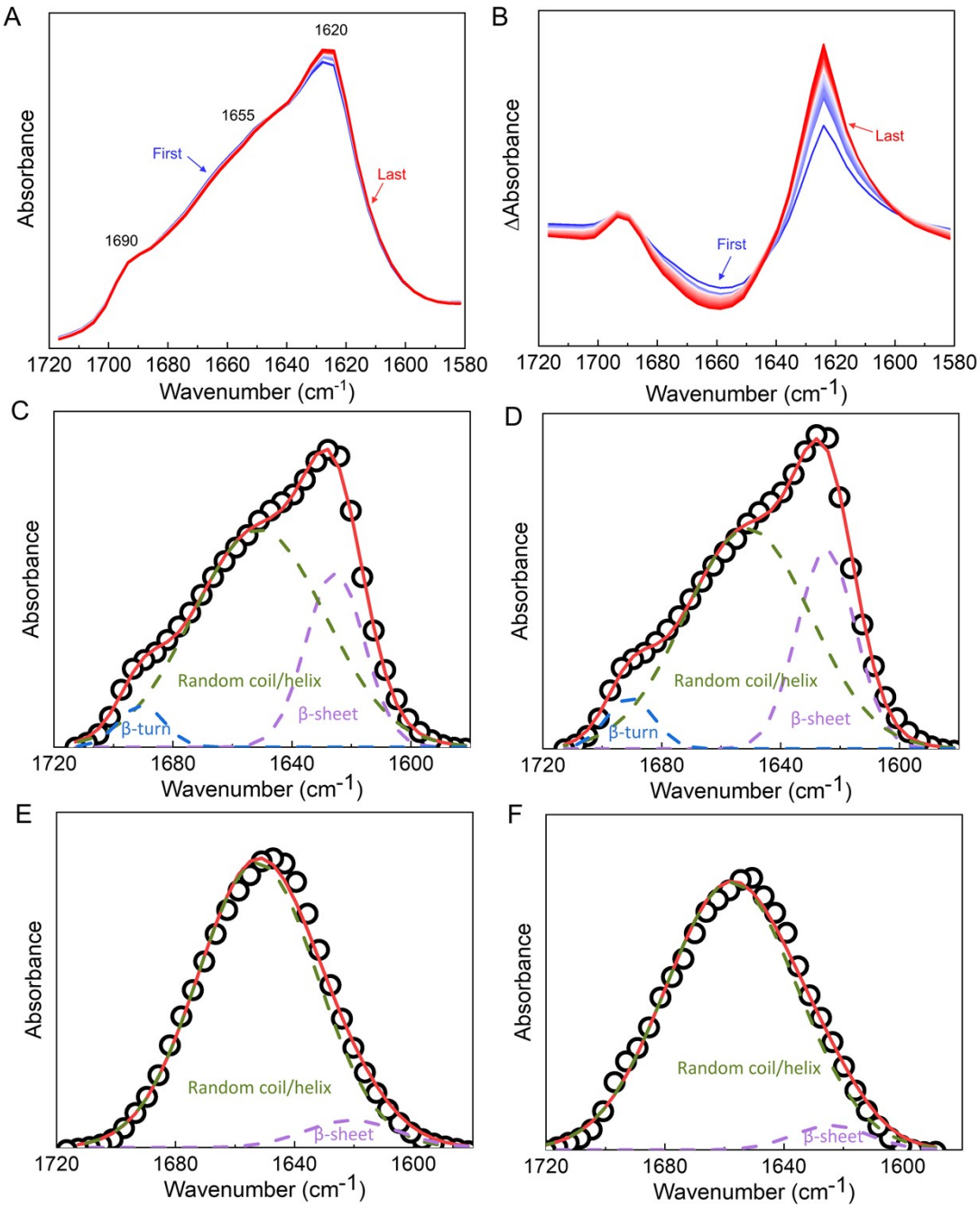

Fig. S1. Conformation transition and deconvolution results of the amide I band of SFMs. TR-FTIR spectra (A) and difference spectra (B) of SFMs from beginning to 30 min after the addition of 75vol% aqueous ethanol. Deconvolution results of the FTIR spectra of SFMs treated with 75vol% aqueous ethanol for 2 min (C) and 20 min (D), and treated with 20wt% aqueous PEG solution for 20 min (E). (F) Deconvolution results of the FTIR spectra of initial SFMs (dry

state).

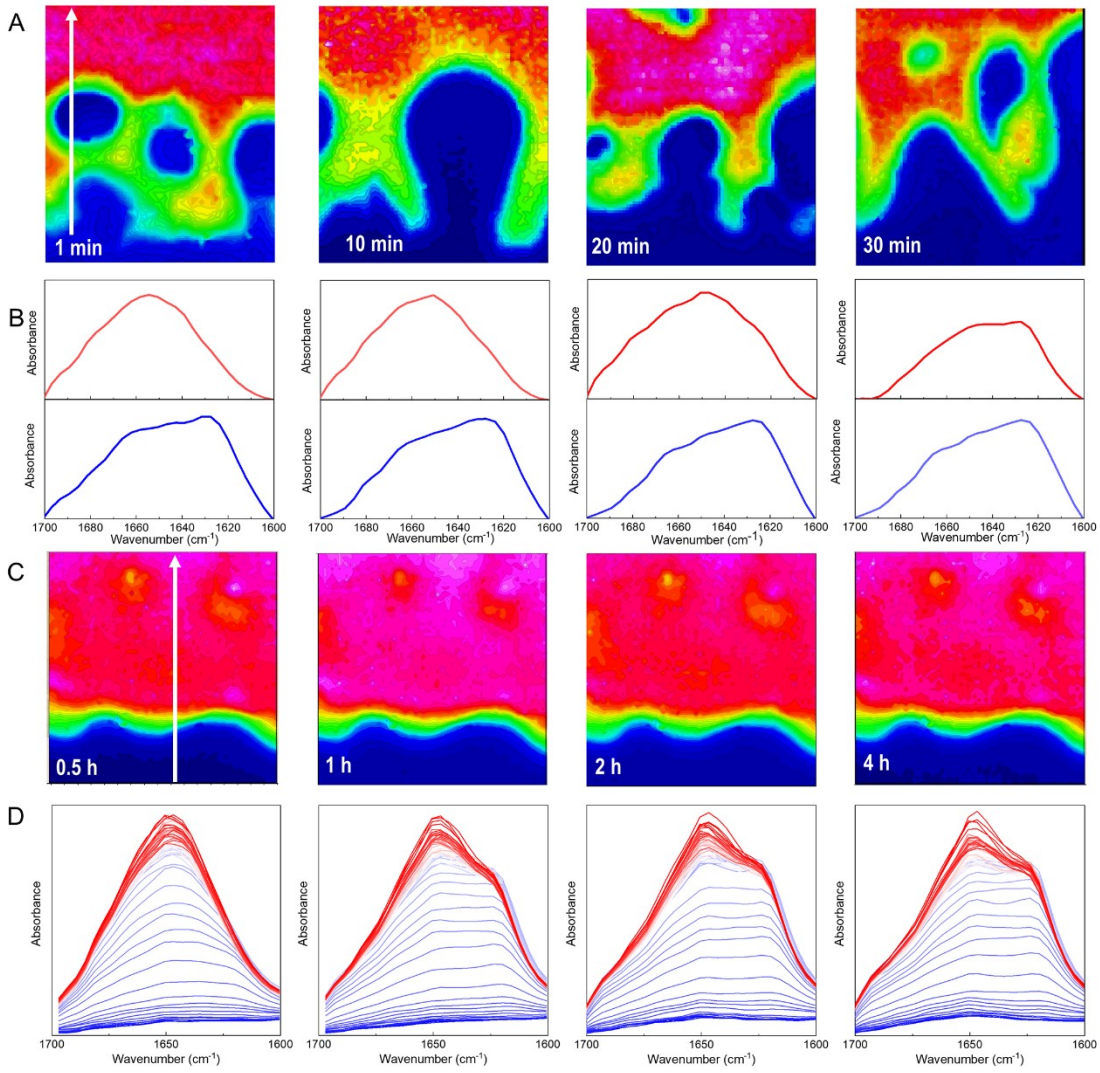

Fig. S2. TR-FTIR imaging of SFMs during ethanol and PEG solution penetration. Univariate imaging maps of the SFMs treated by 75 vol% aqueous ethanol solution at different times by integration of the amide I band (A) and the corresponding FTIR spectra (B). Univariate imaging maps of the SFMs treated by 20 wt% aqueous PEG solution at different times by integration of the amide I band (C) and the corresponding FTIR spectra (D). The FTIR spectra were obtained at the position of the white line in the imaging map.

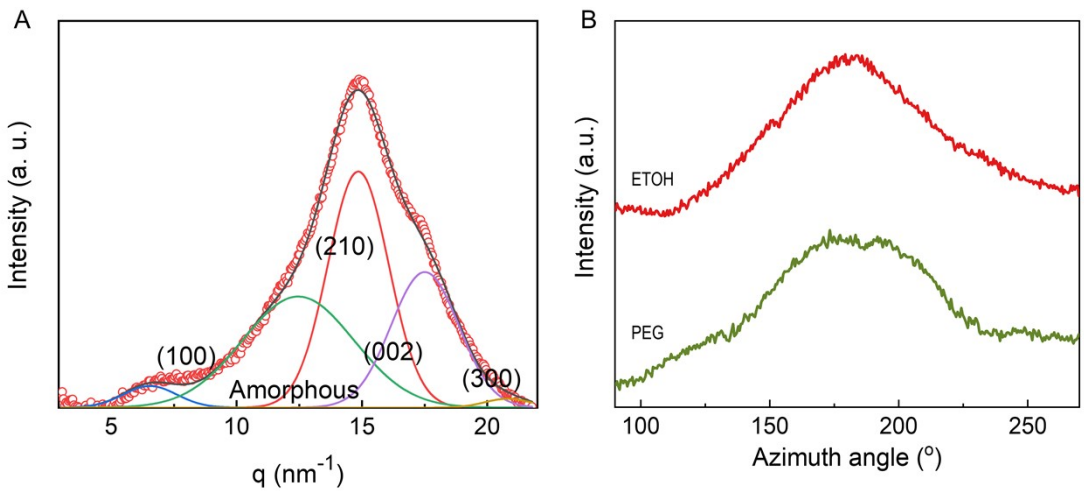

Fig. S3. Structure of MT-SFMs. (A) Deconvolution result of WAXS pattern of ET-MT-SFMs. (B) The measured scattering intensity vs. Azimuthal angle curves of the WAXS pattern of MT-SFMs at 14.8 nm^{-1} (shown in Figure 5D and 5E).

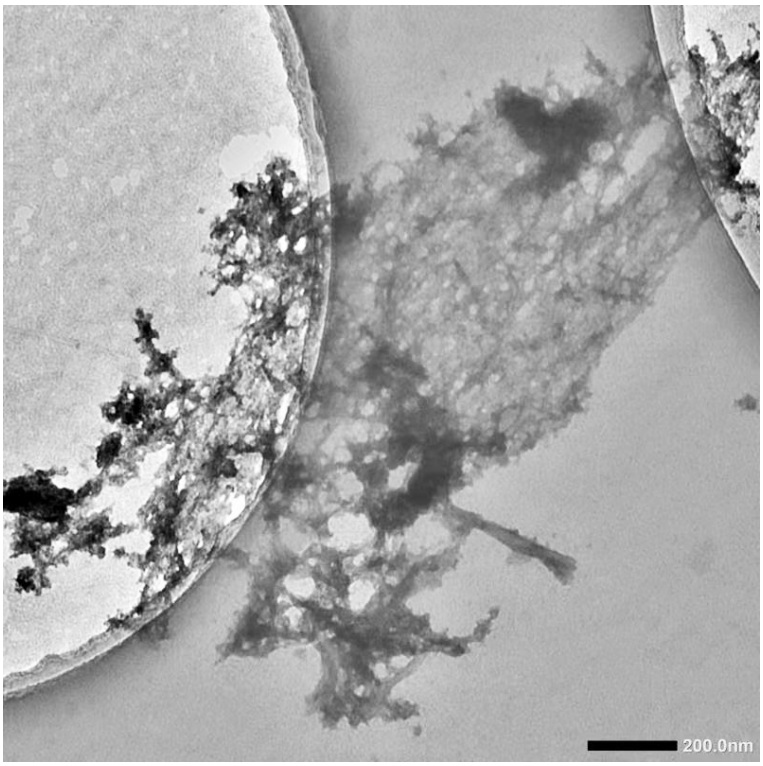

Fig. S4. Transmission electron microscopy image of silk protein solution

Table S1. The number of molecules for several polyAG solution with ethanol coagulation bath.

Ethanol coagulation bath	6-polyAG	9-polyAG	12-polyAG	15-polyAG
No. of polyAG	6	9	12	15
No. of Ca^{2+}/Cl^{-}	15/30	23/46	30/60	38/76
No. of ethanol	351	832	832	1625
No. of water	960	1744	2051	3147

Table S2. The number of molecules for several polyAG solution with PEG coagulation bath.

PEG coagulation bath	6-polyAG	9-polyAG	12-polyAG	15-polyAG
No. of polyAG	6	9	12	15
No. of Ca^{2+}/Cl^{-}	15/30	23/46	30/60	38/76
No. of PEG	1	2	2	3
No. of water	1053	1800	2107	2854

Table S3. The mechanical properties of WS-SFFs.

	Strength (MPa)	Modulus (GPa)
PEG-WS-SFFs-0.5x	40.5±7.7	5.4±1.3
PEG-WS-SFFs-1x	57.5±10.2	6.1±1.1
ET-WS-SFFs-0.5x	32.9±3.6	4.6±0.7
ET-WS-SFFs-1x	40.6±6.0	5.1±0.5

Table S4. **The mechanical properties of MT-SFMs and their control samples in dry state.**

	Strength (MPa)	Modulus (GPa)
PEG-MT-SFMs	60±4	2.9±0.4
ET-MT-SFMs	59±7	2.6±0.7
PEG-SFMs	37±3	1.4±0.4
ET-SFMs	35±4	1.3±0.3
As-cast SFMs	20±3	1.0±0.2

Table S5. **The mechanical properties of MT-SFMs and their control samples in wet state.**

	Strength (MPa)	Modulus (MPa)
PEG-MT-SFMs	5.4±0.5	23.8±1.5
ET-MT-SFMs	4.7±0.9	21.3±2.1
PEG-SFMs	2.2±0.1	5.9±0.6
ET-SFMs	1.9±0.4	4.9±2.2
As-cast SFMs	0.6±0.2	1.7±0.7