Electronic Supplementary information for

Stabilizing oil-oil interfaces with mixed-shell polymeric nanoparticles prepared by PISA and the grafting combination

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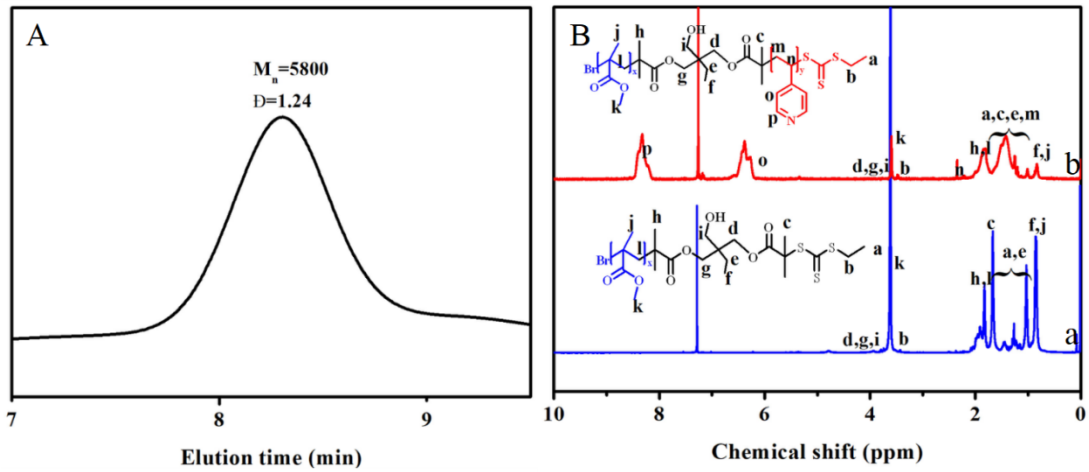

Fig. S1. (A) GPC traces of $PMMA_{24}$-CTA; (B) Typical ^1H NMR spectra of PMMA-CTA and PMMA-*b*-P4VP copolymers recorded in $CDCl_3$

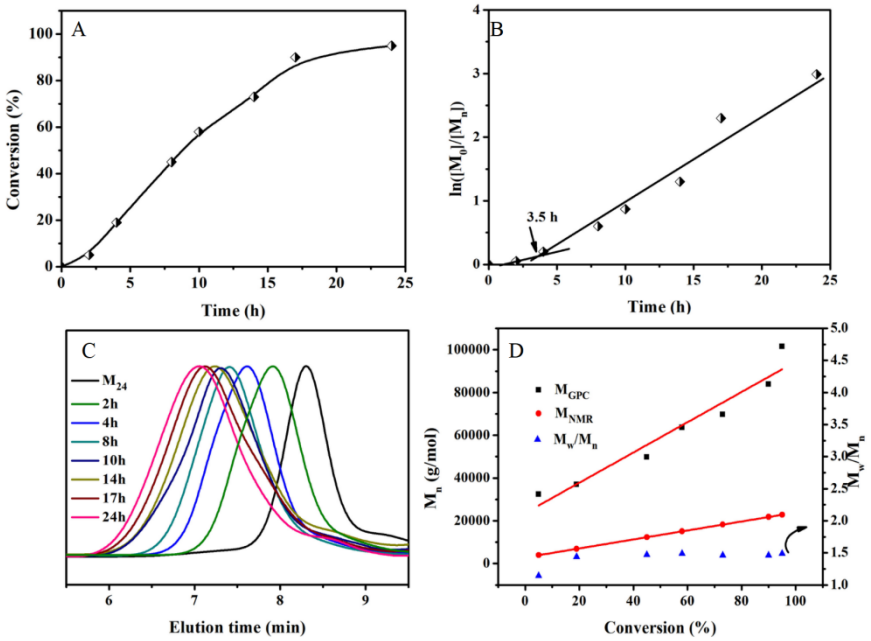

Fig. S2. (A) Monomer conversion vs. time plot; (B) $ln([M]_0/[M])$ vs. time plot for RAFT dispersion polymerization of 4VP mediated by $PMMA_{24}$; (C) GPC traces of $PMMA_{24}$-*b*-$P4VP_x$ copolymers with different DPs of P4VP block; (D) Mns and dispersities of $PMMA_{24}$-*b*-$P4VP_x$ copolymers; Polymerization reaction conditions: $[4VP]_0/PMMA_{24}/[AIBN]_0$ = 1000/5/1; Temperature: 65 °C; Solid content: 20 wt% (w/w)

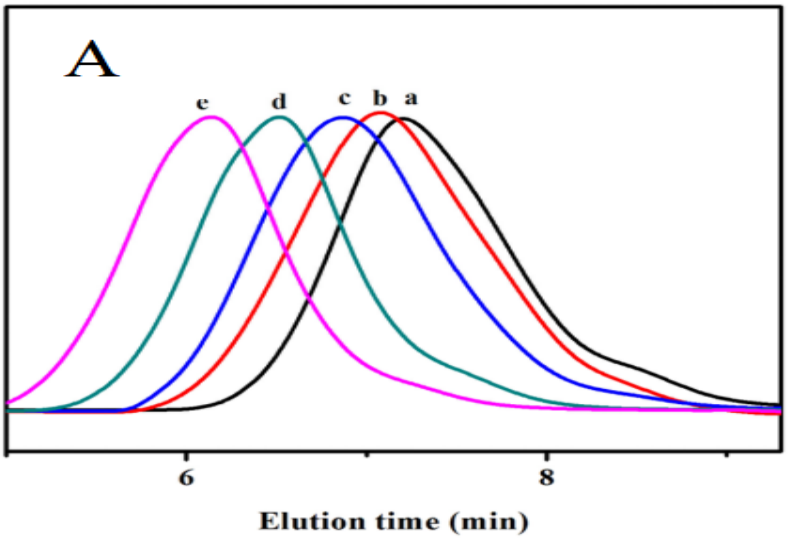

Fig. S3. (A) GPC traces of $PMMA_{24}$-*b*-$P4VP_x$ copolymers with different DPs of P4VP block (a: x = 270; b: x = 376; c: x = 450; d: x = 510; e: x = 900)

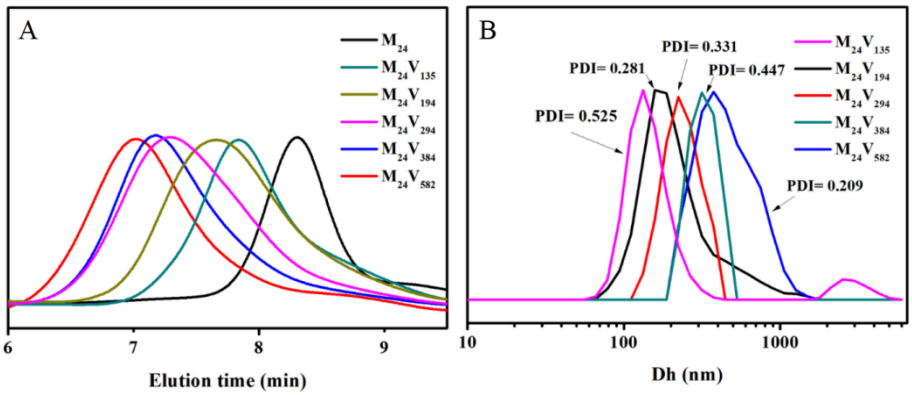

Fig. S4. (A) GPC traces of $PMMA_{24}$-*b*-$P4VP_x$ copolymers with different DPs of P4VP block produced at 30 wt% solid; (B) DLS traces of $M_{24}V_x$ with different DPs of P4VP block at 30 wt% solid

Table S1. The summarized results of linear $PMMA_{24}$-$P4VP_x$ block copolymers and nanoparticles prepared by $PMMA_{24}$-CTA mediated dispersion polymerization of 4-

VP at different conditions

Targeted DP (P4VP block)	Solid wt%	*Conv.* (%)	*calc.* DP (P4VP block)	$M_{n,NMR}$ (PMMA-P4VP)	W_{philic}	Morph. [a]
300	10	97	291	33443	0.073	S
400	10	98	393	44153	0.055	S
500	10	93	465	51713	0.047	S
200	20	58	116	15068	0.203	S
200	20	73	146	18218	0.135	S
200	20	90	180	21788	0.113	W
200	20	95	190	22838	0.107	W
300	20	90	270	31238	0.078	W
500	20	90	450	50138	0.048	W
1000	20	92	920	99488	0.024	W
150	30	90	135	17063	0.145	S+V
200	30	97	194	23258	0.105	S+W+V
400	30	96	384	43208	0.056	V

[a] S: sphere; W: worm; V: vesicle.

S5. Evaluation of the hydroxyl reaction efficiency

The reaction efficiency of hydroxyl groups with $C_{18}NCO$ is roughly calculated according to the following equation:

$$\frac{\left(\frac{m}{M}-a\right)\times n\times 14+a\times(n+1)\times 14}{m+295.5\times a}=11.46\% \quad (1)$$

$$c=\frac{a}{m/M}\times 100\% \quad (2)$$

m is the weight of $M_{24}V_{180}$ polymeric samples, M is the average molecular weight of $PMMA_{24}$-*b*-$P4VP_{180}$, a is the supposed mole number of hydroxyl groups participating

the grafting reaction, n is the degree of polymerization of P4VP block of $PMMA_{24}$-b-$P4VP_{180}$ diblock copolymers, and c is the reaction efficiency of hydroxyl groups.

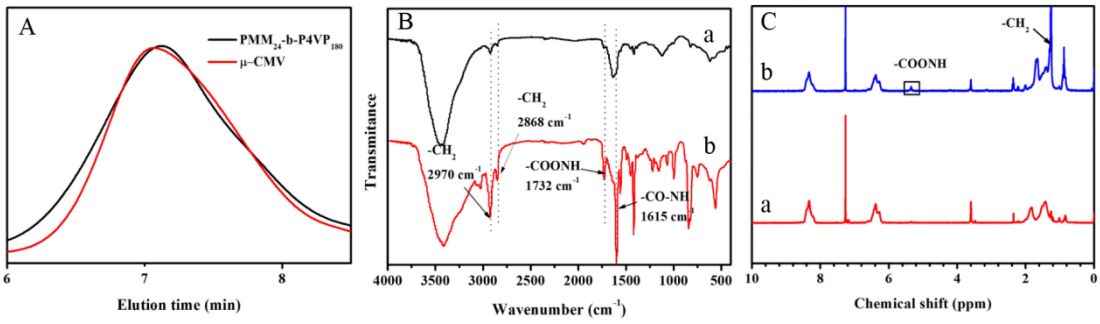

Fig. S6 (A) GPC traces of $PMMA_{24}$-b-$P4VP_{180}$ and μ-C_{18}-$PMMA_{24}$-$P4VP_{180}$ (μ-CMV) recorded in DMF; (B) FT-IR spectra of $M_{24}V_{180}$ worms before (a) and after (b) the grafting of C_{18} alkyl chains; (C) ^{1}H NMR spectra of $PMMA_{24}$-*b*-$P4VP_{180}$ (a) and μ-C_{18}-$PMMA_{24}$-$P4VP_{180}$ copolymers (b) recorded in *d*-$CHCl_3$;

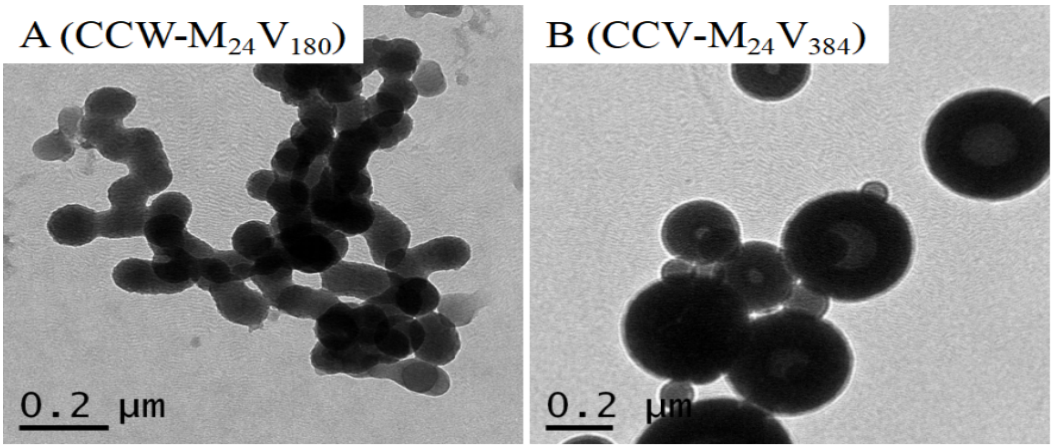

Fig. S7. Representative TEM images of CCW-$M_{24}V_{180}$ (A) and CCV-$M_{24}V_{384}$ (B) originated from their dispersions in DMSO

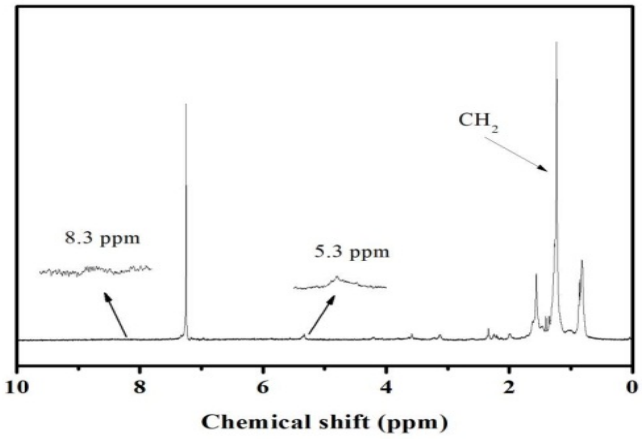

Fig. S8. ^{1}H NMR spectrum of CCW-$C_{18}/M_{24}V_{180}$ recorded in *d*-$CHCl_3$

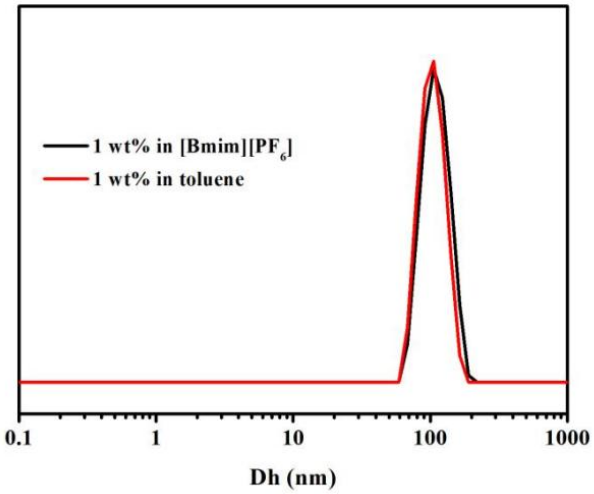

Fig. S9. DLS traces of $C_{18}/M_{24}V_{384}$-S nanoparticles dispersed in toluene and [Bmim][PF_6] at 1.0 wt%

S10. The preparation of $C_{18}/M_{24}V_{384}$-CCS

In a typical reaction, 5 mL of $C_{18}/M_{24}V_{384}$ toluene dispersion (containing 10 mg of $C_{18}/M_{24}V_{384}$ sample) and 15 mL of toluene were added into a 25 mL of round bottom flask. Then, 6 mg of DBB (0.03 mmol) was added. The mixtures were stirred at room temperature. After 24 h, the reaction was stopped. After the centrifugation, the supernatant was separated. The dispersion and the centrifugation operations were then

repeatedly conducted for three times. The resulting samples were re-dispersed in toluene.

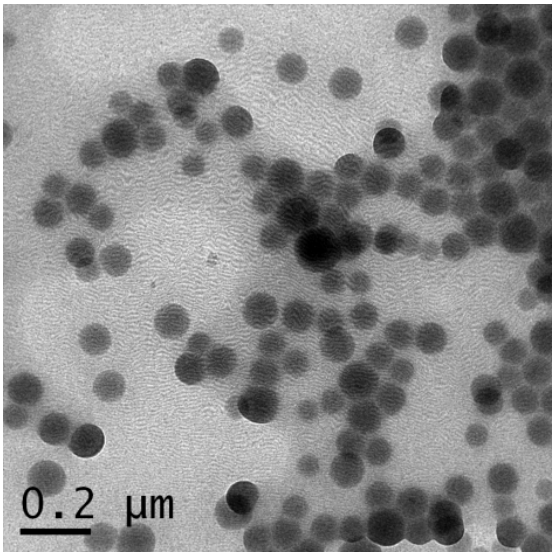

Fig. S10. Typical TEM image of **$C_{18}/M_{24}V_{384}$-CCS,** and TEM sample was prepared by depositing a drop of diluted DMSO suspension onto a carbon-coated copper grid

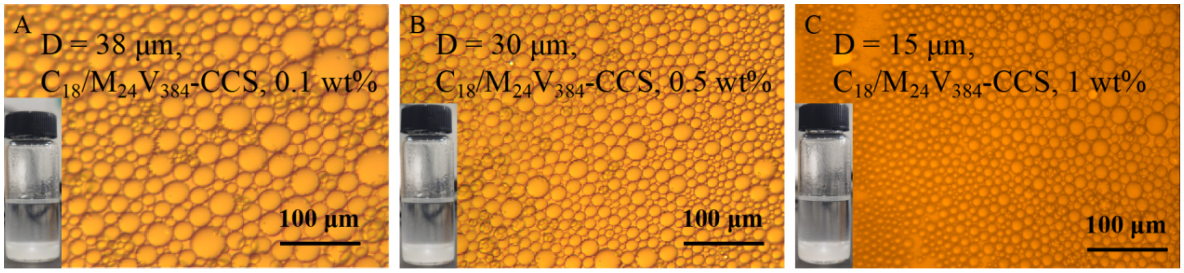

Fig. S11. Optical microscopy images and photographs of [Bmim][PF_6]-in-toluene Pickering emulsions stabilized by $C_{18}/M_{24}V_{384}$-CCS at different concentrations (A: 0.1 wt%; B: 0.5 wt%; C: 1 wt%)

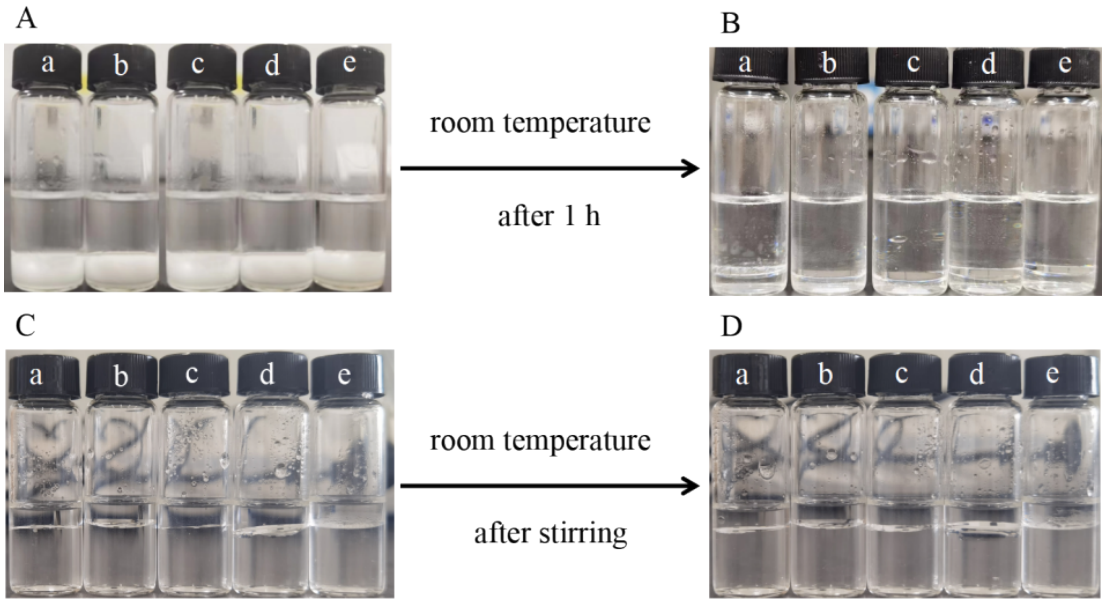

Fig. S12. Emulsifying results of [Bmim][PF_6]/toluene biphases in the presence of 0.5 wt% of CCW-$M_{24}V_{180}$, CCV-$M_{24}V_{384}$, $M_{24}V_{116}$, $M_{24}V_{180}$, $M_{24}V_{384}$; Polymeric nanoparticles were initially dispersed in either toluene (A, B) or [Bmim][PF_6] (C, D)

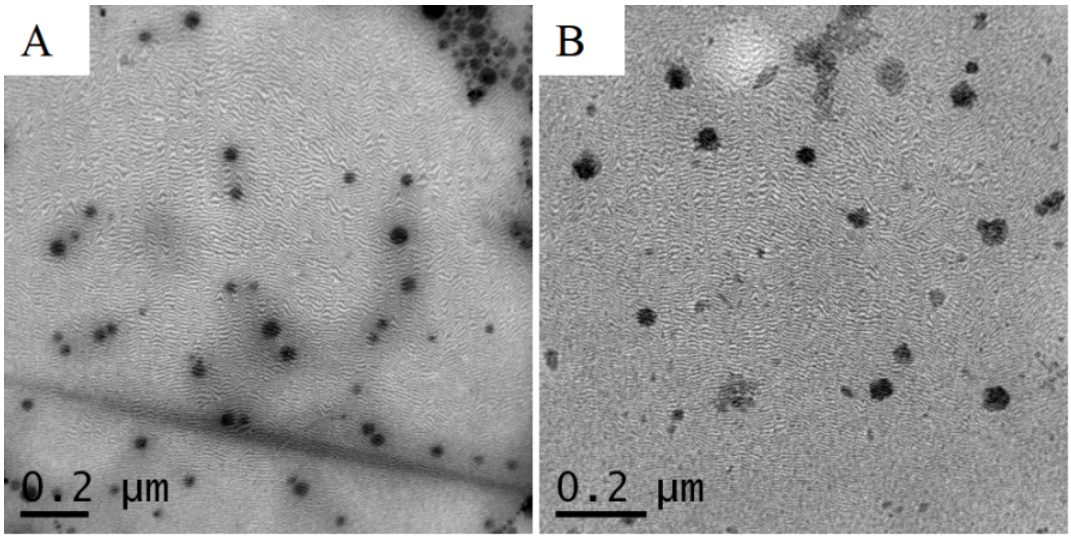

Fig. S13. TEM images of the initial $M_{24}V_{180}$ worms (A) and $M_{24}V_{384}$ (B) vesicles dispersed in toluene after 1 min of homogenization at 14000 rpm