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Supporting Information

Shape-Tunable Polymeric Janus Nanoparticles with Hollow Cavities Derived from Polymerization Induced Self-Assembly Based Crosslinked Vesicles

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Experimental section

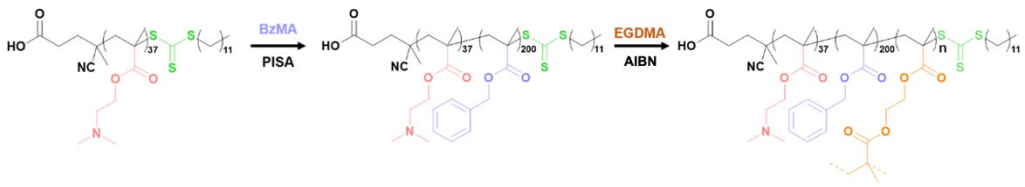
Materials

2-(Dimethylamino) ethyl methacrylate (DMA, Aladdin, 99%), benzyl methacrylate (BzMA, Aladdin, 99%), ethylene glycol dimethacrylate (EGDMA, Aladdin, 99%) and styrene (St, Aladdin, 99%) were passed through a neutral alumina column to remove the inhibitor and stored frozen prior to use. 2,2'-Azoisobutyronitrile (AIBN, Aladdin, 98%) was recrystallization from ethanol for purification. 4-Cyan-4-(dodecylsulfanylthiocarbonyl) sulfanylpentanoic acid (DTTCP, Chengdu Syns Medical Technology Co. Ltd.), ethanol (EtOH, Aladdin, 99.5%), tetrahydrofuran (THF, Aladdin, 99 %), chloroform-d ($CDCl_3$, Aladdin, 99.8%) and dichloromethane (DCM, Aladdin, 99%) were used as received.

Synthesis of PDMA-PBzMA$_{200}$-PEGDMA Copolymer Vesicles via Reversible Addition-Fragmentation Chain Transfer (RAFT)-PISA.

The $PDMA_{37}$ macro-CTA was synthesized as reported in our previous work.[11] Before the dispersion polymerization targeting $PDMA_{37}$-$PBzMA_{200}$-PEGDMA, $PDMA_{37}$ macro-CTA (0.37 g, 0.06 mmol), BzMA (2.11 g, 12 mmol) and AIBN (2 mg, 0.012 mmol) were dissolved in ethanol (9.93 g), and the solution was purged with N_2 for 30 min. The polymerization was conducted at 70 °C for 12 h, followed by injecting a pre-degassed solution of the EGDMA in ethanol into the milky reaction mixture in an N_2 atmosphere. Adequate amount of initiators were also refilled to the system at this stage due to the half-life. The reaction was continued for another 12 h before the polymer

vesicles were obtained via freeze-drying. BzMA conversion reached around 96%, as monitored by ^{1}H NMR. The EGDMA conversion was about 87 % which was determined by the weight difference. The crosslinking degree is defined as the molar ratio of EGDMA to BzMA in this work. Different crosslinking degrees (0 %, 5 %, 10 %, 15 %, and 20 %) of polymer vesicles were synthesized by adding varying amounts of EGDMA. The synthetic route of PDMA-PBzMA$_{200}$-PEGDMA via PISA is shown in Scheme S1.



Scheme S1 The synthetic route of PDMA-PBzMA$_{200}$-PEGDMA.

Preparation of JNPs via Seed Polymerization.

After dispersing polymer vesicles in 10 mL dispersion medium (water or EtOH/water mixtures) for 5 minutes under an ultrasound condition, AIBN (20 mg) and St (2 g) were added in and the mixture was allowed swelling for 90 min at room temperature with a stirring rate at 300 rpm. Then the secondary polymerizations of St with polymer vesicles as seeds was conducted at 70 °C for 10 h. JNPs with various mass ratio of St/vesicles (3/1, 5/1, 10/1, 20/1) were prepared.

Characterizations.

Dynamic light scattering (DLS, Zetazizer ZS90, Malvern, UK) was used to determine the average diameter of nanoparticles. The particle morphology was observed on transmission electron microscope (TEM, HT7700, Hitachi, Japan) operated at 120 kV. The TEM samples of nanoparticles were diluted to concentrations of 0.1~0.5 % in deionized water and stained by uranyl acetate dehydrate before TEM observation.

Supplementary figures

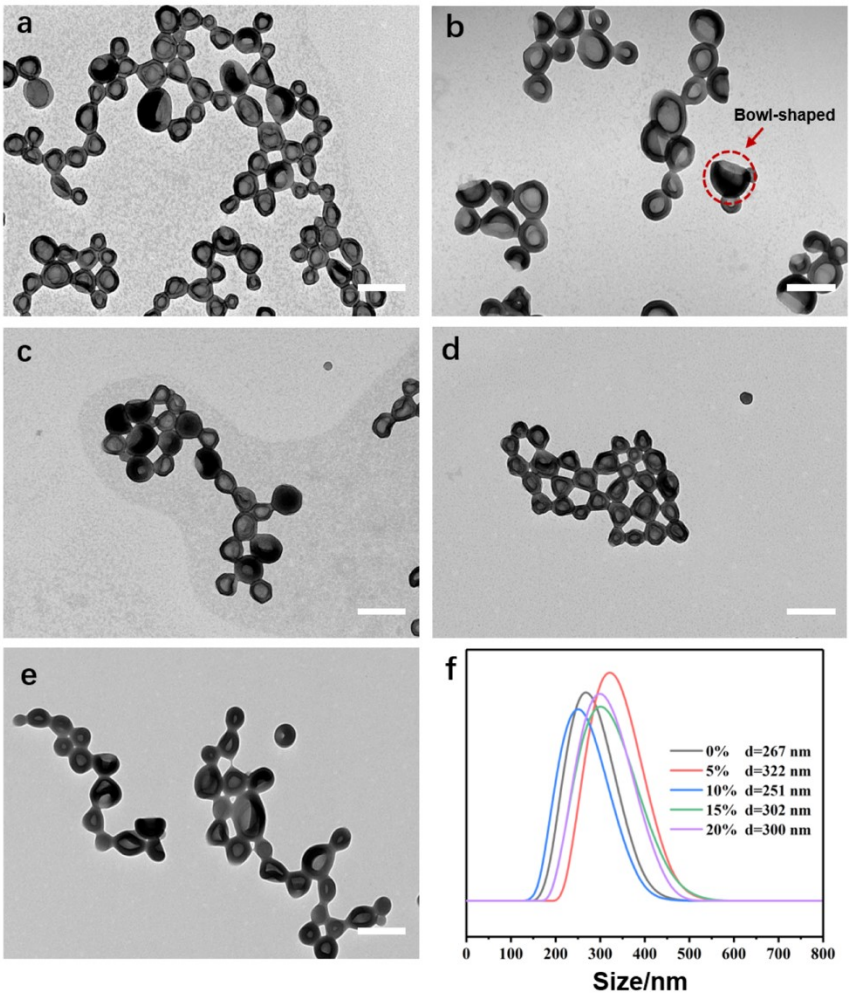


Fig. S1 TEM images of PDMA-PBzMA$_{200}$-PEGDMA copolymer vesicle seeds with crosslinking degree of (a) 0%, (b) 5%, (c) 10%, (d) 15%, (e) 20%. (Scale bar = 400 nm) (f) Corresponding size distributions of vesicle seeds with crosslinking degree from 0 to 20% obtained from the DLS measurement.

TEM images of the nano-scale PDMA-PBzMA$_{200}$-PEGDMA copolymer vesicle seeds with different crosslinking degrees are shown in Fig. S1. Hollow structures were clearly observed for all vesicle seeds. The average sizes of the vesicles measured directly from the TEM images with crosslinking degrees of 0, 5, 10, 15 and 20 % were 221 ± 13, 247 ± 17, 206 ± 10, 203 ± 8 and 227 ± 9 nm, respectively. These results were slightly lower than the data measured from dynamic lights scattering (DLS) (Fig. S1 f), which were measured from fully swollen vesicles in the ethanol solution. As can be seen, the crosslinking degree did not affect the vesicle size significantly. Some interesting bowl-shaped vesicles were found in the TEM images. Optimized uniformity of the copolymer vesicle seed was obtained when the crosslinking degree was 15% (Fig. S1 d).

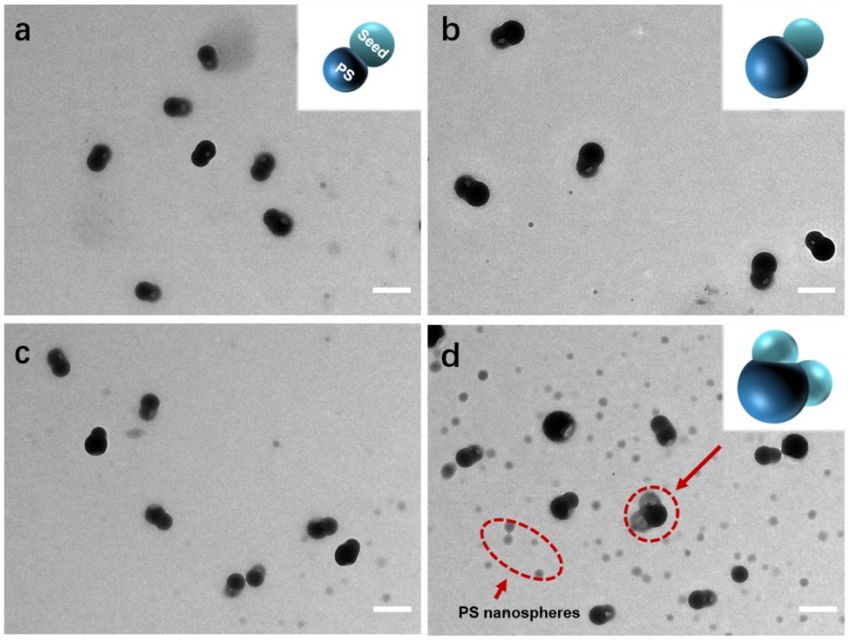


Fig. S2 TEM images of JNPs prepared by using 15% cross-linked PDMA-PBzMA$_{200}$-PEGDMA copolymer vesicle seeds with a swelling ratio (mSt/mVesicle) of (a) 3, (b) 5, (c) 10 and (d) 20. All reactions were performed in an aqueous condition. (Scale bar = 400 nm)

Changing the swelling ratio was considered as a direct method in controlling the lobe size ratios of JNPs in previous studies. Since the most uniform vesicles were obtained with a crosslinking degree of 15% in this study, vesicle seeds prepared in the same batch with a 15% cross-linking degree were employed to investigate the effect of different swelling ratios ($m_{St}/m_{Vesicle}$=3, 5, 10, 20) on the morphologies of JNPs. The TEM images of the prepared particles are shown in Fig. S2. Basically, all particles have two lobes with distinct shades. As can be seen in Fig. S2 a, symmetrical "dumbbell-shaped" JNPs were obtained when the swelling ratio was equal to 3. Starting with the swelling ratio equals to 3 instead of a less number was mainly due to the hollow structure of the seed: the vesicle needs much less mass to form a similar volume compared to a dense PS lobe. Tiny PS protrusions were observed when the swelling ratio was lower than 3.

The volume of the generated protrusions became larger than the seed when the swelling ratio increased to 5 (Fig. S2 b). Interestingly, no significant size change was observed when the swelling ratio was increased from 10 to 20 (Fig. S2 c and d), which may indicate the existence of a maximum swelling ratio. The maximum swelling ratio limits the achievable protrusion size of these JNPs. More nanospheres appeared at higher swelling ratios, revealing the unswollen styrene began polymerizing outside the seed vesicles when the maximum swelling ratio was reached. In addition, two-patch particles were also observed, which indicates the PS protrusion of two individual snowman-like JNPs bumped into each other and got stuck after the polymerization (Fig. S2 d).