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# **Supporting Information**

# One-step Formation of Multiple Pickering Emulsions Stabilized by Selfassembled Poly(dodecyl acrylate-*co*-acrylic acid) Nanoparticles

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#### 1. Materials

Acrylic acid (AA) (Sinopharm Chemical Reagent Co., Ltd. (SCRC), Shanghai, China) were purified by vacuum distillation and store at 4 °C prior to use. Dodecyl acrylate (DA) (J&K Scientific Ltd., Shanghai, China) were eluted through an alkyl AL<sub>2</sub>O<sub>3</sub> column prior to use. 2, 2'azobis-isobutyronitrile (AIBN, SCRC, Shanghai, China) and 2, 2'-azobis-isoheptonitrile (V65, SCRC, Shanghai, China) were recrystallized twice from methanol before use.

#### 2. Synthesis of poly(dodecyl acrylate-co-acrylic acid) (PDAA)

Random copolymers poly(dodecyl acrylate-co-acrylic acid) (PDAA) were synthesized through the free radical copolymerization using dodecyl acrylate (DA) and acrylic acid (AA)as monomers, and 2, 2'-azobis-isobutyronitrile (AIBN) as the initiator. Briefly, DA, AA monomer (at the molar ratio of 1:1, 1:2 and 1:3), initiator AIBN (2 % of the total molar weight of monomers) and 10 mL 1,4-dioxane were charged into a 50 mL round bottom flask with a stirring bar. The flask was degassed by three freeze-evacuate-thaw cycles and sealed under vacuum. Then, the reaction mixture was stirring at 65 °C in an oil bath for 24 h. The obtained copolymer was isolated by pouring the reaction mixture into an excess amount of petroleum ether, and further purified by repeated precipitation for three times. The finally products were dried under vacuum at room temperature for 48 h. In this study, by changing the feed ratio between DA and AA monomers, PDAA with the DA molar content of 44%, 33% and 25% were prepared, as shown in Table S1. The chemical structure of PDAA was analyzed by GPC and <sup>1</sup>H NMR. The molar ratio between DA and AA units was determined through comparison of the integrals of the methylene proton (1.22 ppm,  $CH_2(CH_2)_{10}CH_3$ ) of DA to the proton of carboxyl group (12.02 ppm, COOH) of AA, as shown in Fig. S1.

Sample	Feed Ratio	Yield	DA <sup>a</sup>	$M_{ m n}  imes 10^{4   m b}$	$M_{ m n}/M_{ m w}^{ m b}$	Size of NPs <sup>c</sup>	PDI °
	DA:AA	(%)	(mol%)	(g/mol)		(nm)	
PDAA0.44	1:1	73	0.44	2.72	2.06	$305 \pm 10$	$0.18\pm0.03$
PDAA0.33	1:2	69	0.33	1.58	1.97	$90\pm 8$	$0.13\pm0.02$
PDAA0.25	1:3	80	0.25	2.39	2.28	$43 \pm 12$	$0.12 \pm 0.08$

Table S1. Synthesis of PDAA copolymers.

<sup>a</sup> The molar content of DA were estimated by <sup>1</sup>H NMR;

<sup>b</sup> The molecular weight and polydispersity of PDAA were measured by GPC using DMF as the eluent solvent;

<sup>c</sup> The size and PDI of PDAA micelles were measured at 0.5 mg/mL with 0.01 mM NaCl at the original pH  $5(\text{mean} \pm \text{SD} \text{ of three independent experiments is shown}).$ 



Fig. S1. The <sup>1</sup>H NMR spectrum of PDAA0.44.



Fig. S2. The IR spectra of PDAA0.25, PDAA0.33, and PDAA0.44.

## 3. The self-assembly behavior of PDAA with different DA content



Fig. S3. CWC values of thePDAA0.25, PDAA0.33, and PDAA0.44copolymers. All the initial concentration of copolymer solutions were 2 wt.% in DMF.

#### 4. Three-phase contact angle measurement of PDAA0.44 nanoparticles

Pendant water drop contact angle measurements were carried out in a quartz-cell, filled with paraffin oil. The PDAA0.44 nanoparticles powder sheets substrates were submerged in the quartz cell. A drop of water at various pH values was dripped on the substrate, and images were taken after the drop spread and reached equilibrium. Contact angle was measured by an OCA15EC contact angle measurement instrument (Data physics Ltd., German).Reported values are an average of 3 times measurement. The reported contact angles are always measured through the oil phase.



Fig. S4. Three-phase contact angle of PDAA0.44 nanoparticles against aqueous solution with various pH values.

5. Emulsification performance of PDAA0.44 nanoparticles at various pH value



Fig. S5. Emulsifying performance of PDAA0.44 nanoparticles at different pH value: (a) and (b) are the digital photos of the emulsions placed for 1 day and 4 months, respectively. The concentration of nanoparticles aqueous dispersion was 2 mg/mL.

6. Emulsification performance of PDAA0.44 nanoparticles at various salinity



Fig. S6. Emulsifying performance of PDAA0.44 nanoparticles at different salt concentration: (a) the digital photos of the emulsions, and (b) optical microscopy images of emulsion droplets. The concentration of nanoparticles aqueous dispersion was 2 mg/mL at pH 5.5. The digital and optical microscopy images were taken at 24 h after homogenization.