## Supporting Information

## Large-Scale Fabrication of Polymer Ellipsoids with Controllable Patches via Viscosity-Induced Deformation of Spherical Particles

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## **Experimental section**

**Materials.** Styrene (St, 99%, Shanghai Shan Pu Chemical Co. Ltd.), glycidyl methacrylate (GMA, 95%, Sartomer Company) and divinyl benzene (DVB, 95%, J&L Scientific Ltd.) were distilled under reduced pressure and refrigerated for spar. Azobisisobutyronitrile (AIBN, Shanghai mountain pu chemical co., Ltd.) was purified by recrystallization in methanol solution. Polyvinylpyrrolidone (PVP, BASF Co.), sodium dodecyl sulfate (SDS, Sinopharm chemical reagent co., Ltd.), dibutyl phthalate (DBP, Tianjin bo di chemical co., Ltd.) and anhydrous ethanol (Sinopharm chemical reagent co., Ltd.) were used directly without further purification. Stearic acid and 1-dodecanethiol were obtained from Sinopharm chemical reagent co., Ltd. Deionized water was produced by an apparatus for pharmaceutical purified water (Aquapro Co. Ltd.).

**Preparation of PGMA ellipsoids by RAFT PVP-dispersion polymerization.** 2.0 g of PVP was dissolved in the mixture of 50 mL methyl alcohol and 20 mL water in a 100 mL three-neck round-bottomed flask. Subsequently, AIBN (0.08 g) dissolved in 12.0 g of GMA and 0.2 g of DDMAT was added to the above system. The polymerization system was heated to 70°C and kept for 24 h. The obtained product was washed by centrifugation with ethanol for one time and water for two times, and dried by vacuum freeze-drying for 12 h.

**Preparation of PGMA particles with different CTAs.** The process was the same with the above mentioned. But DDMAT was replaced by Stearic acid or 1-dodecanethiol. The cross-linked PGMA particles were prepared by the addition of 1%

of DVB in the monomer.

**Fabrication of PGMA/PSt patchy ellipsoids via RAFT double-speed seeded emulsion polymerization.** A typical procedure was as follows. First, 0.5 g of PGMA ellipsoids was dispersed in the 50 mL aqueous solution with 2.5 wt% SDS under magnetic stirring. Then, 1.5 g swelling agent DBP and 1.5 g styrene monomer were added, and the swelling was performed at 40°C for 24 h. Subsequently, 1.0 g of styrene dissolved with 0.02 g of AIBN was added into the above swollen seed emulsion. After being purged with nitrogen for 30 min, the system was immerged in the water bath at 70°C for 8 h. The product was washed by centrifugation with ethanol for one time and water for two times, and dried by vacuum freeze-drying for 12 h.

**Characterization.** *OM* (Optical Microscope). The morphology and microstructure of prepared ellipsoids could be directly observed by metallographic microscope (DMM 300C). 1.0 mg/mL of the sample under ultrasonic dispersion was put on the slide to observe their morphology on the objective table. The sample was dispersed in purified water.

*FTIR* (Fourier Transform Infrared Spectroscopy). FTIR spectra were acquired on a TENSOR27 FTIR spectrometer (Bruker). The sample on the tabulating machine was pressed into sheets.

*XPS* (X-ray Photoelectron Spectroscopy). The XPS spectra were measured at a 90° takeoff angle using an AXIS Ultra DLD spectrometer (Kratos Analytical Co. Ltd. UK) equipped with a 300 W monochromatic Al K $\alpha$  X-ray source. The binding energy was referenced to the C 1s line at 284.7 eV from adventitious carbon.

*NMR* (Nuclear Magnetic Resonance). NMR spectroscopy was carried out with a Bruker Avance 400 spectrometer for 1H using DMSO-d<sub>6</sub> and CDCl<sub>3</sub> as solvents at room temperature.

*SEM* (Scanning Electron Microscope).The morphology of the ellipsoids was observed by SEM (AMERY-1000B). The samples were coated on the conductive adhesive and sputtered with platinum by a JFC-1600 auto fine coater at a current of 20 mA for 3 min before examination.

*TEM* (Transmission Electron Microscopy). TEM was employed to investigate the internal structure of PGMA ellipsoids, which were carried out on an H-600 transmission electron microscope (Hitachi, Japan) at an accelerating voltage of 75 kV. The sample was embedded in epoxy resins, which polymerized at 70°C for 3 days. Then, after the sample was microtomed into ~100 nm thick ultrathin sections using a LKBV ultratome, they were collected on TEM grids and stained in RuO<sub>4</sub> vapor for 30 min for observation.



**Figure S1**. Characterization of DDMAT. (a) IF-IR spectrum, (b) <sup>1</sup>H NMR spectrum. (c)

OM image of PGMA ellipsoids.



**Figure S2. System variation of RAFT PVP-dispersion polymerization.** (a) The viscosity of dispersion system, (b) GPC trace of PGMA polymer ellipsoids, (c) particles aspect ratios changed with the polymerization time and (d) monomer conversions of RAFT PVP-dispersion polymerization.

Samples	RAFT (wt%)	M <sub>n</sub> (kg/mol)	M <sub>w</sub> (kg/mol)	PDI
PGMA	0.00	27.64	76.87	2.78
PGMA-RAFT	1.60	5.96	7.57	1.27

**Table S1.** Molecular weights and PDIs of PGMA particles prepared without and withRAFT agent.



Figure S3. RAFT PVP-dispersion polymerization of GMA with the cross-linking agent

of DVB. SEM (a) and OM (b) images of cross-linked PGMA particles.



**Figure S4.** Synthesis of PGMA/PSt patchy ellipsoids with controllable protrusions by adding different St. (a) 1.0 g, (b) 1.5 g and (c) 2.5 g.