Electronic Supplementary Information (ESI)

Tuned Chromic Process for Polydiacetylenes Vesicles: the Influence of Polymer Matrices

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Materials

10,12-pentacosadiynoic acid (PCDA) was purchased from Sigma-Aldrich. *N*-isopropylacrylamide (NIPAm) was purchased from ACROS and recrystallized from hexane before use. *N*,*N*'-methylenebisacrylamide (BIS) from ACROS and *N*,*N*,*N*',*N*'-tetramethylethlenediamine (TEMED) from Sigma-Aldrich were used as received. Ammonium persulfate and chloroform were purchased from Beijing Chemical Co. Deionized water was purified with a Milli-Q system.

Preparation of PPCDA Vesicle Dispersion in Water

10,12-pentacosadiynoic acid (PCDA) was dissolved in chloroform and filtered through a 0.2 μm syringe filter to remove polymerized monomers and rotary evaporated to dryness. Then, 20 mL of deionized water was added to give the desired concentration of vesicles (1 mM). The suspension was heated to 70 °C and sonicated, and then it was allowed to cool to room temperature and kept at 4 °C overnight. Before polymerization, the dispersion was bubbled by N_2 for about 20 min, and then irradiated with UV light (254 nm) to yield a blue colored dispersion. Following the polymerization, the dispersion was filtered through a 0.2 μm syringe filter to remove any undesired aggregate formed during the preparation.

Preparation of PNIPAm Hydrogel

Poly(*N*-isopropylacrylamide) (PNIPAm) hydrogel was prepared by free radical polymerization. Typically, 200 mg *N*-isopropylacrylamide (NIPAm) monomer and 10 mg *N*,*N*'-methylenebisacrylamide (BIS) as a crosslinker were dissolved in 8 mL of deionized water and N_2 was bubbled into the solution for 20 min to remove dissolved oxygen. Then 2.4 mg ammonium persulfate (APS) as an initiator and 20 μL *N*,*N*,*N*',*N*'-tetramethylethlenediamine (TEMED) as an accelerator were mixed with the solution to start the polymerization. The polymerization was carried out for 24 h at room temperature. Then the hydrogel was immersed and washed in an excess of deionized water. The water was replaced every 12 h to remove the residue of unreacted components and the washing was continued for at least 7 days.

Immobilization of PPCDA Vesicles in PNIPAm Hydrogel (PPCDA/PNIPAm Hydrogel)

The as-prepared PNIPAm hydrogel was heated to 70 °C and then in the vacuum oven at 50 °C for several hours to get the PNIPAm dry gel. The dry gel was milled to powder. To immobilize PPCDA vesicles in PNIPAm hydrogel, 0.023 g milled dry gel was mixed with 0.8 mL PPCDA vesicle dispersion and was used after fully swelled for several days.

Instruments

UV light was generated by GY-11 high pressure Hg lamp (100 W, Tianjin Gangdong Co.). A Shimadzu (Tokyo, Japan) UV-2100S UV–vis spectrophotometer was used for the measurement of the UV–vis spectra. To get spectra of PPCDA/PNIPAm hydrogel at different temperatures, the sample was heated at certain temperature for 1 h, then cooled to room temperature for at least 24 h, making sure the gel was fully swelled before UV–vis measurements, since the color transition of PPCDA here is irreversible, proved

by preliminary experiment (not shown). Raman spectra were carried out by using a RM 2000 microscopic confocal Raman spectrometer (Renishaw PLC, England) employing a 633 nm laser beam and a CCD detector with 4 cm^{-1} resolution. A TMS94s cell set made by Linkam Scientific Instruments Ltd controlled the temperature of the samples. Calorimetric data were obtained with a differential scanning calorimeter DSC821e (Mettler-Toledo Co., Switzerland). Scanning electron microscopy (SEM) images were acquired on a field emission (FE) scanning electron microscope (JEOL JSM-7401 F) operated at 1.0 kV.

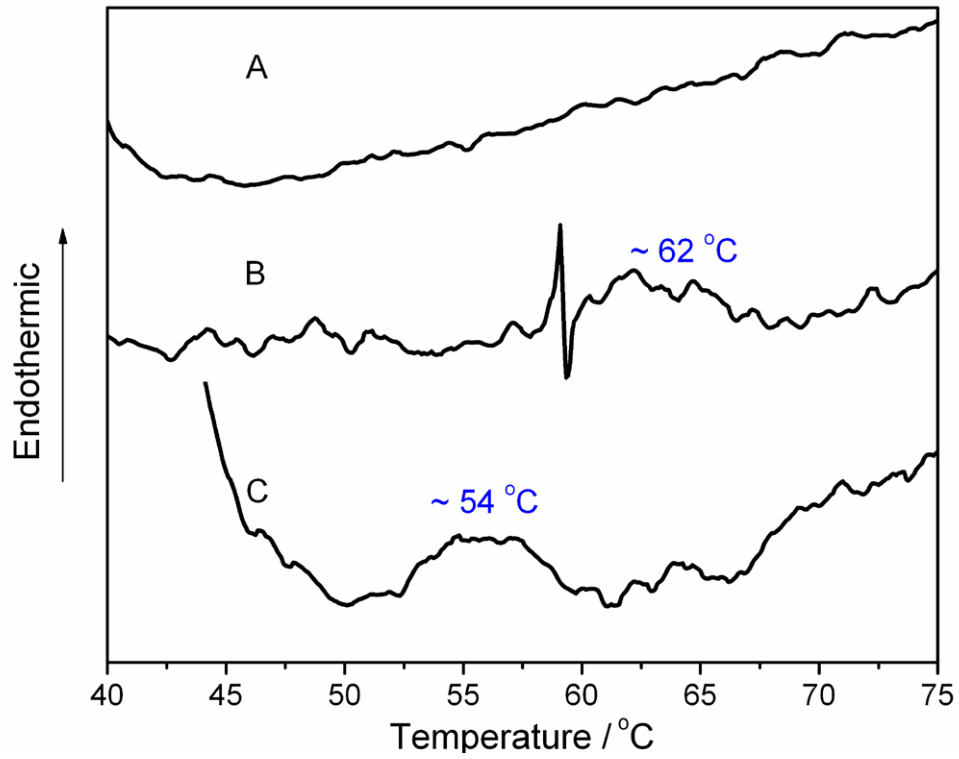

Fig. S1 DSC thermograms of (A) PNIPAm hydrogel, (B) PPCDA vesicle dispersion and (C) PPCDA/PNIPAm hydrogel from 40 °C to 75 °C with a scanning rate of 5 °C/min under N_2 atmosphere. No obvious peak for PNIPAm hydrogel was observed. The peaks for PPCDA vesicle dispersion appeared at about 62 °C and shifted to about 54 °C for PPCDA/PNIPAm hydrogel, which demonstrated the decreased temperature of blue-to-red phase transition for PPCDA/PNIPAm hydrogel. All these are accordant with the UV-vis, C.R. and photograph data. (Noise peaks around 59 °C of plot B.)

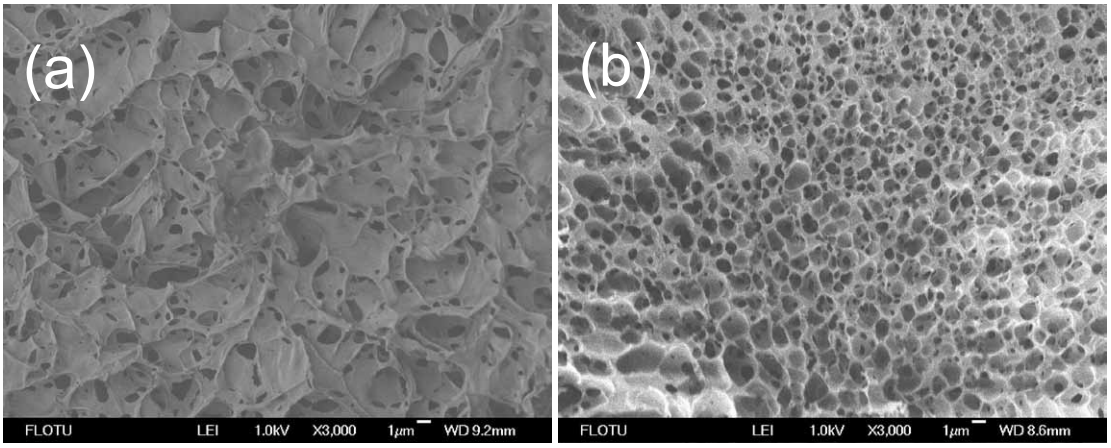

Fig. S2 SEM images for PPCDA/PNIPAm hydrogel (a) swollen in water at 20 °C and (b) shrunk at 50 °C. The size of porous structures was about 5 μm for its swollen state and smaller than 1 μm for its shrunk state.

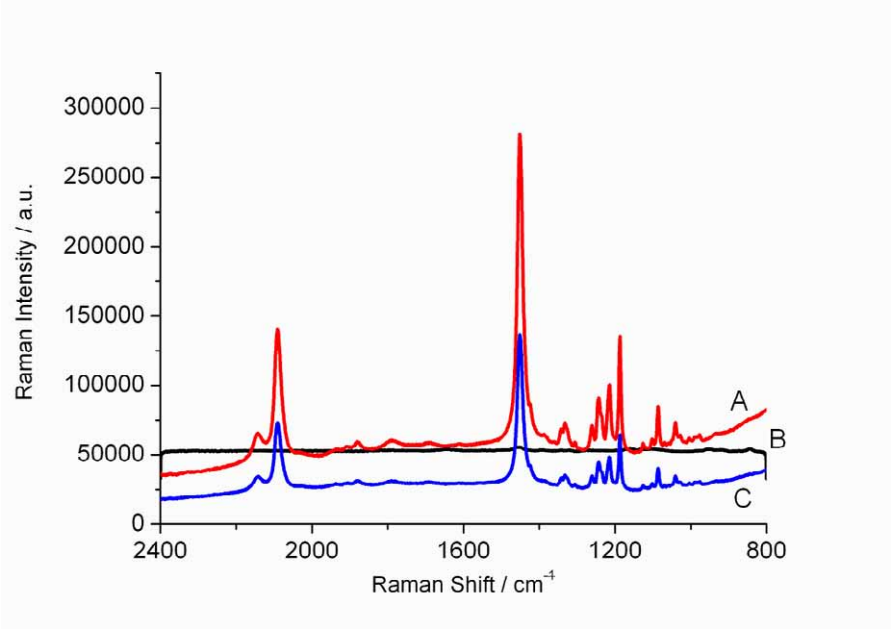

Fig S3. Raman spectra of (A) PPCDA vesicle dispersion, (B) PNIPAm hydrogel and (C) PPCDA/PNIPAm hydrogel at 23 °C. The excitation wavelength was 633 nm.