

Supporting Information

Amphiphilic Diblock Copolymer of Hydrophilic-Functionalized Lactone and Lactide via Switchable Organocatalytic Polymerization

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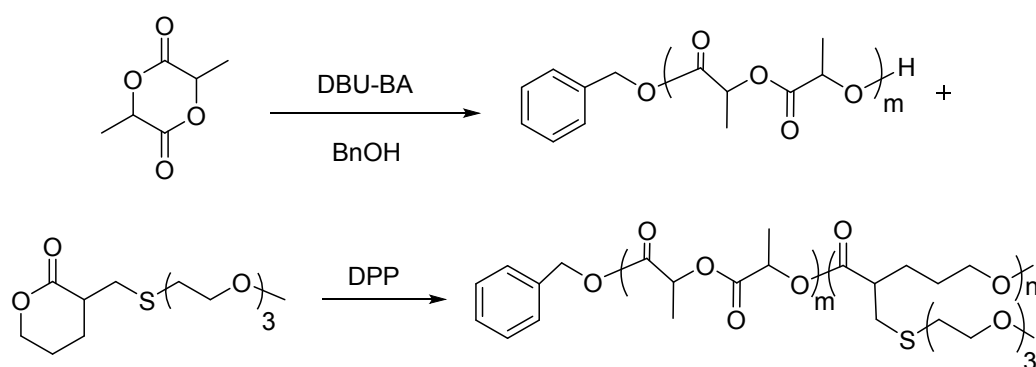
1. Materials and Methods

Chemicals were purchased from commercial sources and used as received unless otherwise noted. The functional δ -valerolactone was synthesized according to reported procedures.¹ Both lactide and the functional δ -valerolactone used in this study were racemic mixtures. The catalyst DBU-BA was synthesized according to reported procedures.² Silica gel for analytical thin layer chromatography (TLC) and column chromatography (200~300 mesh) were purchased from Qingdao Haiyang Chemical Co., Ltd & Special Silica Gel Factory (Qingdao, China). Dialysis was carried out with tubing cellulose membrane (MWCO 1KD, Spectrum Laboratories Inc. USA). The ¹H NMR spectra were recorded at 400 MHz on a Bruker AV400 spectrometer at ambient temperature. Chemical shifts were reported in parts per million (ppm) downfield from TMS (tetramethylsilane). Gel Permeation Chromatography (GPC) in THF was performed using three Agilent PL-gel columns (Mixed C, Mixed C, and Mixed D), a Waters 1515 isocratic HPLC pump, and a Waters 2414 RI detector. THF was used as the eluent at a flow rate of 1.0 mL/min at 35 °C. Polystyrene standards (American Polymer Standards Corp, USA) were used for the calibration. Particle size distributions of the samples dispersed in water were measured with dynamic light scattering (DLS) (Zeta PLUS, Brookhaven Instruments Corporation, NY, USA). The DLS instrument was operated under the following conditions: temperature 25 °C, detector angle 90°, incident laser wavelength 658 nm. SEM images were obtained by a field emission scanning electron microscopy (FESEM, S-8010, Hitachi).

2. General preparation procedures of homopolymers

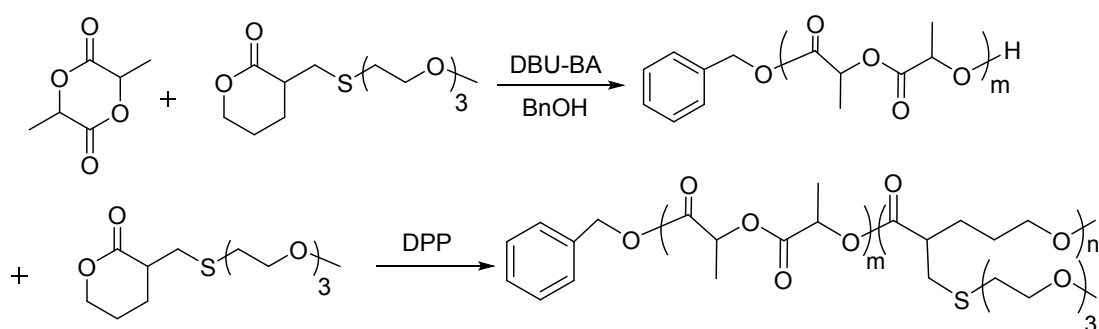
The functional δ -valerolactones (2.19 g, 7.50 mmol), benzyl alcohol (0.05 g, 0.50 mmol), catalyst DBU-BA (0.27 g, 1.00 mmol) and diphenyl phosphate (0.75 g, 3.00 mmol) in 1.5 mL DCM was added to a 25 ml flask equipped with a rubber septum connected to N₂ vacuum line. Moisture and oxygen were removed by freeze-thawing protocol. The polymerization was carried out at room temperature under protection of nitrogen. The monomer conversion was monitored by analyzing aliquots of reaction mixture with ¹H NMR. Upon completion, the reaction mixture was quenched by addition of excess amount of triethylamine, solvent was evaporated under vacuum and residue was dissolved in methanol, then transferred into a dialysis bag (MWCO = 1000) with methanol as dialysis solvent. The solvent was replaced every 12 hours for 3 times. Then the methanol solution was concentrated and the residual solvent was removed via high vacuum pump for 12 h.

3. General preparation procedures of block copolymers



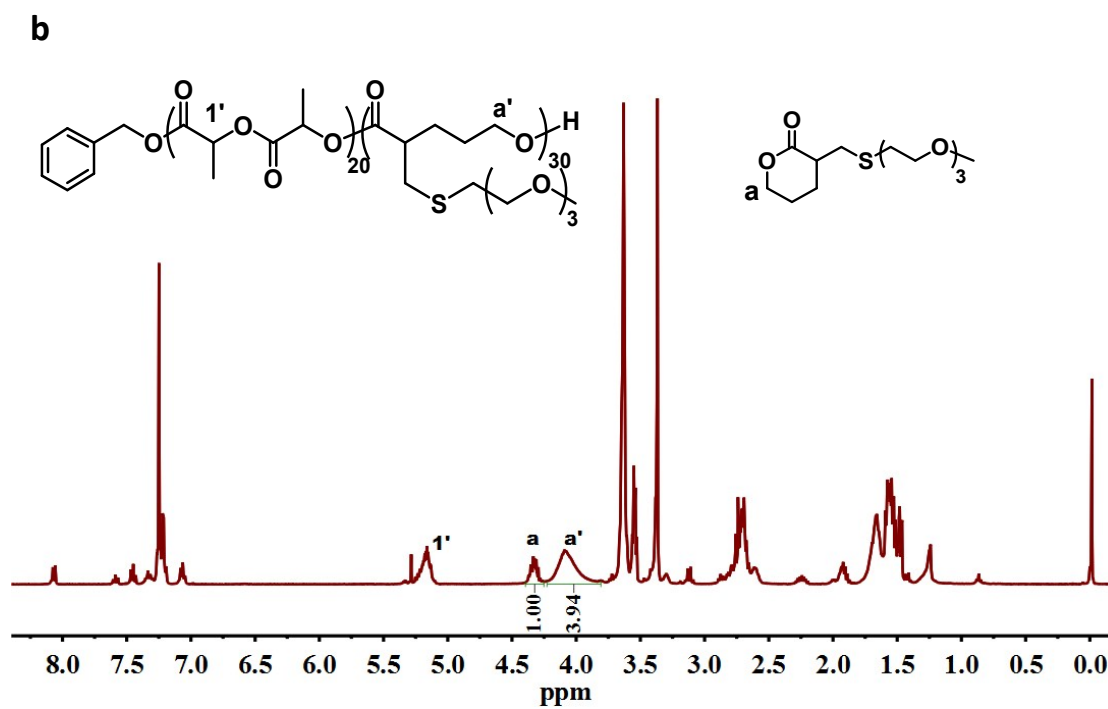
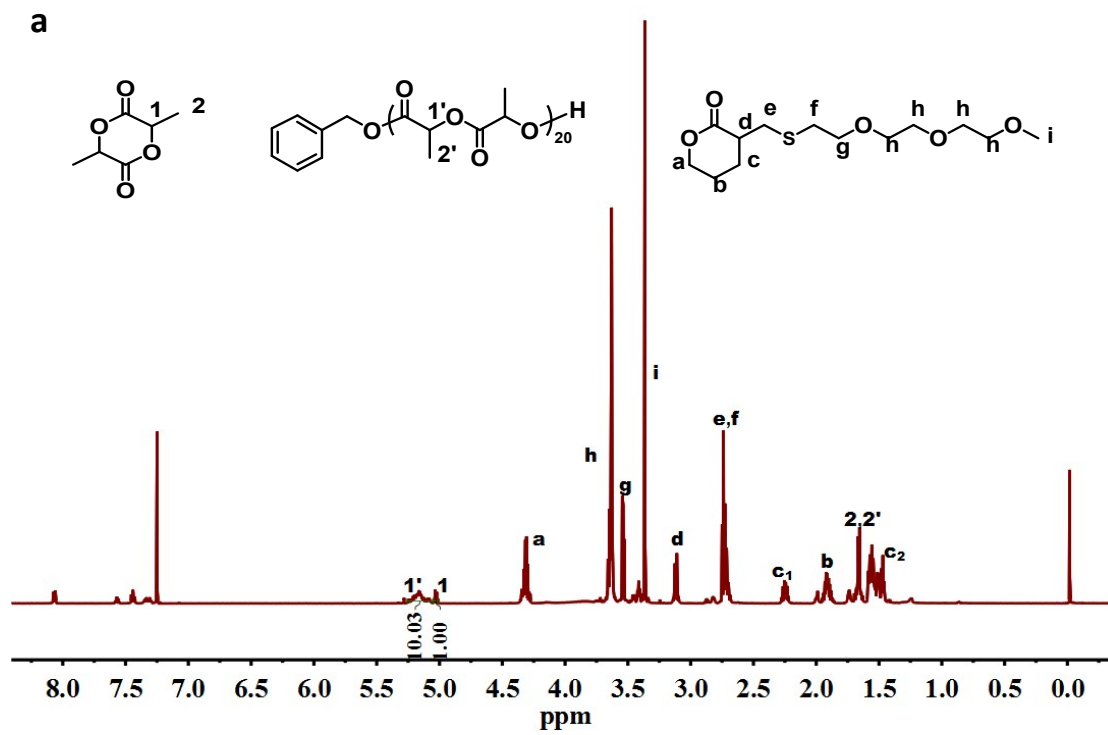
Lactide (1.08 g, 7.50 mmol) was added to a 25 ml flask equipped with a rubber septum connected to N₂ vacuum line. Benzyl alcohol (0.05 g, 0.50 mmol) and catalyst DBU-BA (0.27g, 1.00 mmol) were dissolved in DCM and added to the flask. Moisture and oxygen were removed by freeze-thawing protocol. The polymerization was carried out at room temperature under protection of nitrogen. The conversion of the lactide was monitored by analyzing aliquots of reaction mixture with ¹H NMR.

Upon completion of the PLA block, diphenyl phosphate (0.75 g, 3.00 mmol) in DCM was introduced by a syringe. Before addition of monomers of the second block, the reaction mixture was stirred for 5 min. The functional δ -valerolactones (2.19 g, 7.50 mmol) in DCM was introduced by syringe. The monomer conversion was monitored by analyzing aliquots of reaction mixture with ^1H NMR. Upon completion, the reaction mixture was quenched by addition of excess amount of triethylamine, solvent was evaporated under vacuum and residue was dissolved in methanol, then transferred into a dialysis bag (MWCO = 1000) with methanol as dialysis solvent. The solvent was replaced every 12 hours for 3 times. Then the methanol solution was concentrated and the residual solvent was removed via high vacuum pump for 12 h.



For the one-pot approach, Lactide (0.72 g, 5.00 mmol) and the functional δ -valerolactones (2.19 g, 7.50 mmol) were added to a 25 mL flask equipped with a rubber septum connected to N₂ vacuum line at the beginning. Benzyl alcohol (0.05 g, 0.50 mmol) and catalyst DBU-BA (0.27g, 1.00 mmol) were dissolved in DCM and added to the flask. Moisture and oxygen were removed by freeze-thawing cycles. The polymerization was carried out at room temperature under protection of nitrogen. The conversion of the lactide was monitored by analyzing aliquots of reaction mixture with ^1H NMR. Upon completion of the PLA block, diphenyl phosphate (0.75 g, 3.00 mmol) in DCM was introduced by a syringe. Upon completion, the reaction mixture was quenched by addition of excess amount of triethylamine, solvent was evaporated under vacuum and residue was dissolved in methanol, then transferred into a dialysis bag (MWCO = 1000) with methanol as dialysis solvent. The solvent was replaced every 12 hours for 3 times. Then the methanol solution was concentrated and the residual solvent was removed via high vacuum pump for 12 h.

4. Examples of ^1H NMR Analysis



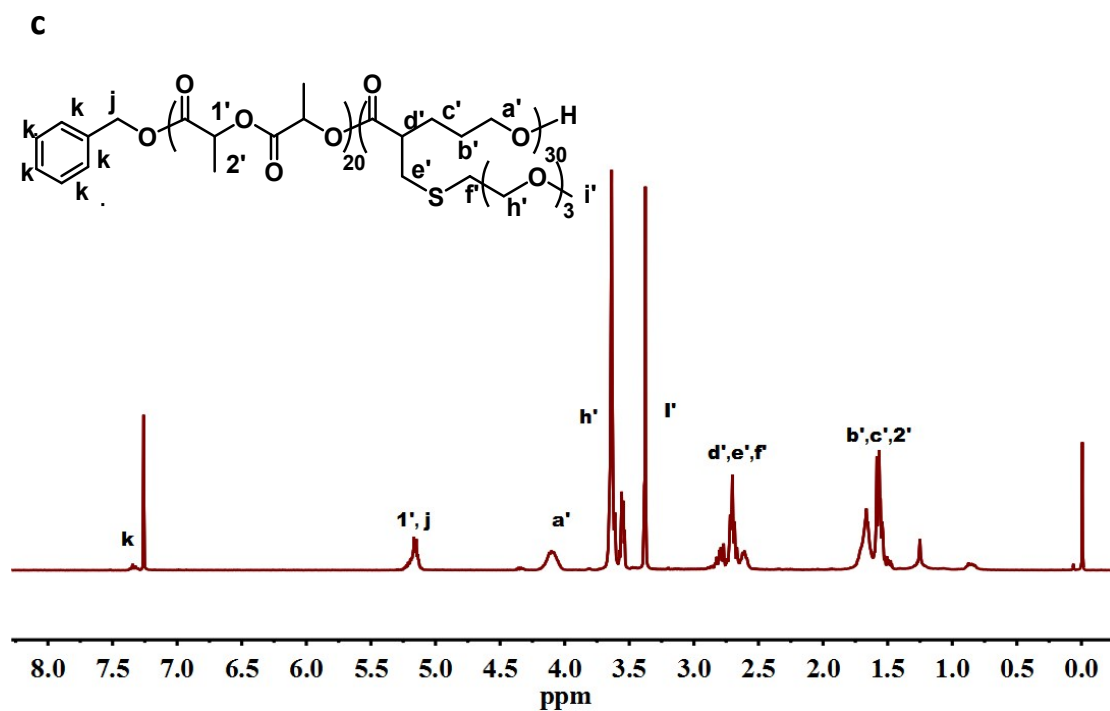
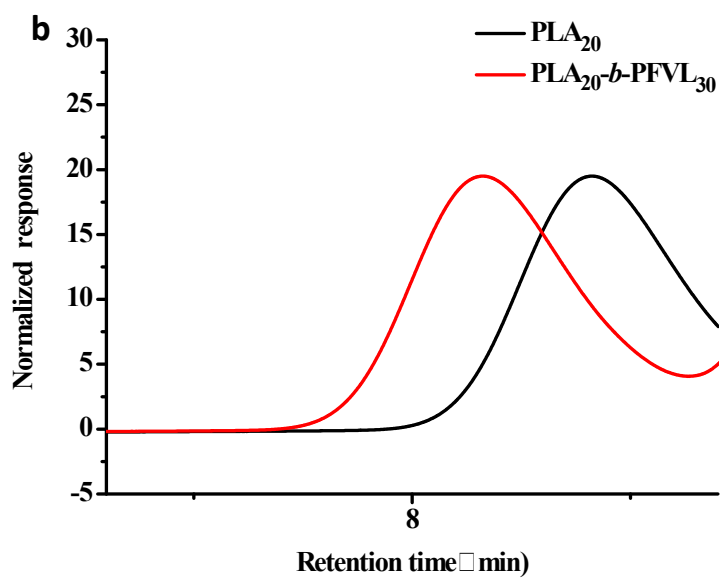
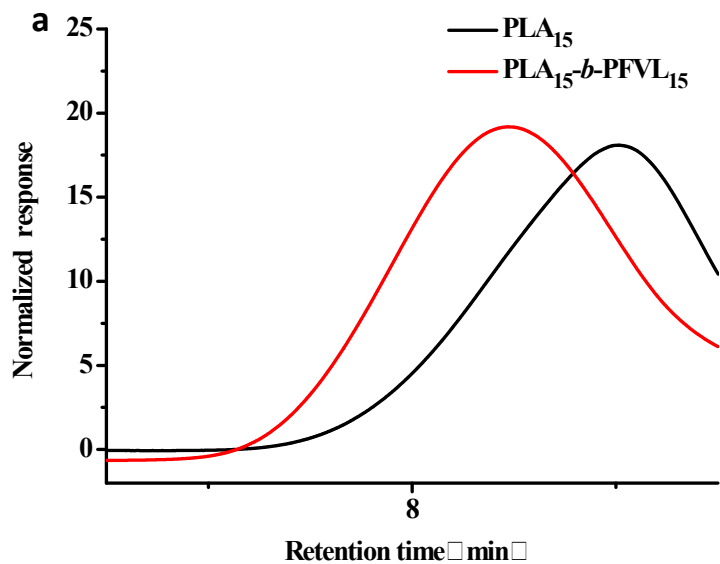


Figure S1. Full ^1H NMR of polymerization with mixtures monomers (a) catalyst in lactide-active mold; (b) catalyst state switched to lactone active mold; (c) ^1H NMR spectra of purified $\text{PLA}_{20}\text{-}b\text{-PFVL}_{30}$ prepared by the one-pot method starting with mixture of LA and FVL.

5. Examples of GPC Analysis



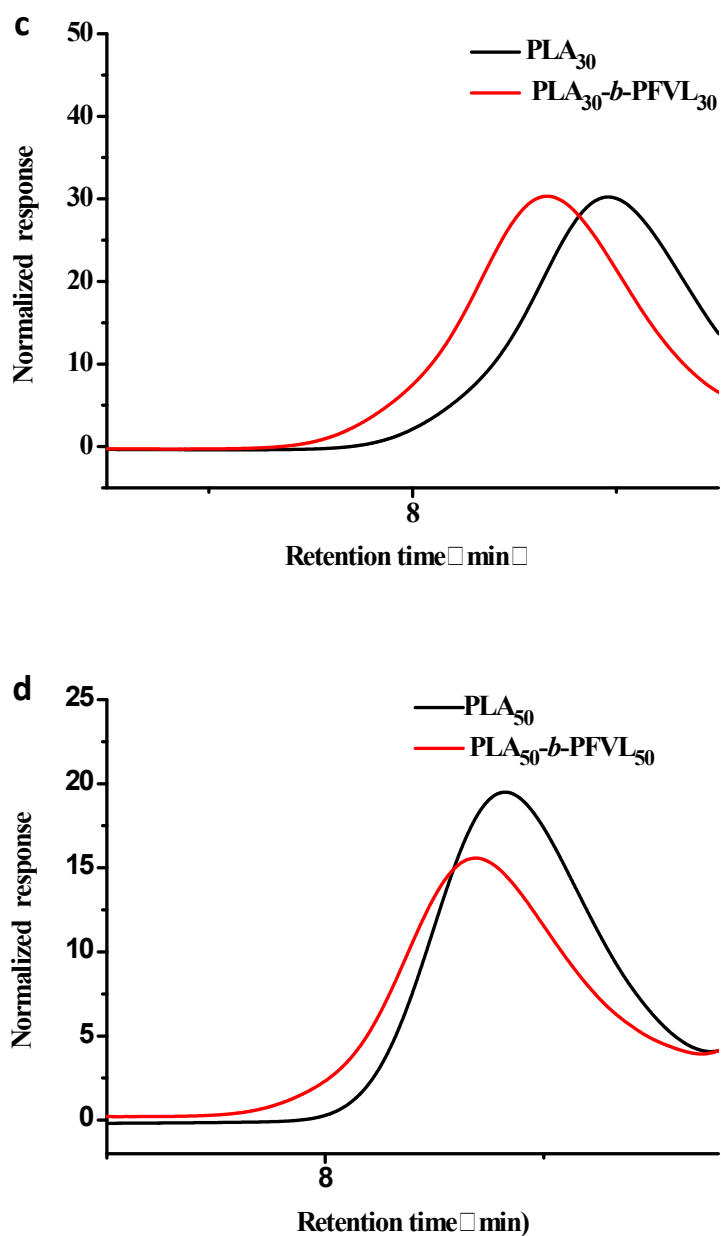


Figure S2. GPC traces of polymers during sequential feeding, the black lines correspond to PLA homopolymer as the first block and the black to the PLA-*b*-PFVL copolymer.: (a) PLA₁₅-*b*-PFVL₁₅, (b) PLA₂₀-*b*-PFVL₃₀, (c) PLA₃₀-*b*-PFVL₃₀ and (d) PLA₅₀-*b*-PFVL₅₀.

6. Critical micelle concentration (CMC) measurement

The CMC of the copolymer was measured using pyrene as a fluorescent probe.³ 10.14 mg (0.05 mmol) pyrene was dissolved in acetone and diluted to 250 mL with a volumetric flask. 0.1 mL of a pyrene stock solution was evaporated in a 10-mL volumetric flask under room temperature overnight. Then 10 mL aqueous solution with concentration in the range from 10.4 mg/L to 130.0 mg/L were added to each pyrene-containing volumetric flask respectively. Then the solutions were allowed to stand at room temperature for 24 h. Then the spectra were recorded in the 340–500 nm wavelength range with an excitation wavelength of 339 nm. The emission of the first (I_1 , 373 nm) and third (I_3 , 384 nm) vibronic bands were measured. All fluorescence measurements were carried out at 25.0 °C. The CMC was given by the copolymer concentration of the inflection point in the plot of pyrene I_1/I_3 ratio as a function of the concentration of the copolymer.

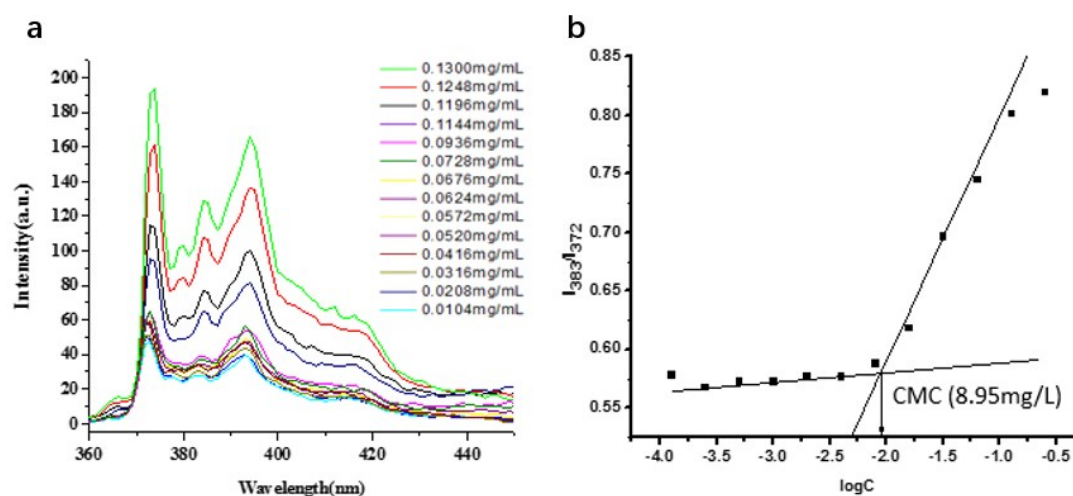


Figure S3. Determination of CMC of PLA₂₀-*b*-PFVL₃₀: (a) Fluorescence emission of pyrene as a function of the concentration of the copolymer; (b) Plots of pyrene I_1/I_3 ratio as a function of the concentration of the copolymer.

7. Micelle preparation

1 mg diblock polymer obtained from evaporation of 60 μL stock solution (16.6 mg/L in methylene chloride) was dissolved with 5 mL acetonitrile in a 25 mL round bottom flask. Acetonitrile was then removed by rotary evaporation at 40 $^{\circ}\text{C}$ *in vacuo* and further dried under high vacuum overnight to form a transparent film on the wall of the flask. Then the resulting polymer film was fully dissolved with 5 mL of ultrapure water at 60 $^{\circ}\text{C}$ to form a clear micelle solution which were filtered through a 0.45 μm membrane before DLS analysis.

8. The result of DLS

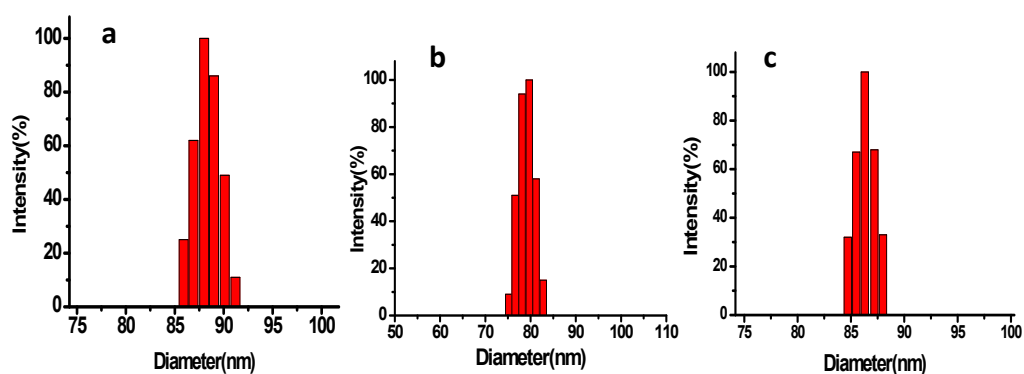


Figure S4. Size distribution of PLA₂₀-b-PFVL₃₀ in 1(a), 8 (b) and 20 days (c).

9. SEM measurements

For SEM, 10 μL of micelle solution was deposited on a clean aluminum foil, and water is allowed to evaporate. A thin layer of gold is coated onto sample prior imaged with a Hitachi (FESEM, S-8010) SEM at an accelerating voltage of 10 kV.

10. References

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