

Supporting information

Fabrication of Monodisperse Poly(ϵ -caprolactone) (PCL) Particles Using Capillary Force Lithography (CFL)

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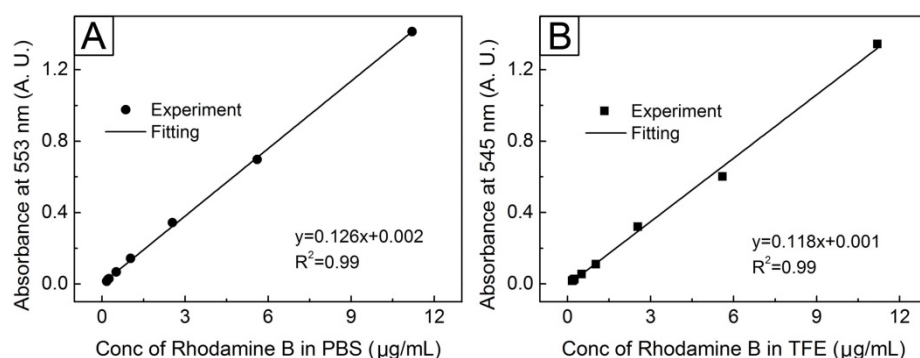


Figure S1. Calibration curves constructed from a series of dye solutions in A) PBS and B) 2,2,2-trifluoroethanol (TFE).

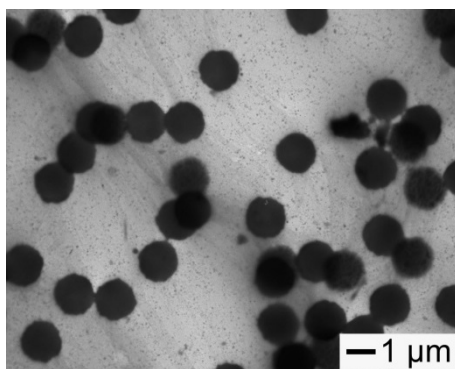


Figure S2. TEM image of the PCL disks released into an aqueous PVP solution.

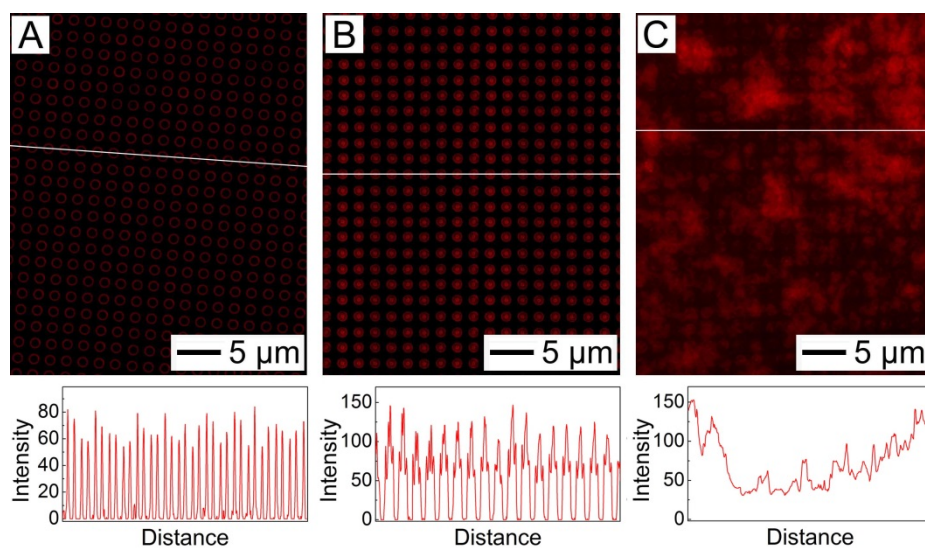


Figure S3. Fluorescence micrographs of the PCL disks generated from PCL films with different thicknesses: A) 17 nm, B) 87 nm, and C) 405 nm. In order to track the PCL chains, a fluorescence dye (Rhodamine B) was added into the PCL solutions used for spin-coating. Fluorescence spectra from (A), (B), and (C) are represented below. The patterns fabricated from the thin PCL films (17 and 87 nm) exhibited fluorescent features with sharp boundary. In contrast, the fluorescence image of the pattern generated from the thicker film (405 nm) was blurry due to the existence of residual layer.

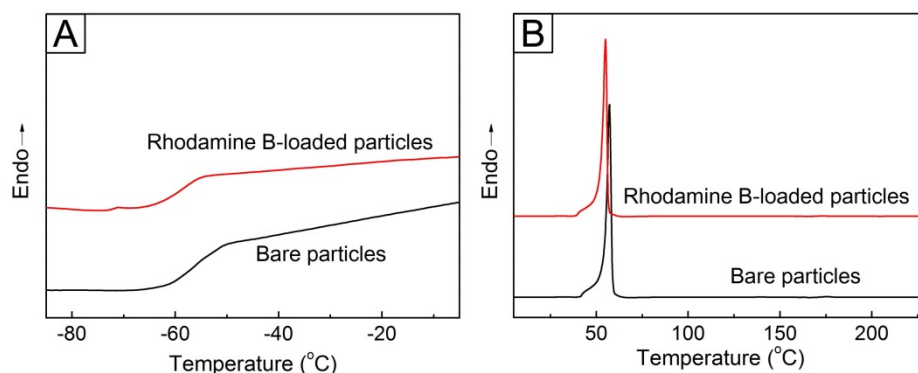


Figure S4. DSC thermograms of bare PCL solid particles and Rhodamine B-loaded particles in the temperature range of: A) from -85 °C to -5 °C and B) from 5 °C to 230 °C. Molecular weight (M_n) of the samples was 10 k. After the heating process for the transformation to a spherical shape, the samples were cooled in ambient air.

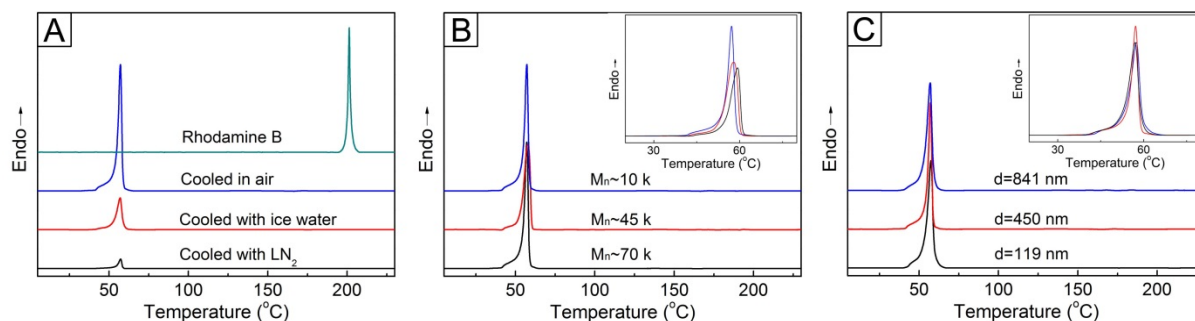


Figure S5. DSC thermograms of the PCL particles loaded with Rhodamine B depending on various controllable factors: A) cooling medium, B) molecular weight (M_n) of PCL, and C) particle size (d).

Table 1. Summary of calculated diffusivity, crystallinity (%), amorphousity (%), and normalized diffusivity and amorphousity.

Molecular Weight (M_n)	Cooling medium	Diameter (nm)	Diffusivity ¹ (D , $\text{cm}^2 \cdot \text{s}^{-1}$)	Crystallinity ² (X_c , %)	Amorphousity ³ (X_a , %)	α^4	β^5
10 k	air	119 ± 37	5.30×10^{-16}	73.3	26.7	0.24	0.28
10 k	air	450 ± 30	5.34×10^{-16}	72.5	27.5	0.24	0.29
10 k	air	841 ± 42	5.25×10^{-16}	72.8	27.2	0.23	0.28
45 k	air	461 ± 27	7.56×10^{-16}	65.8	34.2	0.34	0.36
70 k	air	453 ± 34	9.32×10^{-16}	56.2	43.8	0.41	0.46
10 k	ice water	448 ± 38	1.73×10^{-15}	26.2	73.8	0.77	0.78
10 k	LN ₂	452 ± 31	2.25×10^{-15}	5.5	94.5	1	1

¹ From a theoretical model, $M_t/M_\infty = 6(Dt/\pi r^2)^{1/2} - 3Dt/r^2$ describing the release behavior in particle matrix system, diffusivity for each sample was obtained.

² Crystallinity (X_c , %) = $\Delta H_f \times 100 / \Delta H_f^\circ$ where ΔH_f and ΔH_f° are the apparent heat of fusion per gram of the sample and the thermodynamic heat of fusion per gram of 100% crystalline PCL, respectively. ΔH_f° is 135.31 J/g.

³ Amorphousity (X_a) = $100 - X_c$

⁴ Normalized diffusivity (α) = $D / (2.25 \times 10^{-15})$

⁵ Normalized amorphousity (β) = $X_a / 94.5$

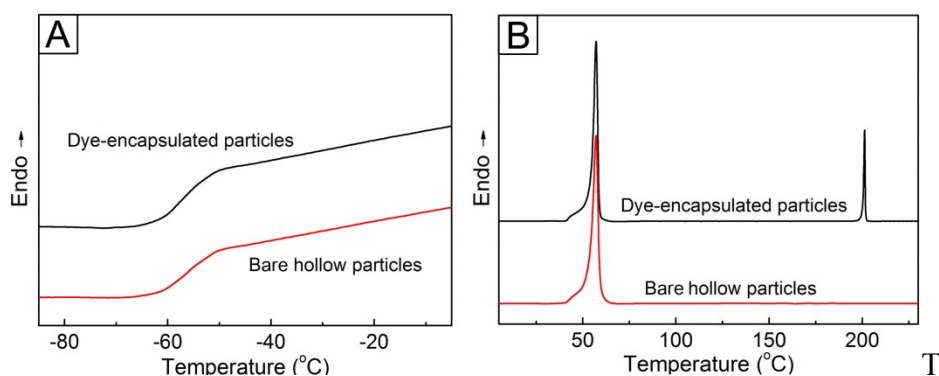


Figure S6. DSC thermograms of bare PCL hollow particles and Rhodamine B-encapsulated hollow particles in the temperature range of: A) from -85 °C to -5 °C and B) from 5 °C to 230 °C. The loading content of the dye-encapsulated PCL hollow particles was $19.2 \pm 0.5\%$.

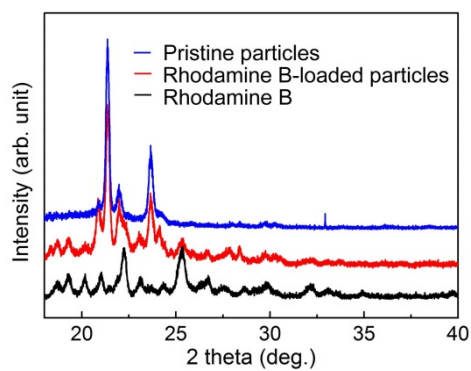


Figure S7. XRD patterns of bare PCL hollow particles, Rhodamine B, and Rhodamine B-encapsulated PCL hollow particles. The loading content of the dye-encapsulated PCL hollow particles was $19.2 \pm 0.5\%$.