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## **Electronic Supporting Information**

## A silk composite fiber reinforced by telechelic-type polyalanine and its strengthening mechanism

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Fig. S1 <sup>1</sup>H NMR spectrum of TPA in DMSO-*d*<sub>6</sub>/TFA-*d* (5/1 volume ratio).



Fig. S2 Aggregation observed for 1 wt % Silk/LPA dope.



Fig. S3 Peak fitting results of silk fibers and TPA after deconvolution within amide I region.



Fig. S4 Stress-strain curves of silk only fiber, silk composite fiber, cocoon silk and De-silk. The test number for each sample is eight.



Fig. S5 The representative stress-strain curve of (a) silk composite fibers, De-silk and cocoon silks with the detailed mechanical property in terms of (b) tensile strength, (c) Young's modulus, (d) strain and (e) toughness. \* Significant difference between groups at p < 0.05. The testing number for each sample is eight.



Fig. S6 SEM images of breaking silk only fiber (a, f), Silk/TPA-0.5 fiber (b, g), Silk/TPA-1 fiber (c, h), Silk/TPA-3 fiber (d, i) and Silk/TPA-5 fiber (e, j) after the tensile test. (f)-(j) is the magnification of (a)-(e), respectively.



Fig. S7 Surface morphology of the (a) cocoon silk and (c) degummed silk. (b) and (d) show the magnification from (a) and (c), respectively.



Fig. S8 Outline of BL05 XU at SPring-8 for WAXD measurement with the sample setup.



**Fig. S9** Structure analysis of pristine silk fibers by WAXD. (a) 1D integrated profile and (b) azimuthal intensity profile at (020) peak. The arc lines in 2D pattern were showed to obtain the relevant azimuthal intensity. (c) Crystallinity. (d) Crystallite size. (e) Orientation degree.

\* Significant difference between groups at p < 0.05.



Fig. S10 Peak fitting results of silk fibers for the calculation of the crystallinity and crystallite

size.



Fig. S11 Peak fitting results of pristine silk fibers for the calculation of the crystallinity and crystallite size.



Fig. S12 The sample setup for the simultaneous tensile deformation during WAXD

measurement in SPring-8.



**Fig. S13** Simultaneous tensile deformation of silk composite fibers during WAXD measurement. The stress-strain curve of Silk/TPA-0.5 (a) and Silk/TPA-1 (b) fibers. The WAXD results of Silk/TPA-0.5 (c) and Silk/TPA-1 (d) fibers corresponding to specific strains in (a) and (b).



Fig. S14 AFM images of TPA particles and nanofibrils.

## Video caption

Video S1 Simultaneous stretching of Silk/TPA-1 fibers during WAXD measurement.