Supplementary Information

Preparation of Core-Shell Nanoparticles *via* Emulsion Polymerization Induced Self-Assembly Using Maleamic Acid-α-Methyl styrene Copolymer as macro-inisurf

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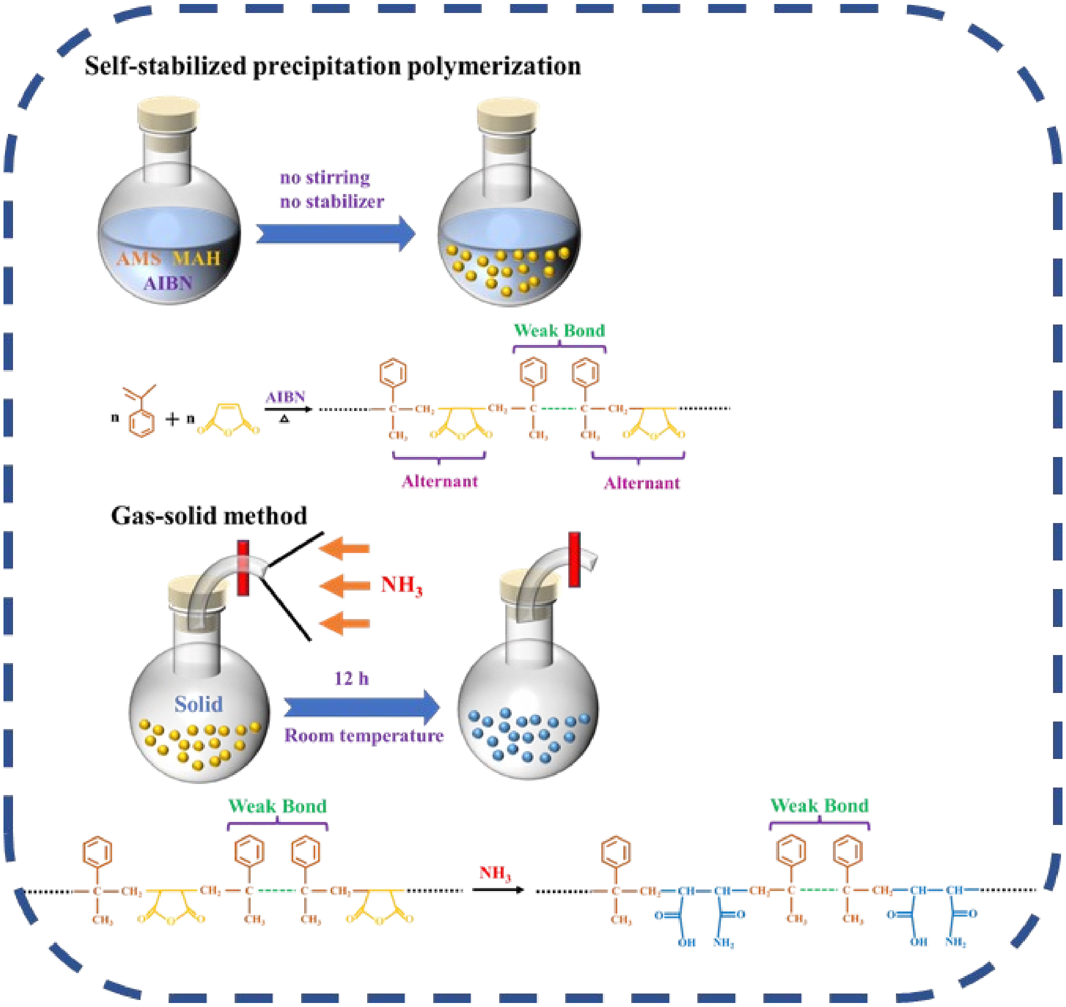

Scheme S1. Schematic illustration of the macro-initisurf prepared by AMS, MAH and NH_3.

Table S1 The formulations of emulsion PISA initiated by macro-initisurf.

Run	MAA-*alt*-AMS (g)	BA (g)	MMA (g)	Water (g)	$NH_3 \cdot H_2O$ (g)	Temperature (°C)
1	1.95	10.9	8.54	50	0.5	90
2	1.95	7.6	11.87	50	0.5	90
3	1.95	5.83	13.66	50	0.5	90
4	1.95	14.01	5.47	50	0.5	90
5	1.95	15.45	4.02	50	0.5	90

6	3.57	10.03	7.83	50	1	90
7	3.57	6.97	10.89	50	1	90
8	3.57	5.34	12.52	50	1	90
9	3.57	12.84	5.02	50	1	90
10	3.57	14.18	3.7	50	1	90
11	4.95	9.25	7.23	50	1.5	90
12	4.95	6.43	10.05	50	1.5	90
13	4.95	4.93	11.55	50	1.5	90
14	4.95	11.78	4.63	50	1.5	90
15	4.95	13.08	3.41	50	1.5	90
16	6.12	8.59	6.71	50	1.9	90
17	6.12	5.97	9.33	50	1.9	90
18	6.12	4.58	10.73	50	1.9	90
19	6.12	11.01	4.3	50	1.9	90
20	6.12	12.15	3.16	50	1.9	90
21	6.12	4.58	10.73	50	1.9	80
22	6.12	4.58	10.73	50	1.9	70
23	6.12	8.59	6.71	50	1.9	80
24	6.12	8.59	6.71	50	1.9	70
25	6.12	12.15	3.16	50	1.9	80
26	6.12	12.15	3.16	50	1.9	70
27	9.52	7.12	16.89	50	3	90
28	9.52	13.37	10.44	50	3	90
29	9.52	18.89	4.92	50	3	90
30	14.28	10.68	25.03	50	4.4	90
31	14.28	20.05	15.66	50	4.4	90
32	14.28	28.34	7.38	50	4.4	90

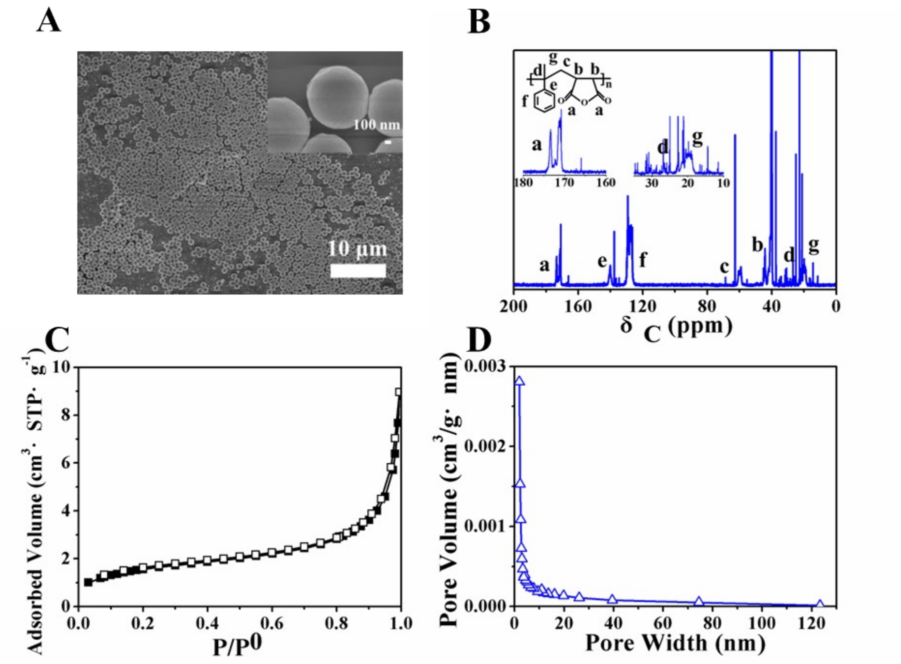

Fig. S1 (A) SEM images of MAH-*alt*-AMS microspheres, (B) ^{13}C NMR spectra of MAH-*alt*-AMS microspheres, (C) N_2 adsorption isotherms and (D) the pore size distribution of MAH-*alt*-AMS microspheres.

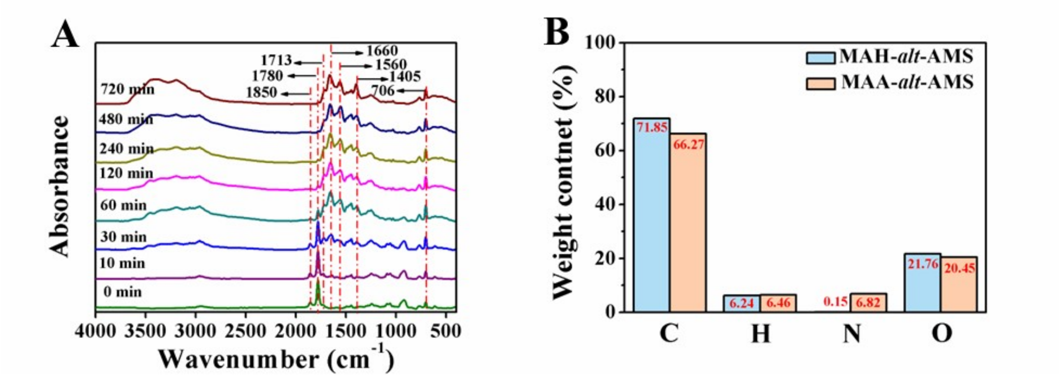

Fig. S2 (A) FTIR spectra of MAH-*alt*-AMS at different time intervals during gas-solid reaction and (B) weight content of different elements in MAH-*alt*-AMS and MAA-*alt*-AMS.

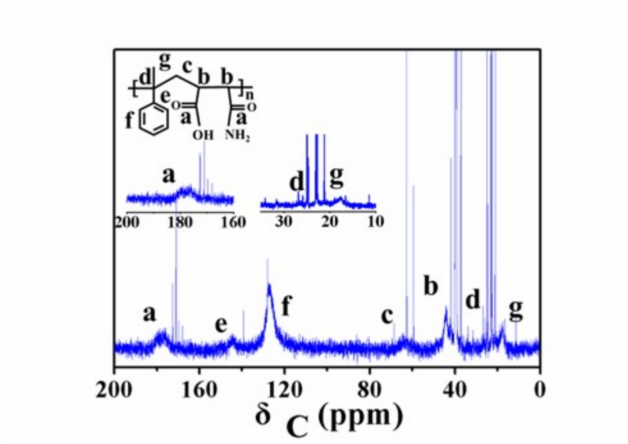

Fig. S3 ^{13}C NMR spectra of macro-initisurf.

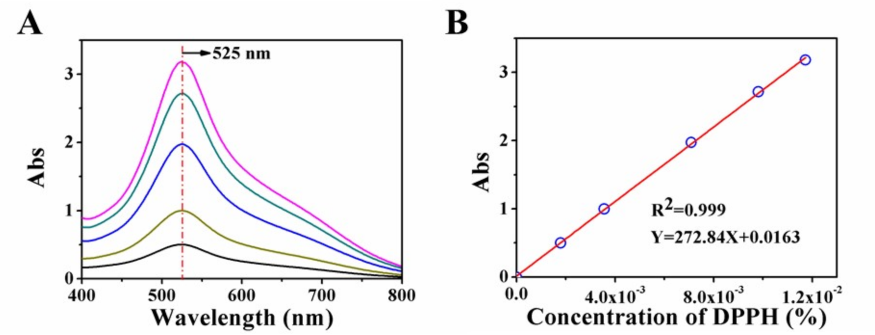

Fig. S4 (A) UV-vis absorption spectrum of DPPH-DMSO, and (B) the relation curve that absorbance at 525 nm varies with DPPH concentration.

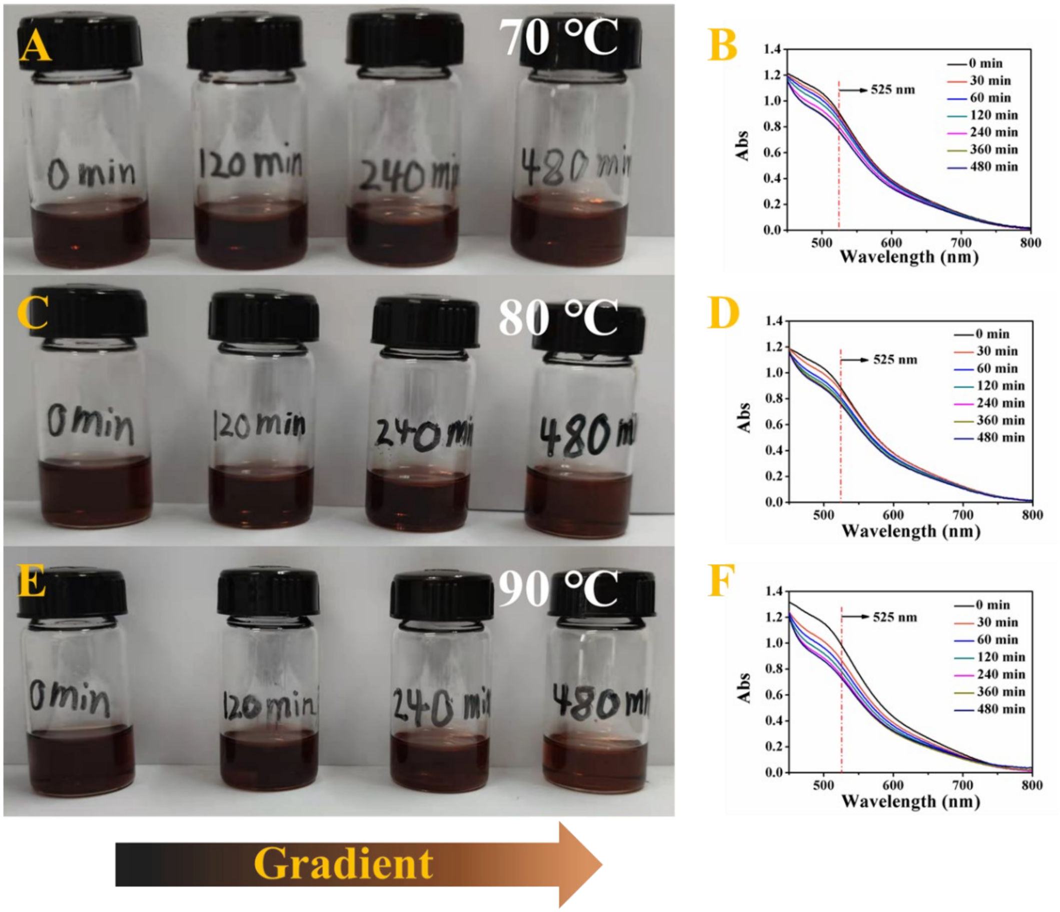

Fig. S5 The photos of mixture of MAA-*alt*-AMS and DPPH in DMSO at different temperatures, (A) 70 °C, (C) 80 °C and (E) 90 °C , and their corresponding UV-vis absorption spectra, (B) 70 °C, (D) 80 °C and (F) 90 °C.

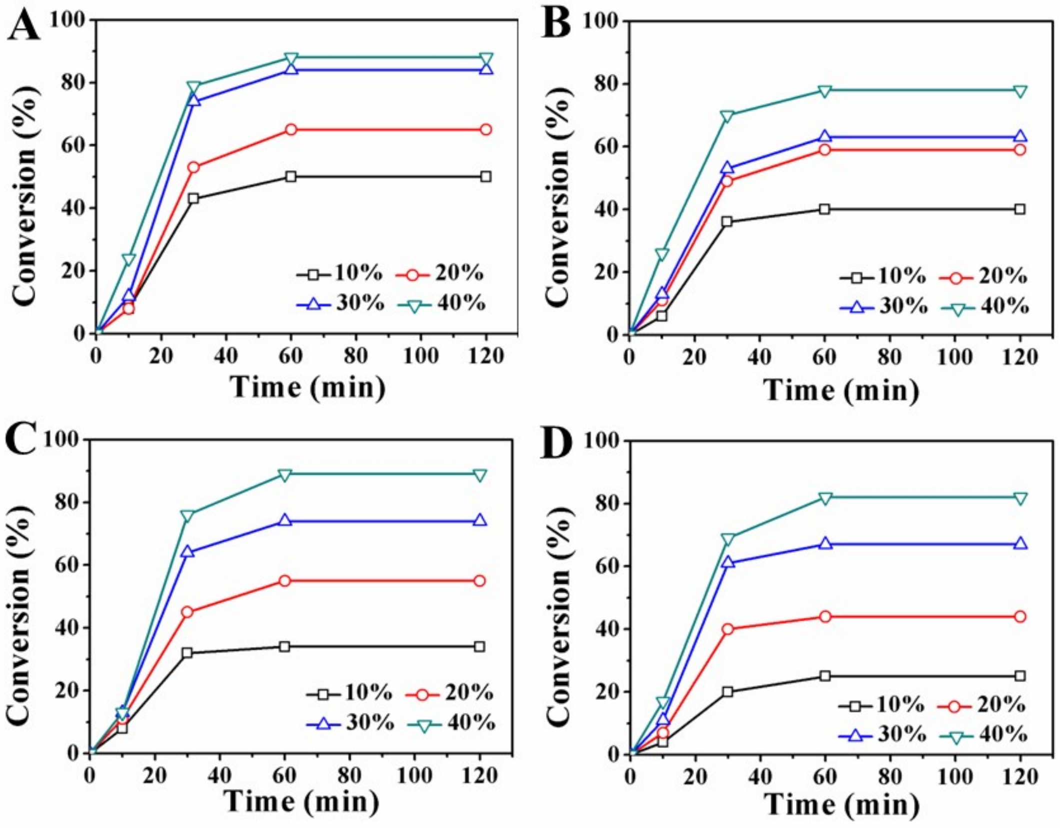

Fig. S6 Monomer conversion of emulsion PISA initiated by different amount of macro-initisurf, macro-initisurf /monomers, *w/w*. (A) BA/MMA=1/2, (B) BA/MMA=1/1, (C) BA/MMA=2/1 and (D) BA/MMA=3/1 (molar ratio).

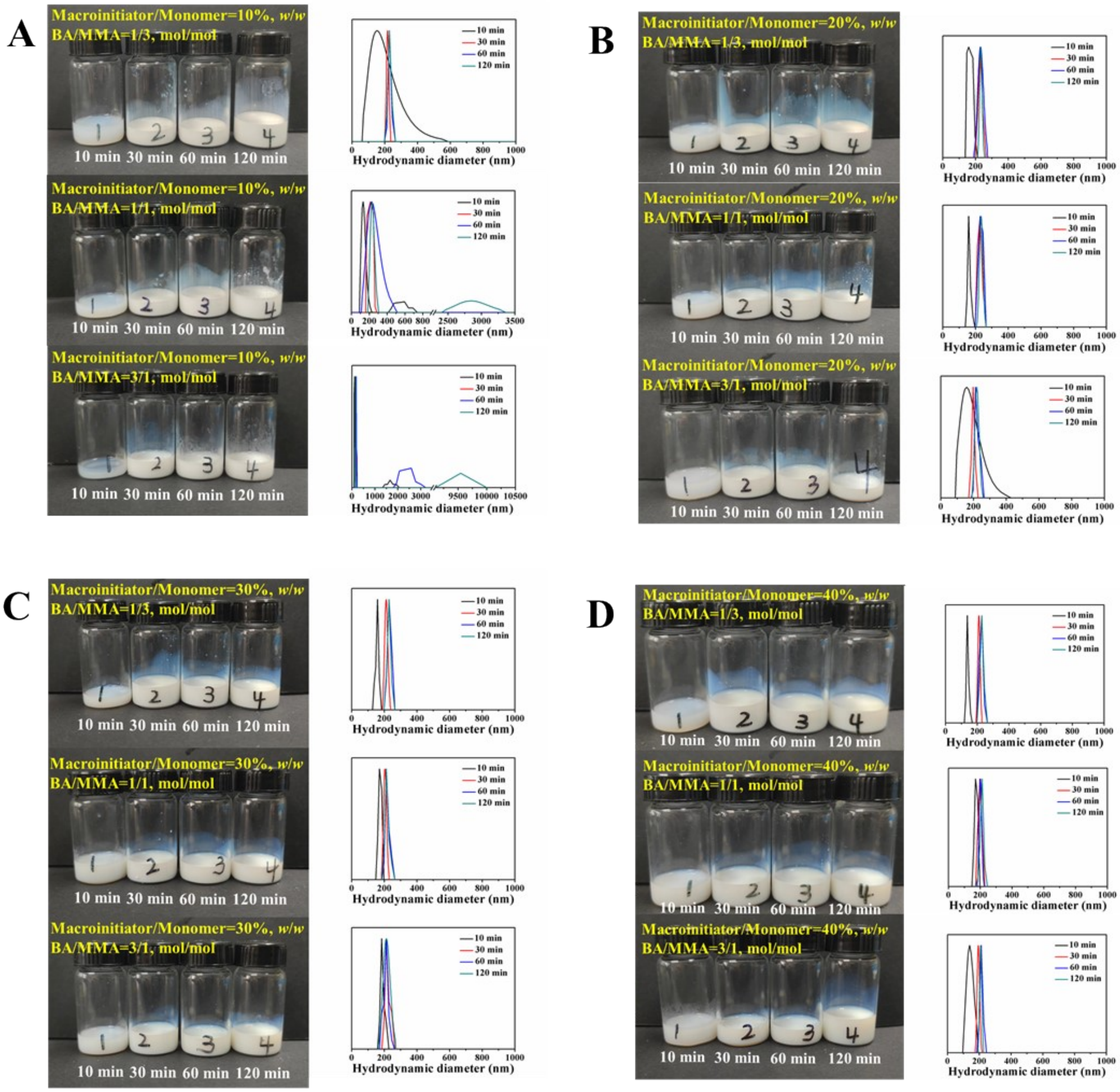

Fig. S7. DLS intensity traces of latex during emulsion PISA. Macro-initisurf /monomers (*w/w*) =10%, (A), 20% (B), 30% (C) and 40% (D).

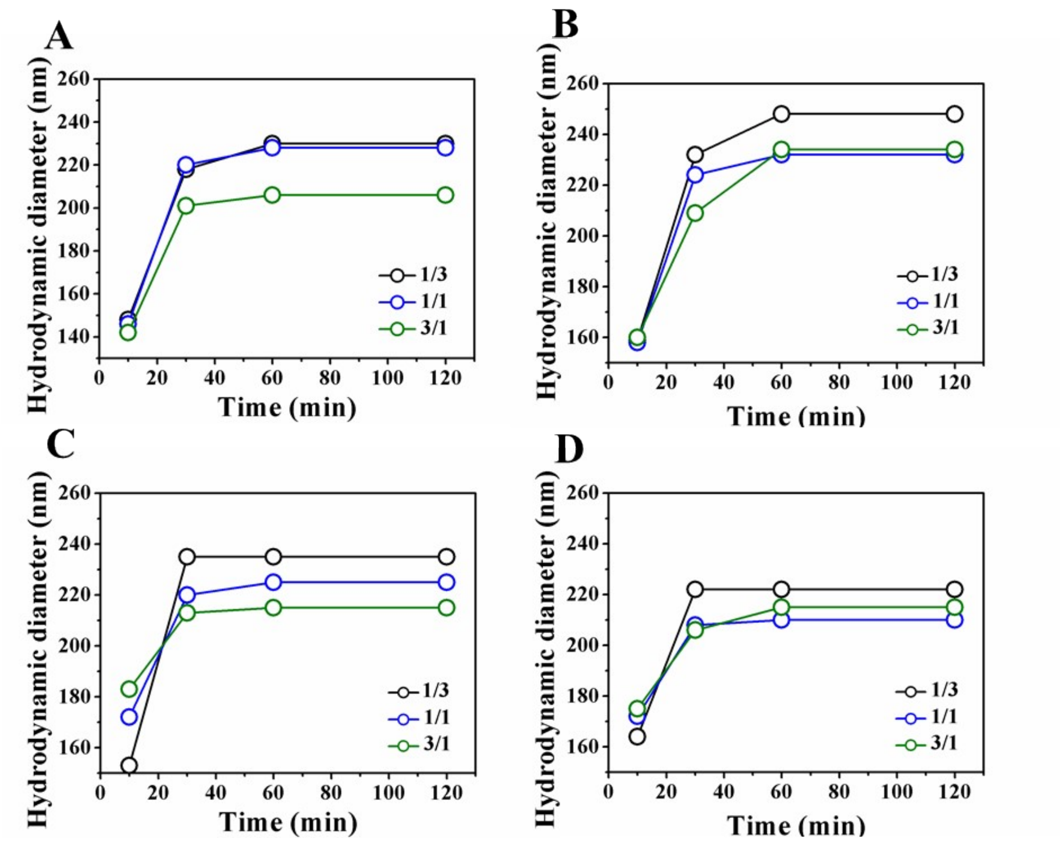

Fig. S8 Evolution of nanoparticles size during emulsion PISA initiated by different amount of macro-initisurf. Macro-initisurf /monomers=10%, *w/w*. (A), 20% (B), 30% (C) and 40% (D).

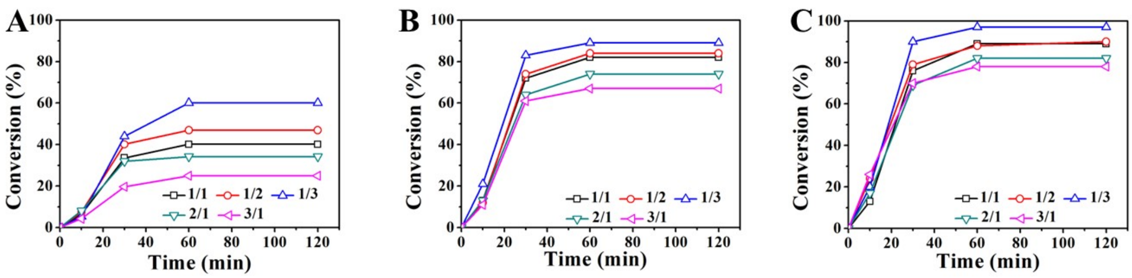

Fig. S9 Monomer conversion of emulsion PISA initiated by macro-initisurf at different monomers ratios, (A) macro-initisurf /monomers=10%, (B) macro-initisurf /monomers=30% and (A) macro-initisurf /monomers=40%, *w/w*.

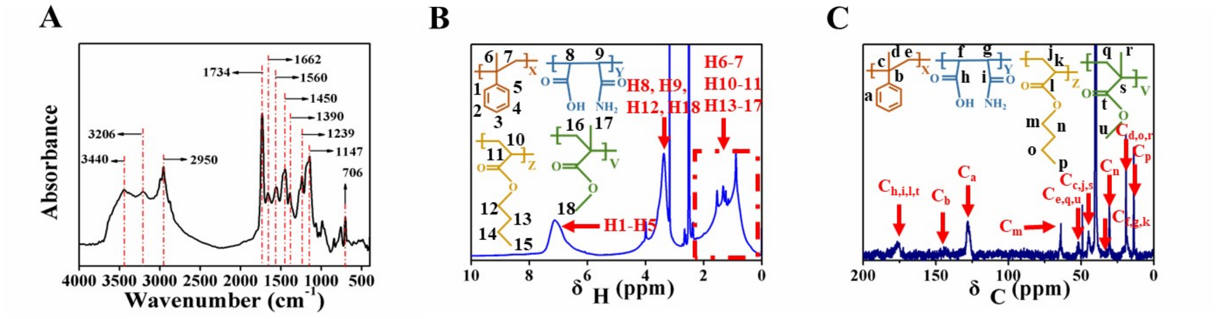

Fig. S10 (A) FTIR spectrum, (B) ^{1}H NMR spectrum and (C) ^{13}C NMR spectrum of nanoparticles.

The FTIR signals of benzene ring (1450 cm^{-1}, 758 cm^{-1}, and 706 cm^{-1}), amide (3440cm^{-1}, 3206cm^{-1}, 1662cm^{-1}, 1560cm^{-1} and 1390cm^{-1}) and ester bonds (1734cm^{-1}, 1239cm^{-1} and 1147cm^{-1}) appeared, indicated that macroinitiator indeed reacted with BA and MMA. In ^{1}H NMR, the signals 6.00 – 7.50 ppm stands for the chemical shift of aromatic H in AMS moiety, the signal covering a wide range of 3.00 – 4.50 ppm stands for OCH_3 in MMA moiety, OCH_2 in BA moiety and CH_2 in MAA moiety. Other signals that located from 0.70 ppm to 2.80 ppm arise from CH_2 and CH_3 of AMS and MMA moieties plus remaining CH, CH_2 and CH_3 from BA moiety. In ^{13}C NMR, the signals representing different C atoms in AMS, MAA, BA and MMA also appeared, 173 – 180 ppm was the chemical shift of carbonyl C in BA, MMA and MAA, 142 – 148 ppm and 124 – 130 ppm stands for the phenyl C in AMS, other signals of $-O-CH_2-$ in BA (63 – 65 ppm), $-O-CH_3$ in MMA (50 – 52 ppm), $-CH_3$ in AMS (17 – 22.2 ppm), $-CH_2-$ in MMA and AMS (53 – 55 ppm), -CH- in BA (36 – 40 ppm) and $-CH_2CH_2CH_3-$ in BA (29.5 – 31, 18.9 – 19.1, 13.1 – 13.6 ppm) can also match the chemical structure of BA, MMA, AMS and MAA.

Table S2 MMA, BA, AMS and MAA molar fractions in nanoparticles (F_{MMA}, F_{BA}, F_{AMS} and F_{MAA}).

Run	F_{MMA}	F_{BA}	F_{AMS}	F_{MAA}
1	0.438	0.089	0.227	0.246
2	0.501	0.051	0.216	0.233
3	0.531	0.021	0.216	0.233
4	0.140	0.226	0.305	0.329
5	0.130	0.306	0.29	0.313
6	0.350	0.228	0.204	0.220
7	0.510	0.267	0.111	0.112
8	0.654	0.157	0.092	0.099
9	0.256	0.301	0.213	0.230
10	0.186	0.393	0.202	0.219
11	0.409	0.288	0.131	0.145
12	0.534	0.221	0.118	0.127
13	0.636	0.192	0.083	0.089
14	0.474	0.263	0.127	0.136
15	0.590	0.236	0.084	0.091
16	0.402	0.373	0.109	0.118
17	0.424	0.174	0.194	0.209
18	0.627	0.218	0.074	0.080
19	0.303	0.515	0.087	0.095
20	0.142	0.427	0.173	0.187
21	0.635	0.205	0.077	0.083
22	0.599	0.224	0.085	0.088
23	0.341	0.460	0.096	0.103
24	0.443	0.300	0.124	0.128
25	0.186	0.586	0.110	0.118
26	None	None	None	None
27	0.638	0.205	0.075	0.082

28	0.413	0.414	0.083	0.090
29	0.205	0.608	0.090	0.097
30	0.639	0.203	0.076	0.082
31	0.413	0.417	0.082	0.088
32	0.213	0.607	0.086	0.094

Table S3 The polydispersity of nanoparticles at different time.

BA/MMA=1/3

Reaction time (min) **Macro-initisurf content (%)**	**10**	**30**	**60**	**120**
10	0.134	0.044	0.027	0.016
20	0.083	0.031	0.011	0.005
30	0.040	0.040	0.040	0.034
40	0.051	0.040	0.030	0.020

BA/MMA=1/1

Reaction time (min) **Macro-initisurf content (%)**	**10**	**30**	**60**	**120**
10	0.1843	0.144	0.167	0. 168
20	0.040	0.038	0.030	0.020
30	0.050	0.045	0.040	0.020
40	0.046	0.040	0.030	0.020

BA/MMA=3/1

Reaction time (min) **Macro-initisurf content (%)**	**10**	**30**	**60**	**120**
10	0.234	0.144	0.227	0.332
20	0.040	0.038	0.030	0.020
30	0.090	0.045	0.040	0.020
40	0.046	0.040	0.030	0.020

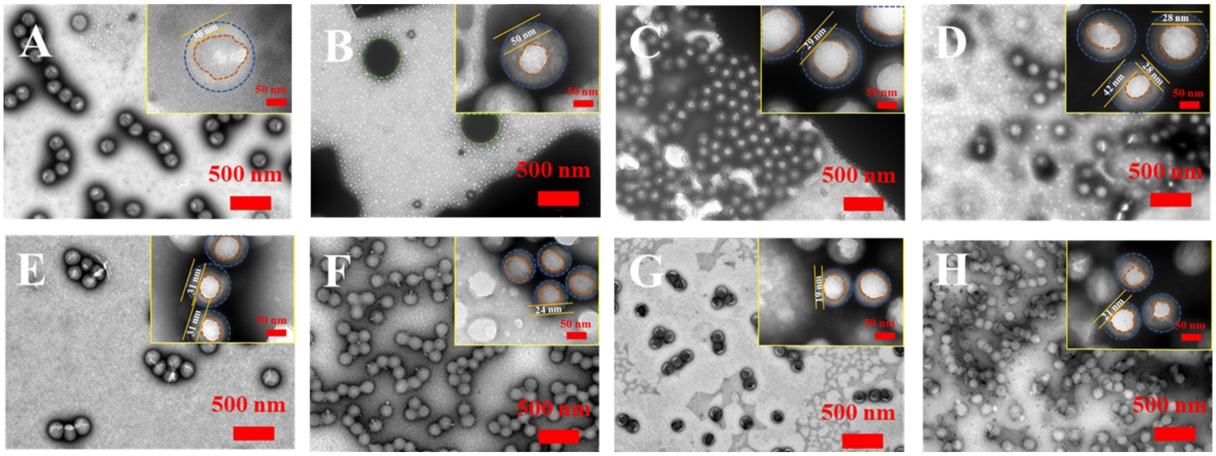

Fig. S11 TEM images of nanoparticles, reaction temperature=90 °C. (A), (B): BA/MMA=1/2, 2/1, macro-initisurf content=10%; (C), (D): BA/MMA=1/2, 2/1, macro-initisurf content=20%; (E), (F): BA/MMA=1/2, 2/1, macro-initisurf content=30%; (G), (H): BA/MMA=1/2, 2/1, macro-initisurf content=40%

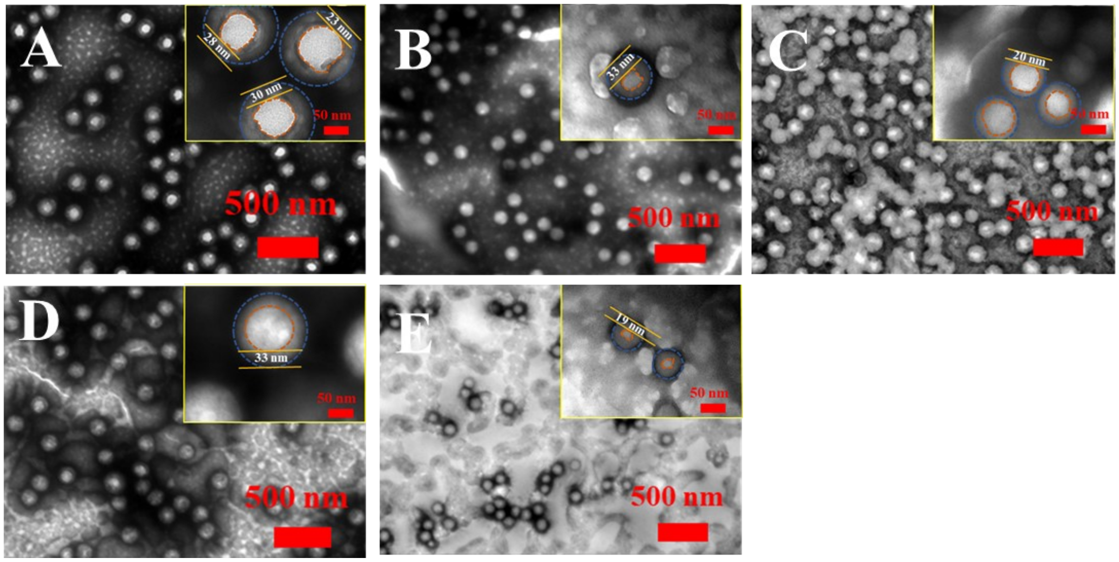

Fig. S12 TEM images of nanoparticles. (A) – (C): BA/MMA=1/3, 1/1, 3/1, macro-initisurf =40%, reaction temperature=80 °C; (D) – (E): BA/MMA=1/3, 1/1, macro-initisurf =40%, reaction temperature=70 °C.

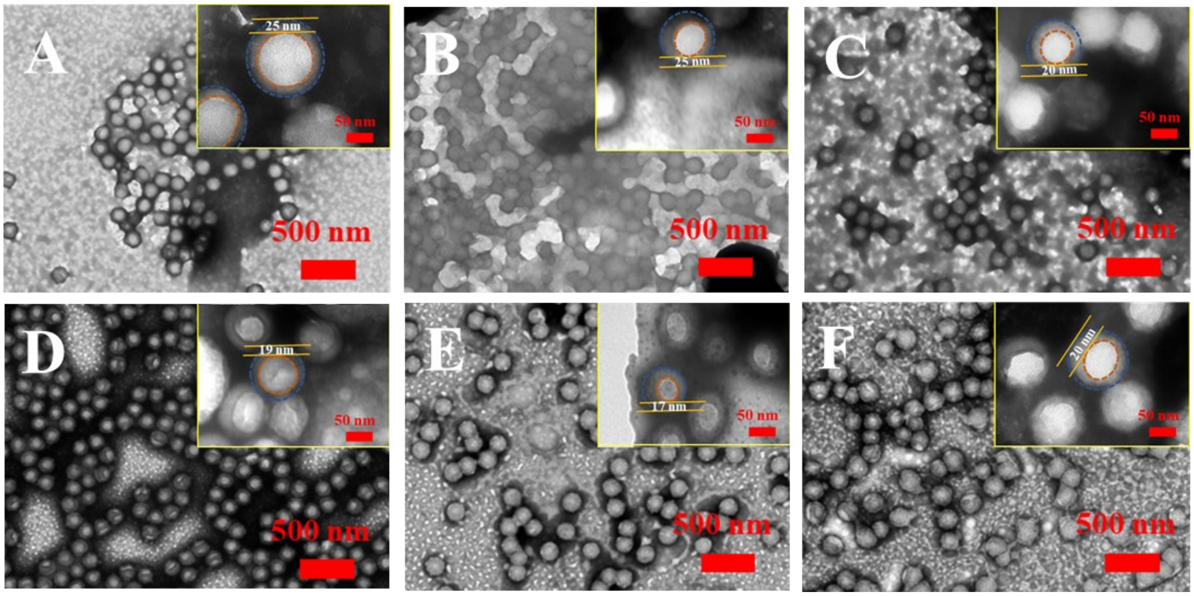

Fig. S13 TEM images of nanoparticles. (A) – (C): BA/MMA=1/3, 1/1, 3/1, macro-initisurf =40%, reaction temperature=90 °C, solid content=40%; (D) – (F): BA/MMA=1/3, 1/1, 3/1, macro-initisurf =40%, reaction temperature=90 °C, solid content=50%.

Table S4 The diameter of nanoparticles that determined by TEM measurement.

Temperature (°C) **BA/MMA (mole ratio)**	70	80
1/3	140	145
1/1	60	85
3/1	None	80

Table S5 The diameter of nanoparticles that determined by TEM measurement.

Solid content (%) **BA/MMA (mole ratio)**	40	50
1/3	147	140
1/1	155	168
3/1	138	179

In order to obtain particles with other morphologies, we carried out the polymerization in the presence of ethanol to help BA and MMA to dissolve in the medium. The formulations were summarized in Table S6 and the polymerization temperature was 90 ℃.

Table S6 The formulations of PISA

	BA/g	MMA/g	Macro-initisurf/g	H_2O/g	EtOH/g	Stirring	pH
1	3.2	2.5	1.71	25.94	8.65	Yes	7
2	3.2	2.5	1.71	23.05	11.53	Yes	7
3	3.2	2.5	1.71	17.29	17.29	Yes	7
4	3.2	2.5	1.71	17.29	17.29	No	7
5	3.2	2.5	1.71	17.29	17.29	No	9

As shown in Fig. S15, when the reaction medium was EtOH/H_2O=1/1, the system was clear and transparent before polymerization. With the polymerization proceeds, the system gradually turned semitransparent, no matter with stirring or not. However, when the reaction medium was EtOH/H_2O=1/3 and 1/2, stirring was necessary. Otherwise, the system was not stable, and monomers would float on water. Additionally, due to the existence of -COOH and -$CONH_2$ in macro-initisurf, pH of reaction medium could also affect the morphology of particles, so we also conduct PISA in an alkalic medium (pH=9).

EtOH/H_2O=1/1 (*w/w*), Solid content=30%, BA/MMA=1/1 (molar ratio), Macro-initisurf/monomers=30%

Fig. S14 Photos of different stages of PISA in EtOH/H_2O

The photo of latex prepared under different conditions was shown in Fig.S16. Clearly, $1^{\#}$ and $2^{\#}$ were milk-white, $3^{\#}$ and $4^{\#}$ were blueish. Although $5^{\#}$ was also white, it was lighter than $1^{\#}$ and $2^{\#}$.

Fig. S15 Photos of latex prepared under different conditions

TEM images of $1^{\#}$ and $2^{\#}$ were shown in Fig. S17. Particles in $1^{\#}$ were 400 nm microspheres with a regular shape. While the particles in $2^{\#}$ were vesicular-like, and their diameter was approximate 900 nm. And the shell thickness was around 70 – 100 nm.

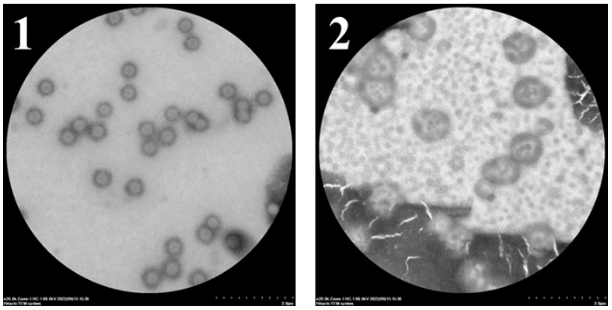

Fig. S16 TEM images of nanoparticles (Condition 1 and 2)

TEM images of $3^{\#}$ to $5^{\#}$ were shown in Fig. S18. Obviously, the particles were still spherical and having nothing to do with stirring, the polymer chains can spontaneously form spheres. Conversely, as adjusting pH to 9, abnormal rod-like particles can be obtained, as shown in Fig. S 18-1 to 18-4. The reason may be that the polymer chains of macro-initisurf can stretch more easily in alkalic environment as the salinization of -COOH, which can lead to deprotonation. So, the aggregation of macro-initisurf polymer chains can be weakened, which supply the possibility of forming particles with other morphologies.

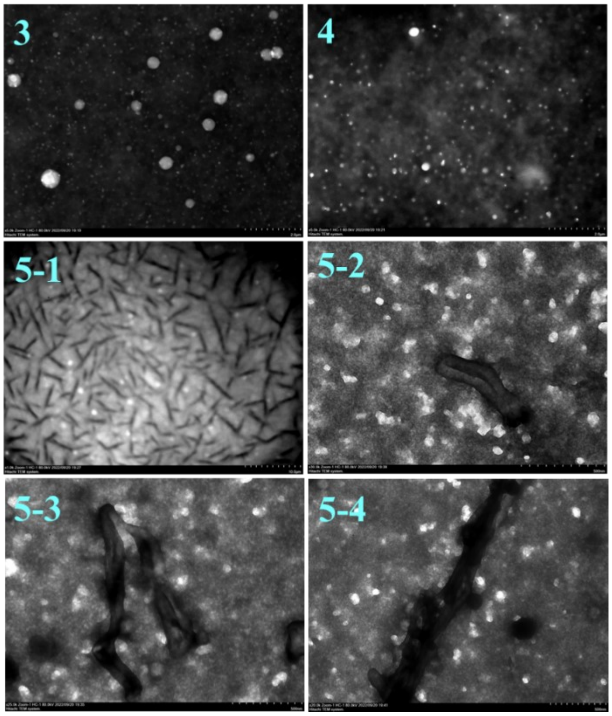

Fig. S17 TEM images of nanoparticles (Condition 3-5)