Electronic Supplementary Information

Fabrication of Nanofibers through a Unique Morphological Transformation of Poly(lactic acid) particles in Water

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Contents

1. Materials and methods

PLLA (M_w = 30,000, M_w/M_n = 2.4) and PDLA (M_w = 26,000, M_w/M_n = 2.4) were prepared by the ring-opening polymerization of L-lactide and D-lactide, respectively.[1] PDLLA (M_w = 20,000) was purchased from *Polysciences, Inc*. The weight-average molecular weights and the distribution of PLLA and PDLA were measured by gel permeation chromatography (Tosoh System HLC-8120GPC) with polystyrene standards, where two commercial columns (TSKgel GMHXL and TSKgel SuperHM-M) were connected in series, and chloroform was used as an eluent. The ^{1}H NMR and ^{13}C NMR spectra were measured with a JEOL JNMECS-400 spectrometer. The morphologies of the PLA particles and nanofibers formed in this study were observed with SEM (Scanning Electron Microscopy) and TEM (Transmission Electron Microscopy). The SEM measurements were performed with a JEOL JSM-6701F microscope operating at 5 kV. The SEM samples were prepared by deposition on a glass substrate and then sputtering with OsO_4. The TEM measurements were performed with a JEOL JEM-1200EX microscope operating at 80 kV. TEM samples of the PLA particles and nanofibers were prepared by depositing a droplet of the water dispersion on a copper grid covered with polyvinylformal films, and allowing it to air-dry overnight, and then staining with RuO_4 vapor.

2. ^{1}H and ^{13}C NMR spectra of PLLA and PDLA

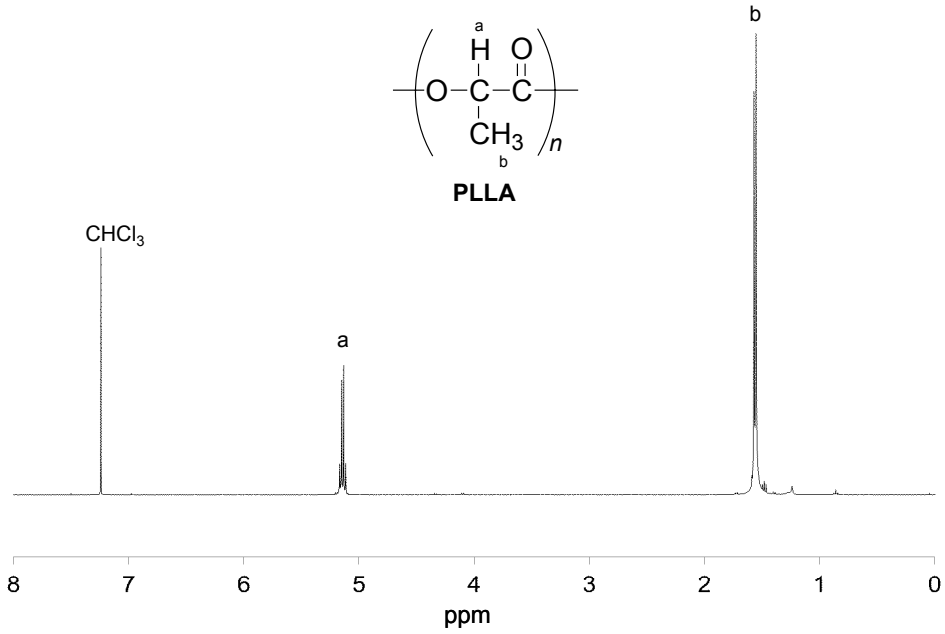

Fig. S1 ^{1}H NMR spectra of PLLA in $CDCl_3$ at 20 °C.

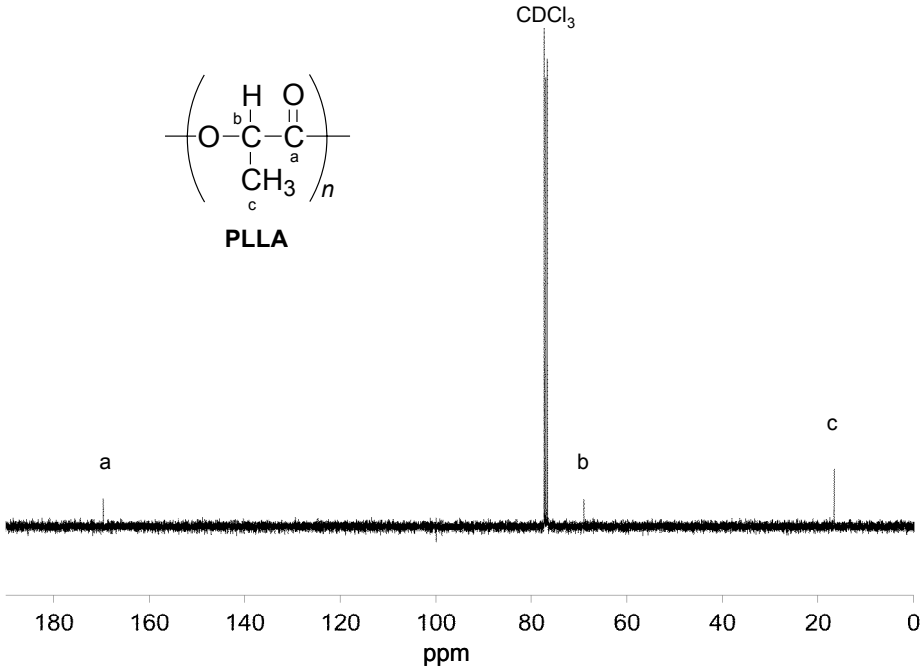

Fig. S2 ^{13}C NMR spectra of PLLA in $CDCl_3$ at 20 °C.

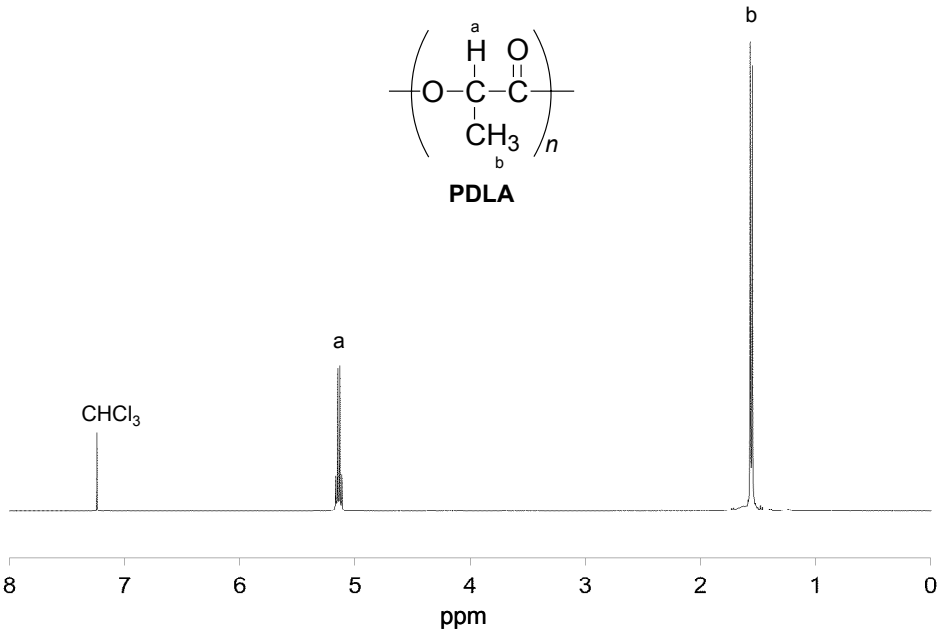

Fig. S3 ^{1}H NMR spectra of PDLA in $CDCl_3$ at 20 °C.

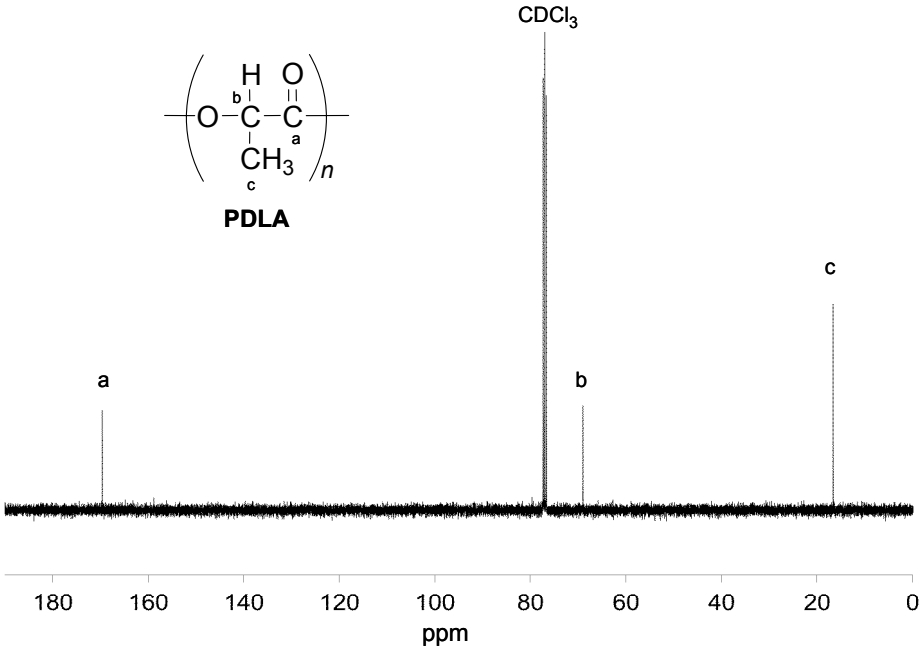

Fig. S4 ^{13}C NMR spectra of PDLA in $CDCl_3$ at 20 °C.

3. Preparation of PLA particles and nanofibers

Particles composed of PLLA and PDLLA were prepared by the self-organizing precipitation (SORP) method.[2] PLLA (M_w = 30,000) and PDLLA (M_w = 20,000) were each dissolved in THF to prepare the corresponding 0.1 g L^{-1} solution. Pure water (1 mL) was added to the PLA solution (1 mL) with stirring, and the THF was evaporated at room temperature under atmospheric pressure over 2 days. The preparation of PLLA/PDLA stereocomplex particles was performed by the re-precipitation of a mixed solution of PLLA and PDLA. 5 milligrams of PLLA (M_w = 30,000) and PDLA (M_w = 26,000) were dissolved in chloroform (1 mL). This polymer solution was added to ethanol (10 mL) with stirring, and the resulting precipitate was washed with ethanol several times and then re-dispersed in pure water to give PLLA/PDLA stereocomplex particles.

PLA nanofibers were fabricated by heating a water dispersion of PLA particles above 30 °C for a prescribed time and subsequently cooling it to ambient temperature.

4. SEM images of PLA particles

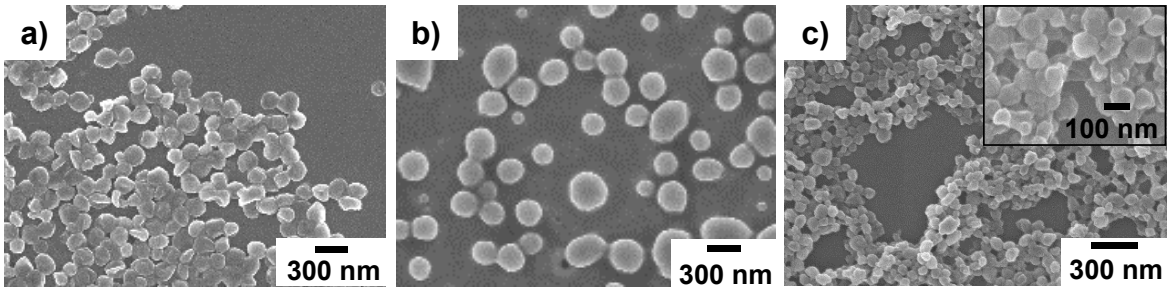

Fig. S5 SEM images of particles composed of (a) PLLA, (b) PDLLA and (c) PLLA/PDLA stereocomplex.

5. SEM images of PLA helical nanofibers

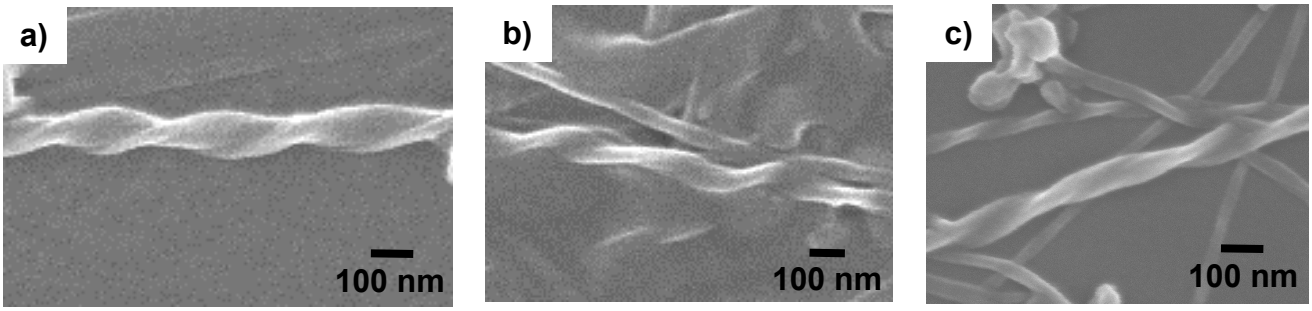

Fig. S6 SEM images of helical fibers composed of (a) PLLA, (b) PDLLA and (c) PLLA/PDLA stereocomplex.

6. FT-IR/ATR spectra of PLLA particles and nanofibers

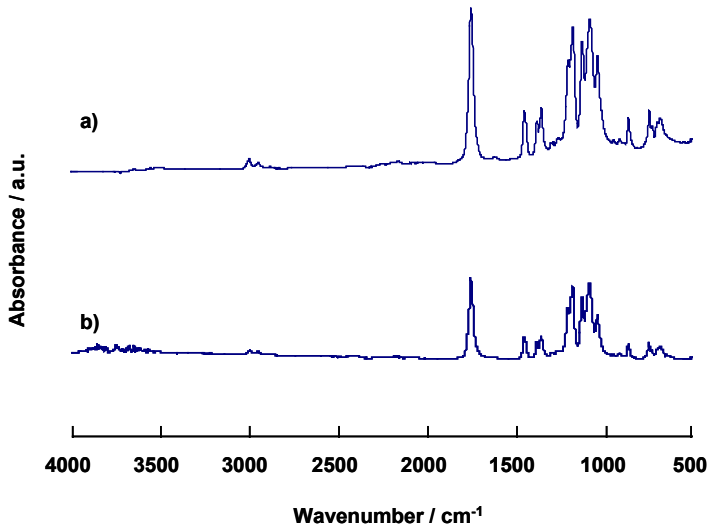

Fig. S7 FT-IR/ATR spectra of (a) PLLA particles and (b) PLLA nanofibers obtained by heating the PLLA particles in water at 90 °C for 1 h.

7. Static contact angle measurement and AFM image of PLLA nonwoven

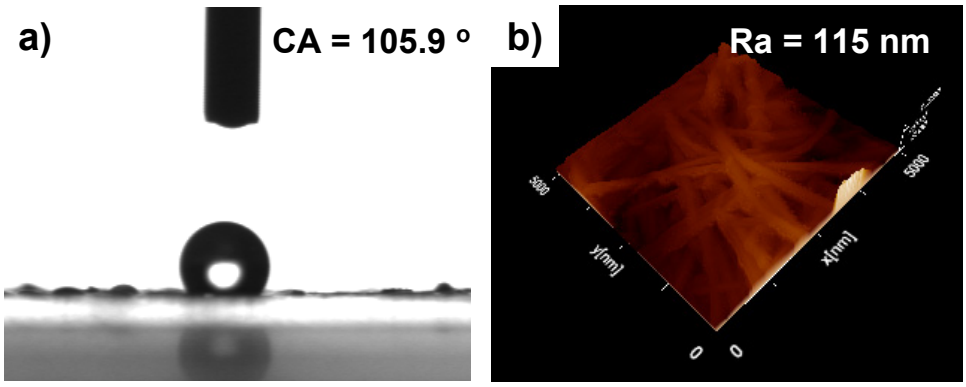

Fig. S8 (a) Photograph of a water droplet on the surface of PLLA nonwoven and (b) AFM image of PLLA nonwoven.

8. References

1 a) R. K. Kulkarni, E. G. Moore, A. F. Heygyelli and F. Leonard, *J. Biomed. Matter Res*. 1971, **5**, 109; b) V. W. Dittrich and R. C. Schulz, *Angew. Makromol. Chem.* 1971, **5**, 169.

2 T. Higuchi, A. Tajima, K. Motoyoshi, H. Yabu, and M. Shimomura, *Angew. Chem. Int. Ed.* 2009, **48**, 1.