Supporting Information for:

Dual responsive macroemulsion stabilized by Y-shaped amphiphilic AB_2 miktoarm star copolymers

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S1. The photographs of o/w macroemulsion and the optical microscope of emulsion droplets stabilized by Y-shaped amphiphilic PS_{32}-$(PDMAEMA_{80})_2$ miktoarm star copolymers

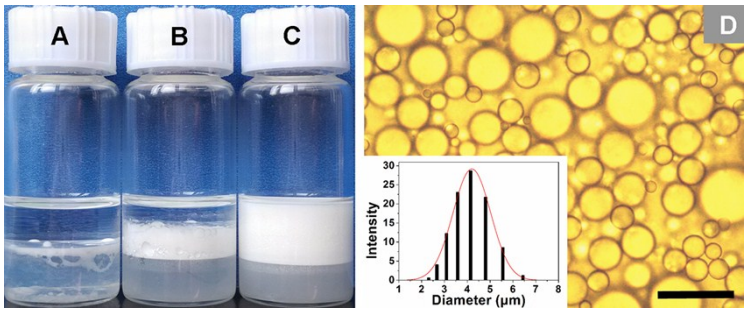

Fig S1: （A-C）Photographs of emulsions with pH5 water stabilized by varied contents of PS_{32}-$(PDMAEMA_{80})_2$: (A) 0.06 wt%; (B) 0.08 wt%; (C) 0.10 wt%; (D) The optical microscope of o/w macroemulsion droplets shown in C, which were stabilized by 0.10 wt% of PS_{32}-$(PDMAEMA_{80})_2$ with 50 % (volume fraction) of pH5 water. All the photographs were taken after 24 h of standing at room temperature. The inset displayed in D was the corresponding droplets size distribution histogram. Scale bar: 6 μm.

S2. Synthesis of linear PS_{30}-b-$PDMAEMA_{259}$ block copolymer by ATRP technique

Synthesis of PS-Br: In a typical reaction, St (6.24 g, 60 mmol), Ethyl 2-bromo-2-methylpropionate (195 mg, 1 mmol), CuBr (143.5 mg, 1 mmol) and PMDETA (0.205 mL, 1 mmol) were charged into a round bottomed flask. After three freeze-pump-thaw cycles, the degassed flask was sealed and then immersed in 75 ^{o}C oil bath for polymerization under N_2 atmosphere. After 5 h of polymerization, the reaction was stopped by diluting with THF and then passed through a short neutral alumina column to remove the metal salt. The solution was concentrated by evaporation, and the concentrated mixture was dropped into a large amount of methanol, producing a white precipitation. The precipitation was filtered, and washed with methanol. The precipitation, filtration and washing operations were repeated for three times, and the purified product was dried under vacuum at room temperature. GPC analysis indicated Mn was 3300 g/mol with 1.12 of PDI (Fig.S2A). According to GPC analysis, the polymerization degree of PS block was 30.

Synthesis of PS-*b*-PDMAEMA: PS-*b*-PDMAEMA block copolymer was synthesized by ATRP in THF at 60 ^{o}C using PS and CuBr/PMDETA as macroinitiator and catalyst, respectively. In a typical reaction, 0.2 g of PS macroinitiator, CuBr (7.2 mg, 0.05 mmol), PMDETA (0.01 mL, 0.05 mmol), DMAEMA

(1.26 g, 8 mmol) and 1.5 mL fresh THF were charged into a round bottomed flask. The flask was degassed by three freeze-pump-thaw cycles and then immersed in an oil bath at 60 °C for polymerization under N_2. After 4 h of polymerization, the reaction was stopped by diluting with THF and then passed through a short basic alumina column to remove the metal salt. The solution was concentrated by evaporation, and the concentrated mixture was dropped into a large amount of hexane, producing a white precipitation. The precipitation was filtered, and washed with hexane. The precipitation, filtration and washing operations were repeated for three times, and the purified product was dried under vacuum at room temperature. GPC analysis indicated Mn was 44000 g/mol with 1.29 of PDI (Fig.S2B). According to GPC analysis, the polymerization degree of PDMAEMA block was 259.

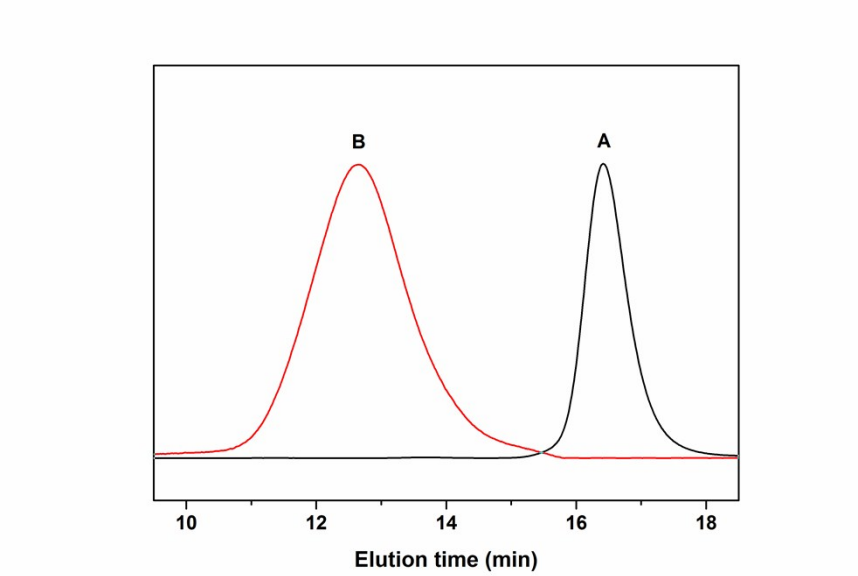

Fig S2. GPC traces of PS macroinitiator (A) and linear PS-b-PDMAEMA block copolymer (B)

S3: Photographs of w/o and o/w emulsions stabilized by PS_{32}-$(PDMAEMA_{121})_2$

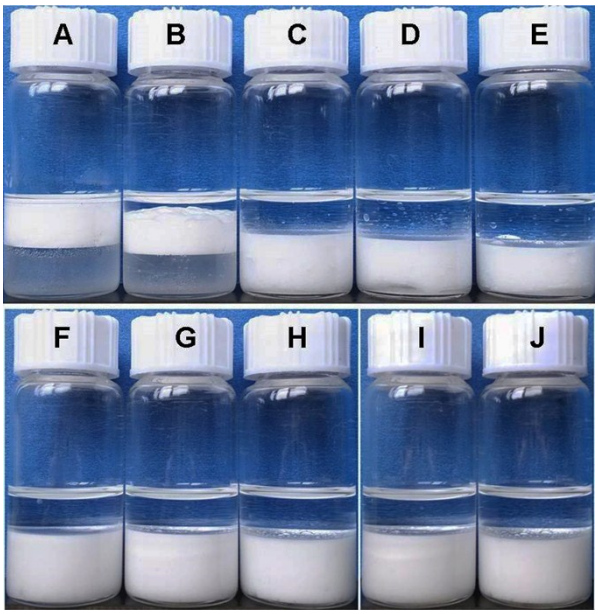

Fig S3: (A-E) Photographs of emulsions stabilized by 0.06 wt% of PS_{32}-$(PDMAEMA_{121})_2$ with varied volume fractions of pH7 water: (A) 49%; (B) 48%; (C) 47%; (D) 45%; (E) 40%; (F-H) Photographs of w/o emulsions stabilized by 0.12 wt% of PS_{32}-$(PDMAEMA_{121})_2$ with 45 % (volume fraction) of varied pHs water: (F) 5; (G) 6; (H) 9; (I-J) Photographs of w/o emulsions with 45 % of pH7 water (volume fraction) stabilized by varied contents of PS_{32}-$(PDMAEMA_{121})_2$: (I) 0.19 wt%; (J) 0.26 wt%. All the photographs were taken after 24 h of standing at room temperature.