## Supporting Information for:

## **Polymer Patchy Colloids with Sticky Patches**

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**Fig. S1** Chemical structures of the monomers, initiators, and polymers mentioned in this study: **a**) dodecyl methacrylate (DMA); **b**) 1,4-divinylbenzene (DVB); **c**) azobisisobutyronitrile (AIBN); **d**) potassium persulfate (KPS); **e**) 2,2-dimethoxy-2-phenylacetophenone (DMPA); **f**) poly(dodecyl methacrylate) (PDMA); **g**) poly(vinyl formal) (PVF).



**Fig. S2** <sup>1</sup>H NMR spectra of the dispersion (Entry 7 in Table 1) diluted in DMSO- $d_6$  after polymerizing at different times. Xylene (7.02~7.16 ppm) was used as the external standard while the arrows showing the integral of protons near carbon-carbon double bond (6.0 ppm and 5.66 ppm) in DMA decreased with reaction time.



**Fig. S3** Cross-section TEM micrographs for PPs (Entry 1 of Table 1) showing the core-shell structure of PPs and two distinct phases on the particles surface. The scale bars represent 200 nm.



**Fig. S4** SEM micrograph of the obtained PVF/PDMA nanoparticles showed that there was no multiple patches on particle surface when the photo-induced polymerization was carried out at room temperature.



**Fig. S5** SEM micrographs of PVF nanoparticles with different DMA contents (wt.% compared to the total amount of monomers) before polymerization: **a**) 10% (Entry 5 in Table 1); **b**) 20% (Entry 6 in Table 1); **c**) 40% (Entry 7 in Table 1); **d**) 60% (Entry 8 in Table 1). The scale bars represent 500 nm.



**Fig. S6** SEM micrographs of PVF nanoparticles (Entry 9 in Table 1) prepared with a DMA content (wt.% compared to the total amount of monomers) of 80% **a**) before, and **b**) after polymerization. The scale bars represent 500 nm.



**Fig. S7** SEM micrographs of PPs (Entry 6 of Table 1) annealed at 90 °C in water for different times: **a**) 0 h; **b**) 1 h; **c**) 2 h; **d**) 3h. The scale bars represent 500 nm.



Fig. S8 DSC curves of PPs powder (Entry 1 in Table 1) before annealing and after annealing at 120 °C for 24 h.



**Fig. S9 a)** SEM micrographs and **b)** AFM phase image of the crosslinked PPs (Entry 10 of Table 1, 15 wt.% DVB). The patchy domains could not be easily identified from the phase image when the initial amount of DVB was 15 wt.%.