Supporting Information

Poly(lactic acid) stereocomplex microspheres as thermally tolerant optical resonators

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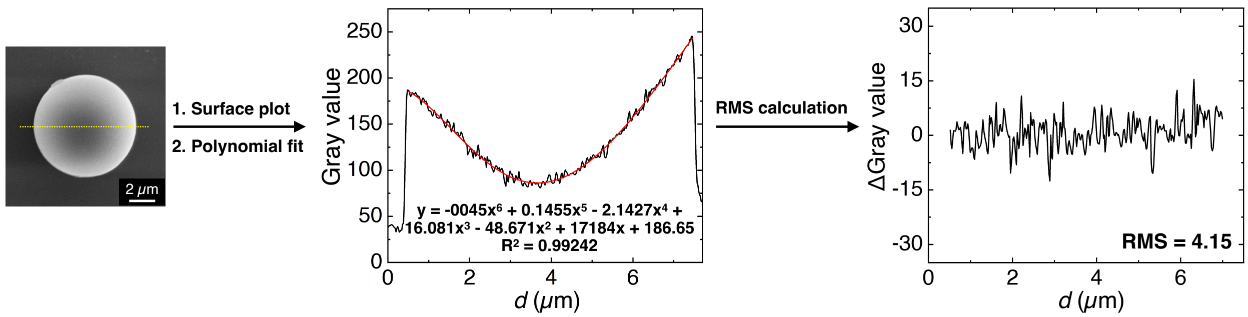
Materials. Poly(L-lactide) (PLLA, M_n = 40 kg mol^{-1}), poly(D-lactide) (PDLA, M_n = 90 kg mol^{-1}), poly(vinyl alcohol) (PVA, M_w = 31–50 kg mol^{-1}), and solvents were purchased from Sigma-Aldrich Co. Ltd. Zinc(II) tetraphenylporphyrin was purchased from Tokyo Chemical Industry Co., Ltd. All the materials were used without purification.

Preparation of Various Mixing Ratios of Stereocomplex PLA Microspheres. The homochiral (HC) and stereocomplex (SC) of poly(lactic) acid (PLA) microsphere resonators were prepared by oil-in-water miniemulsion method. Tupically, 10 mg of PLLA, PDLA, or their blends with different weight ratios (L/D = 9/1, 7/3, 5/5, 3/7, 1/9) and 0.1 mg zinc(II) tetraphenylporphyrin dye were dissolved in 0.2 mL of dichloromethane. For emulsification, the solution was then added to 3 mL of the aqueous PVA solution with a concentration of 1% and homogenized using a handy micro homogenizer (physcotron NS-360D) under stirring at 10 krpm for 10 min. The microsphere was collected by centrifugation at 100 krpm for 1 min. After centrifugation, the precipitation was washed three times by deionized water to remove all residual PVA.

Scanning Electron Microscopy (SEM). The surface morphology of the HC- and SC-PLA microspheres was observed by scanning electron microscopy (SEM, Hitachi S-3700N). All the sample was dispersed in EtOH, and the suspension was drop-cast on a silicon substrate and air dried. The surface was coated with thin gold layer (~ 30 nm) for observation.

Root-mean-square (RMS) roughness. The surface roughness of the single microsphere was evaluated by ImageJ software to determine the distribution of gray values in the SEM micrograph of the microspheres. The RMS roughness was calculated by plotting between the difference of gray values and the distance (d), as shown below.

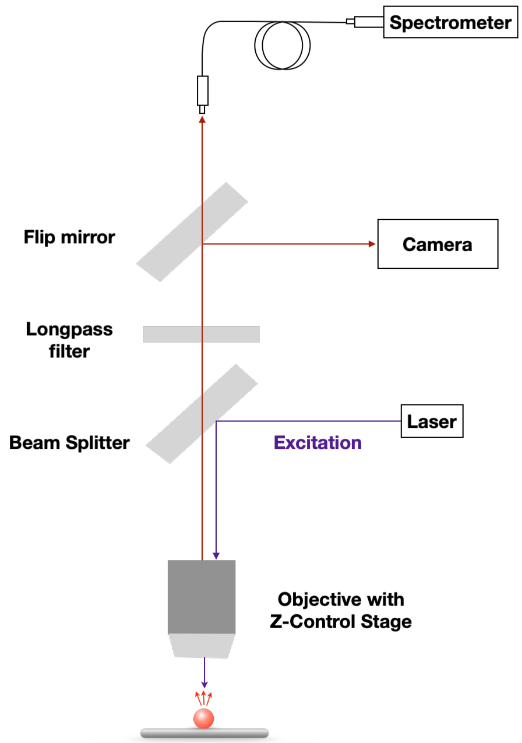


Differential Scanning Calorimetry (DSC). The DSC thermograms of PLLA, PDLA and SC-PLA were measured using DSC instrument (Seiko Instruments X-DSC7000). The powder samples of HC-PLLA, HC-PDLA and SC-PLA (~ 5 mg) were placed into an aluminum pot, and the thermogram was measured in the DSC instrument in temperature range of 30–250 °C at the rate of 10 °C min^{-1}.

Thermogravimetry Differential Thermal Analysis (TG/DTA). The TG/DTA measurements were carried out with TG/DTA instrument (SEICO Inst., TG/DTA7300)**.** The powder samples of HC-PLLA, HC-PDLA and SC-PLA approximately 5 mg were analyzed in temperature range of 30–250 °C at the heating rate of 10 °C min^{-1}.

Powder X-Ray Diffraction (PXRD) Analysis. PXRD analyses of the HC- and SC-PLA microspheres were performed on a Rigaku model MiniFlex 600 diffractometer operated 40 kV and 15 mA with the Cu *K*α radiation (λ = 1.5418 Å) in the scan range 5–40° at a scanning speed of 1° min^{-1}. The variable-temperature XRD was performed at temperature in the range of 25–220 °C. The relative percentage of the crystallites (X_c) of HC- and SC-PLA was calculated by comparing the diffraction peak area of the HC- or SC-PLA with the total diffraction peak area of the amorphous, HC- and SC-PLA.

Micro Photoluminescence (μ-PL) Spectroscopy: μ-PL spectra of the PLA microspheres were observed with a spectrometer (Lambda Vision model LV-MC3/T) upon photoexcitation with a focused laser (cw, λ = 405 nm) to a single microsphere of PLA on a quartz substrate. The schematic illustration of the optical measurement system is shown below. The microspheres on a quartz substrate were heated for 2 s at temperature from 30 to 240 °C with every 10 °C and subsequently cooled down to 25 °C. All the μ-PL measurements were conducted at 25 °C



Analysis of TE and TM modes from PL spectra from a single microsphere: Simulations of the WGMs were conducted using eq. 1 and eq. 2 for transverse electric (TM) and magnetic (TE) mode emissions, respectively.[S1]

$$\lambda_l^E = 2\pi r(\varepsilon\mu)^{\frac{1}{2}}\left[l+\frac{1}{2}+1.85576(l+\frac{1}{2})^{\frac{1}{3}}-\frac{1}{\varepsilon}\left(\frac{\varepsilon\mu}{\varepsilon\mu-1}\right)^{\frac{1}{2}}\right]^{-1} \quad \text{(eq. S1)}$$

$$\lambda_l^H = 2\pi r(\varepsilon\mu)^{\frac{1}{2}}\left[l+\frac{1}{2}+1.85576(l+\frac{1}{2})^{\frac{1}{3}}-\frac{1}{\mu}\left(\frac{\varepsilon\mu}{\varepsilon\mu-1}\right)^{\frac{1}{2}}\right]^{-1} \quad \text{(eq. S2)}$$

where λ_l^E and λ_l^H are the wavelengths of the l-th TM and TE mode photoemission, respectively, ε (= n^2) is the dielectric permittivity, μ (= 1) is the magnetic permeability, and r is the radius of the sphere. Here, higher-order terms were neglected. For simulation of the PL lines, TE and TM modes were calculated using Eqs. S1 and S2. Within the margin of error of the radius of the sphere (obtained by optical microscopy), the simulation adapts a radius so that both TE and TM modes agree well for given orders l, effectively determining the radius with much higher precision.

Supporting Figures

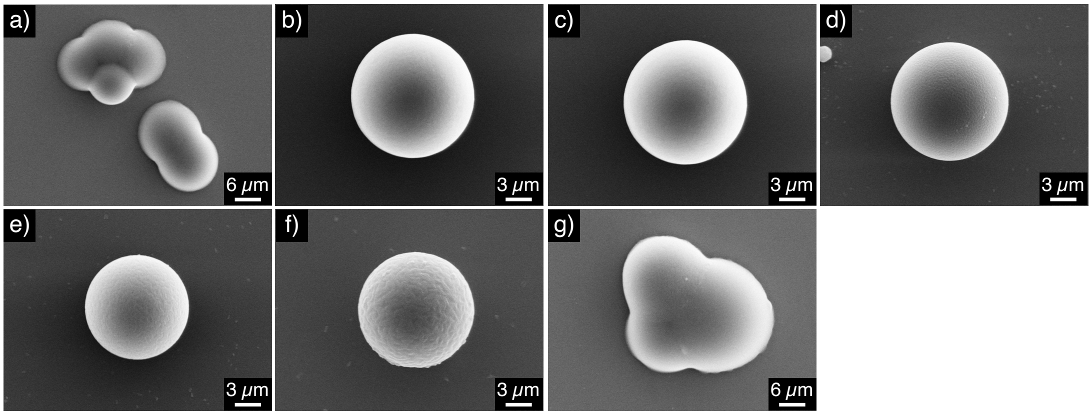


Figure S1. Surface Morphology of HC- and SC-PLA microsphere prepared by oil-in-water solvent evaporation method at varying mass ratio of PLLA/PDLA after heated at 200 °C. The L/D ratio: (a) 10/0, (b) 9/1, (c) 7/3, (d) 5/5, (e) 3/7, (f) 1/9, (g) 0/10.

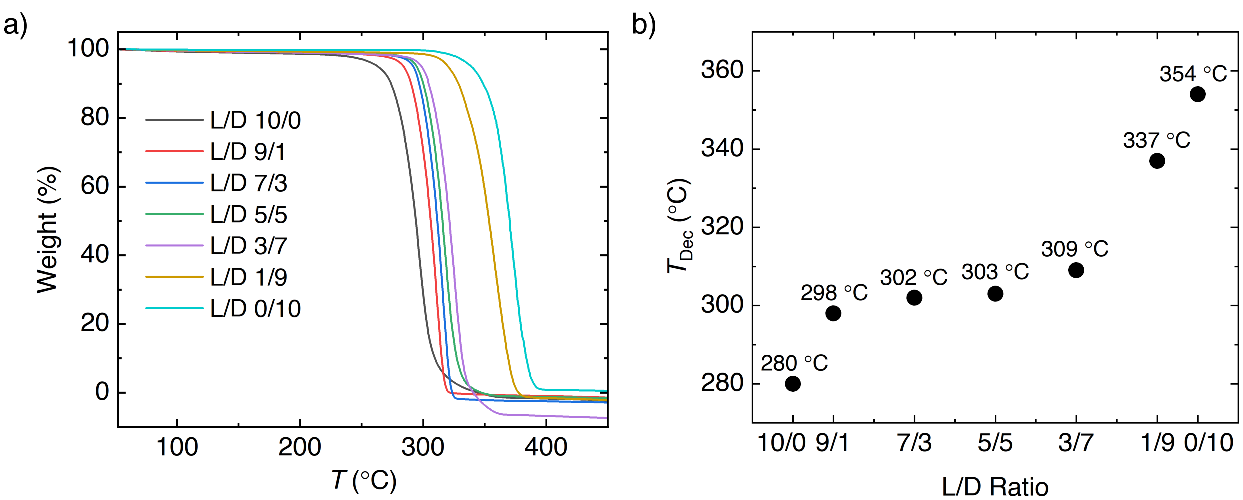


Figure S2. (a) TGA profiles of HC- and SC-PLA microspheres with various L/D ratios. (b) Plot of T_{dec} versus L/D ratio.

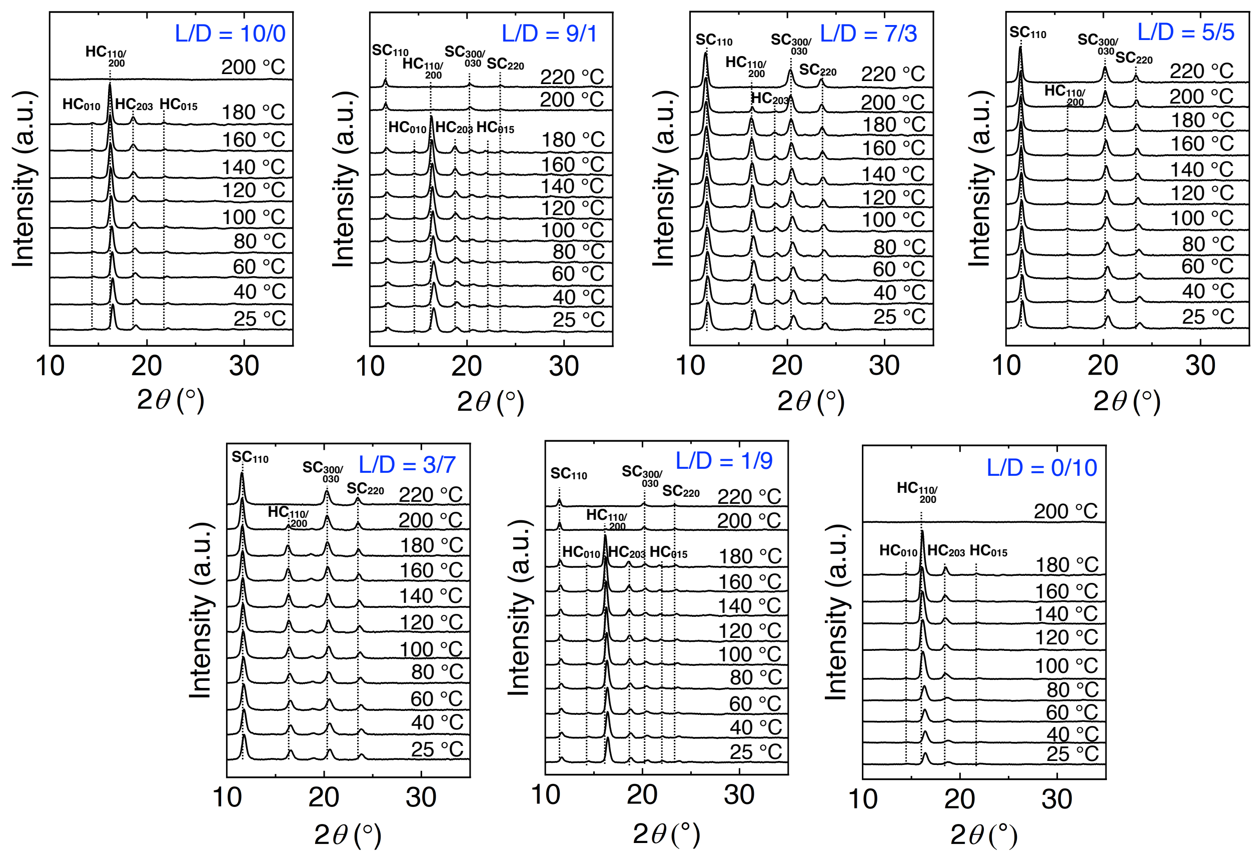


Figure S3. Temperature dependence of powder XRD patterns of HC- and SC-PLA with various L/D ratios.

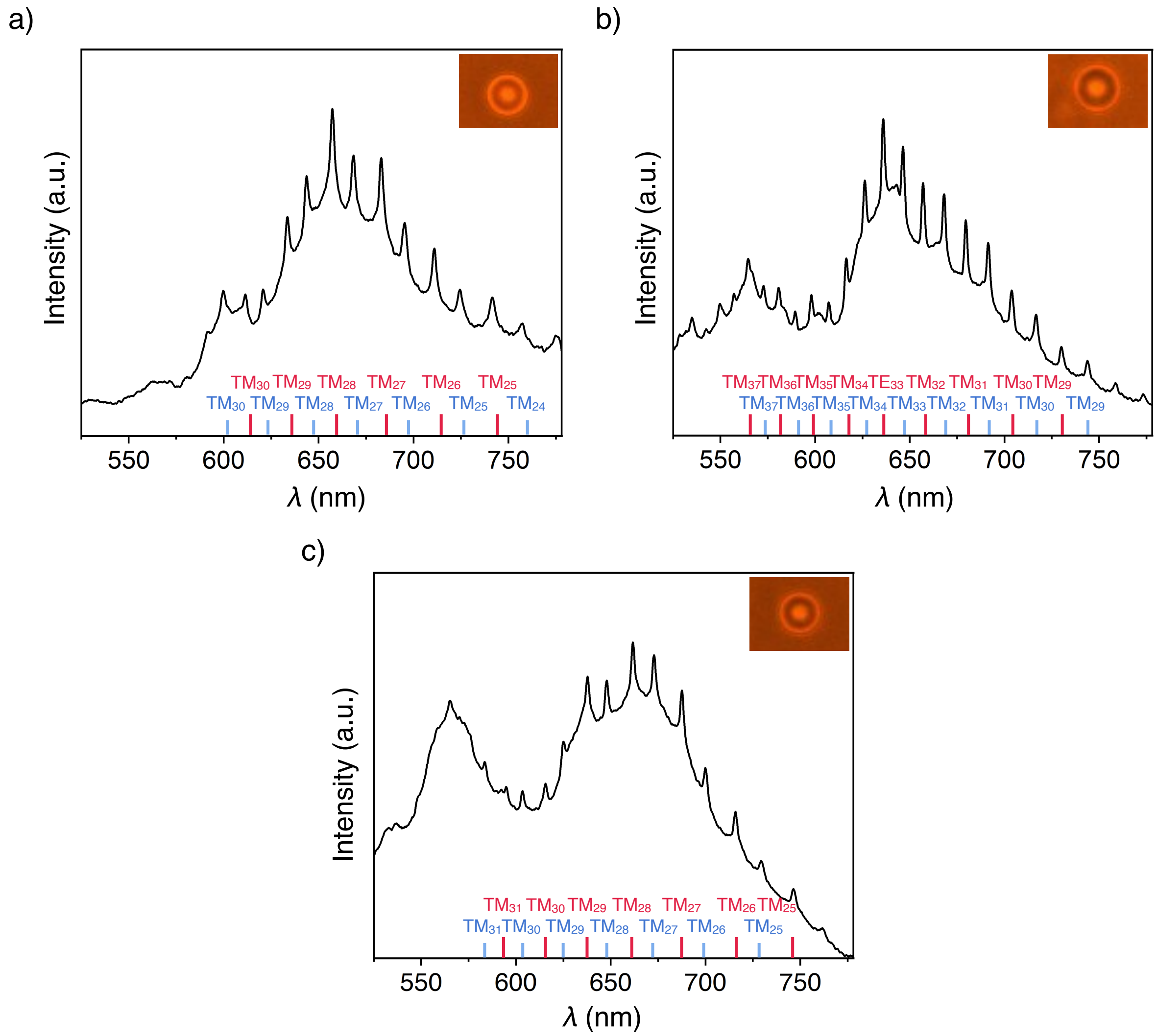


Figure S4. PL spectra of single microsphere at 30 °C upon excitation with a cw 405-nm laser with the calculated mode number of the observed resonant peaks, the insets show the image of the single microsphere under excitation. The L/D ratio: 10/0 (a), 9/1 (b), 7/3 (c). The TE and TM mode numbers of the resonant peaks are shown on the bottom of the spectra.

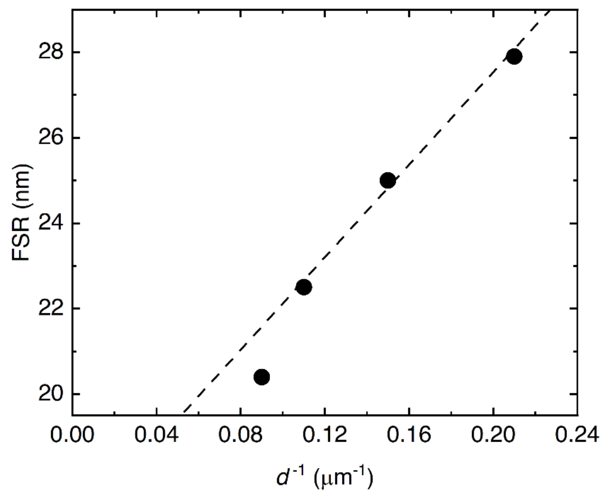


Figure S5. Plot of FSR versus d^{-1} for PLLA microspheres with different d.

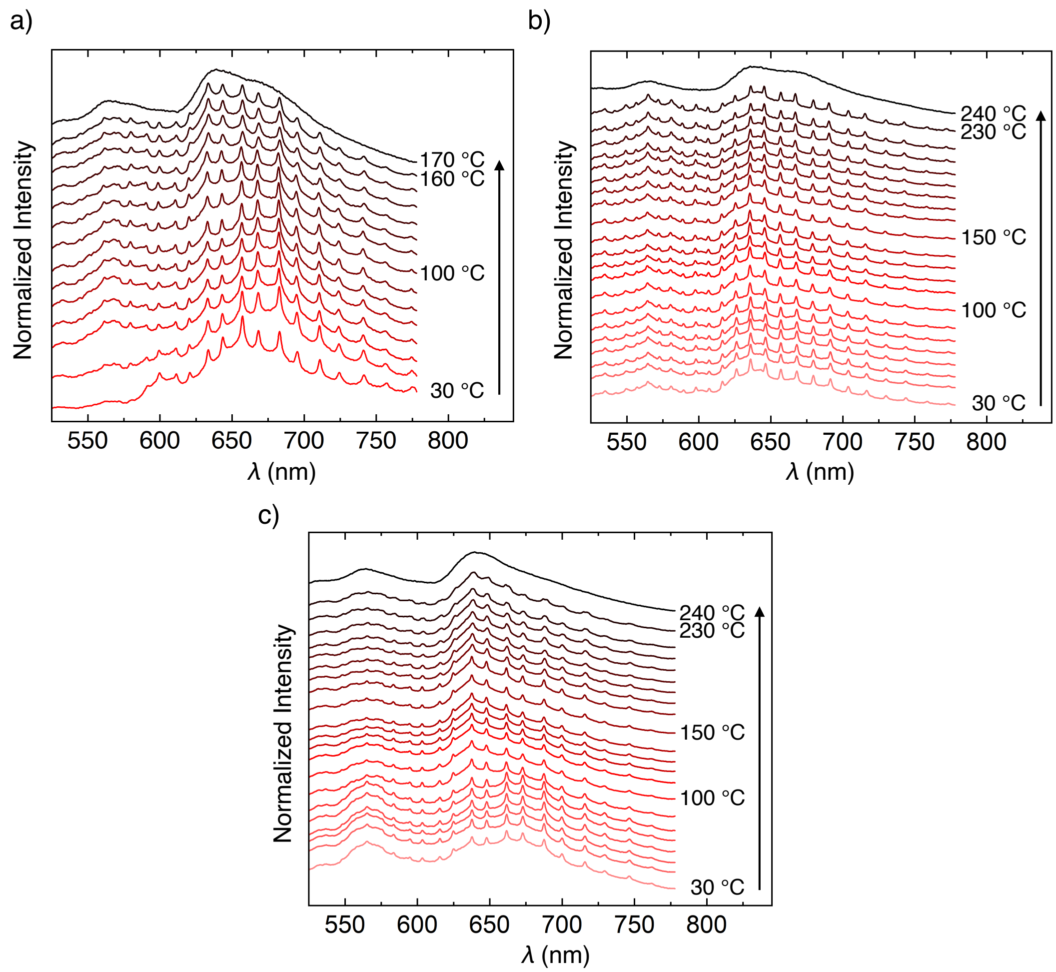


Figure S6. Variable-temperature PL spectra of a single PLA microsphere after heating for 2 s at 30–240 °C for every 10 °C upon excitation with a cw 405-nm laser. The L/D ratio: (a) 10/0, (b) 9/1, (c) 7/3.

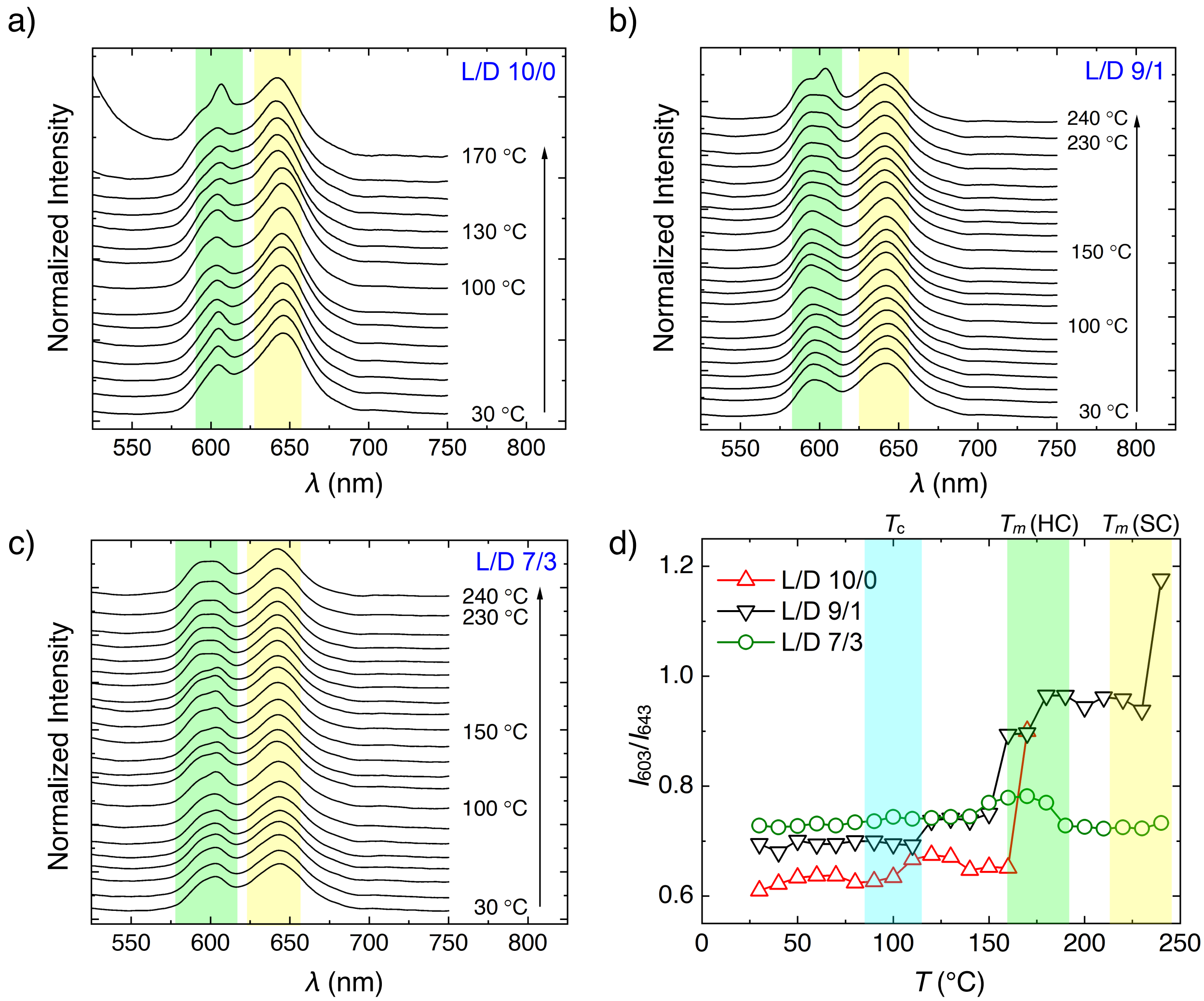


Figure S7. (a–c) PL spectra of cast films of PLA microspheres with L/D ratio of 10/0 (a), 9/1 (b), and 7/3 (c), annealed at each temperature for 2 s. (d) Plots of PL Intensity ratio at 603 and 643 nm (I_{603}/I_{643}) versus annealing temperature.

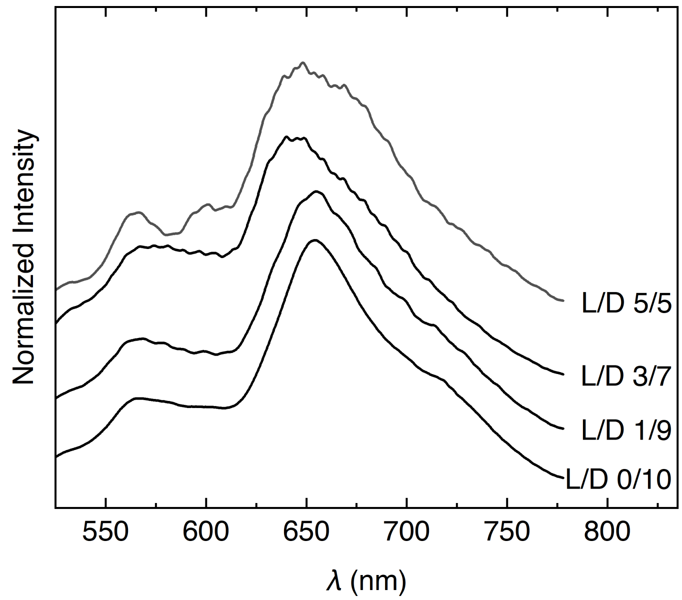


Figure S8. PL spectra of a single PLA microsphere upon excitation with a cw 405-nm laser. The L/D ratio: 5/5 (a), 3/7 (b), 1/9 (c), 0/10 (d).

Supporting reference

[S1] A. N. Oraevsky, *Quant. Elect*. 2002, 32, 377.