

**Supporting Information for:**

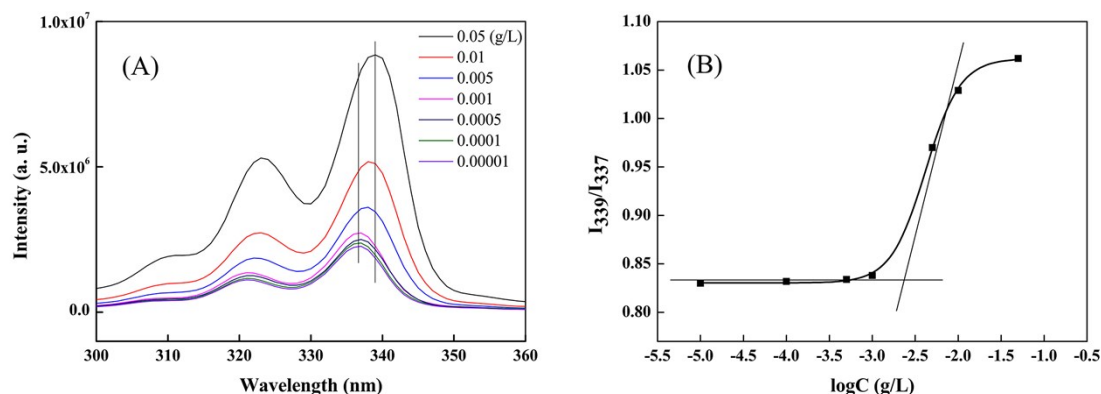
Efficient synthesis of narrowly dispersed amphiphilic double-brush copolymers through the polymerization reaction of macromonomer micelle emulsifiers at oil-water interface

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## S1. Determination the critical micelle concentration (CMC) of the macromonomer



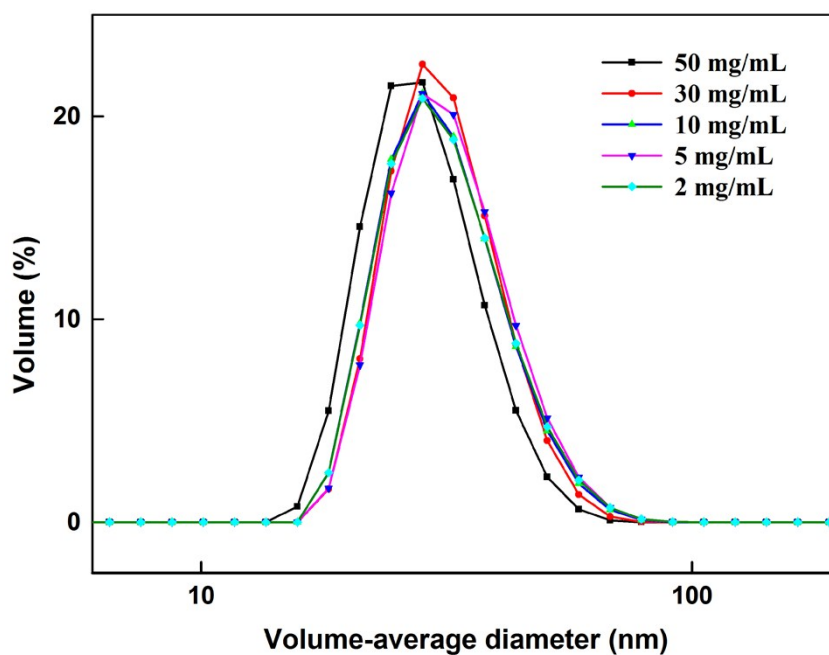
**Figure S1:** (A) Excitation spectra recorded for pyrene equilibrated with macromonomers in water at various polymer concentrations. Pyrene concentration:  $5 \times 10^{-9}$  mol/mL. (B) Plots of the fluorescence intensity ratios  $I_{339}/I_{337}$  from the excitation spectra of pyrene probe as a function of polymer concentrations.

For the determination of CMC of the macromonomer, a series of macromonomer aqueous solutions with different concentrations were prepared by successive dilution of a stock solution (a solution of the macromonomer polymer at 6 mg/mL in water). And 5 mL of ( $5 \times 10^{-9}$  mol/mL) pyrene solution was added to each macromonomer solution. All of the solutions were left to stand at room temperature overnight to achieve equilibrium. Fluorescence spectra were recorded on spectrofluorometer (FP-6500, JASCO, Japan). MA-PMMA-*b*-PDMA/pyrene solutions were scanned from 230 to 360 nm at room temperature, with an emission wavelength of 390 nm and a bandwidth of 5 nm. The intensity ratios of  $I_{339}$  to  $I_{337}$  were plotted as a function of logarithm of MA-PMMA-*b*-PDMA concentrations. The critical micelle concentration

(CMC) was determined using pyrene as a fluorescence probe. The CMC value was taken from the intersection of the tangent to the curve at the inflection with the horizontal tangent through the points at low concentrations. The CMC values of MA-PMMA-*b*-PDMA were determined to be 2.0 mg/L.

## **S2: The size of micelles prepared by different initial concentration of macromonomer**

The core-shell structure micelles were prepared at different initial concentration of MA-PMMA-*b*-PDMA using the self-assembly method. The initial polymer concentration was 50, 30, 10, 5, 2 mg/mL, respectively. In a typical experiment, 100 mg of MA-PMMA-*b*-PDMA polymer was firstly dissolved in 2 mL of DMF, and 8 mL of deionized water was added dropwise into the mixture with gently stirring. The mixture was then dialyzed against deionized water for 24 h at room temperature using a cellulose membrane bag (MWCO 8,000-14,000). The obtained dispersion was measured by DLS. DLS curves of dispersions obtained at different initial polymer concentration were shown in Fig. S2, and the detailed data was displayed in the **Table S1**. DLS experiment indicated that the  $\langle D_{h,v} \rangle$  of aggregates formed by self assembly of MA-PMMA-*b*-PDMA macromonomer at 2 mg/mL of the initiated polymer concentration was 37.4 nm with 0.067 of PDI. And the  $\langle D_{h,v} \rangle$  value of MA-PMMA-*b*-PDMA macromonomer at 50 mg/mL of the initial polymer concentration was 32.8 nm with 0.049 of PDI. Evidently, the initiated polymer concentration has a minor effect on the morphologies of aggregates for the current system.



**Figure S2:** Volume-average distribution of the hydrodynamic diameters of macromonomer micelles prepared at different initial macromonomer concentrations.

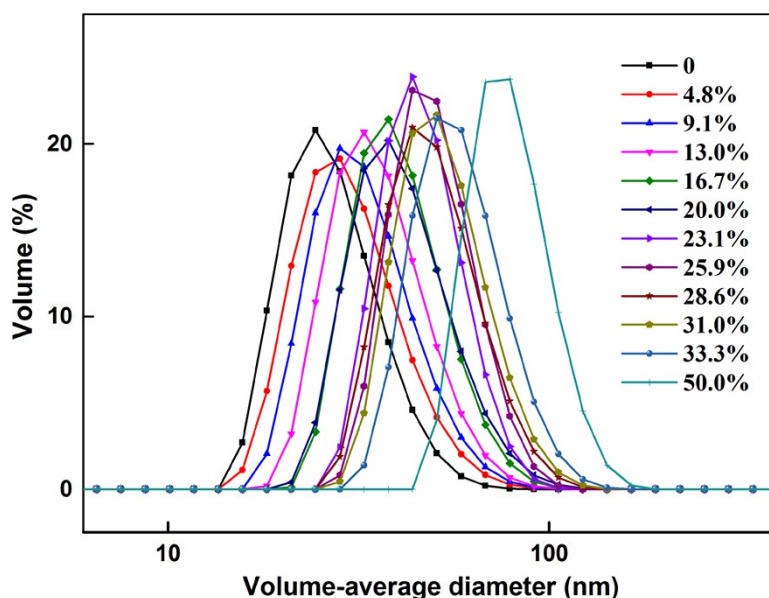
**Table S1:** DLS analysis results of micelles prepared at different initial macromonomer concentrations.

Initial polymer concentration (mg/mL)	$\langle D_{h,v} \rangle$ (nm)	PDI
50	32.8	0.049
30	35.9	0.036
10	36.9	0.064
5	38.4	0.118
2	37.4	0.067

**S3: The size dependent of macromonomer micelles on the content of**

## DMF in the DMF/H<sub>2</sub>O binary mixed solvent

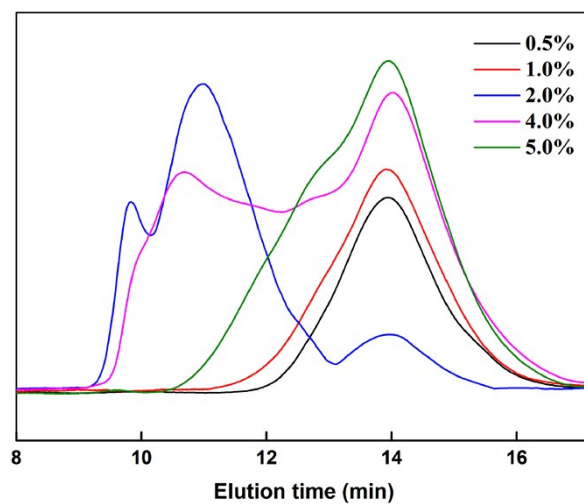
The content of co-solvent in the cores is usually very low and can be ignored after dialysis, and the vitrifiable core retain their structural integrity. The existing co-solvent will affect the dimension of the core. In order to investigate the effect of the co-solvent on the micelle size, DMF, which are good solvent for both the core and the shell, was added stepwise to the micelle aqueous solutions. For each addition, 24 h of standing at room temperature was required. And then, the  $\langle R_h \rangle$  of the formed micelles dispersion in the mixed solvent was measured by DLS (Fig. S3). The volume fraction of DMF in the mixed solvent ranged from 0~50%. DLS measurements indicated that the  $\langle D_{h,v} \rangle$  of the micelles increased from 32.8 nm to 82.4 nm when the volume fraction of co-solvent of DMF increased from 0 to 50%, and the detailed data was displayed in the **Table S2**.



**Figure S3:** Volume-average distribution of the hydrodynamic diameters of macromonomer micelles in DMF/H<sub>2</sub>O with different DMF contents.

**Table S2:** DLS analysis results of macromonomer micelles in DMF/H<sub>2</sub>O

The volume fraction of DMF	$\langle D_{h,v} \rangle$ (nm)	PDI
0	32.8	0.049
4.8%	37.0	0.094
9.1%	39.7	0.077
13.0%	42.4	0.080
16.7%	47.2	0.075
20.0%	50.1	0.083
23.1%	52.3	0.059
25.9%	56.2	0.005
28.6%	57.9	0.022
31.0%	61.0	0.052
33.3%	66.9	0.047
50.0%	86.4	0.006

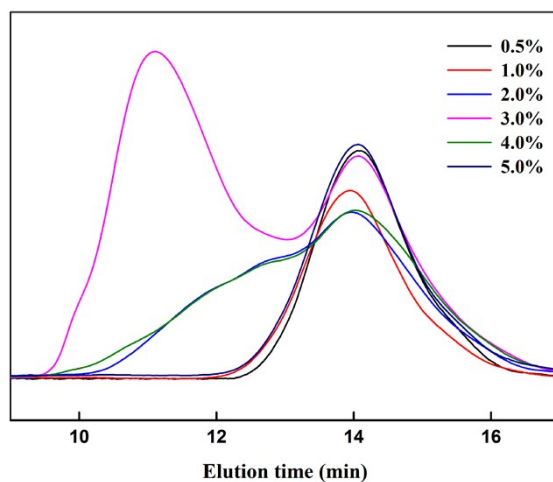
**S4: GPC traces of DBCs obtained at different AIBN contents**

**Figure S4:** GPC curves for PMA-g-PMMA/PDMA DBCs obtained by Pickering emulsion template directed radical polymerization reactions initiated by varied AIBN contents ranging from 0.5 wt% to 5.0 wt%.

**S5: GPC traces of the DBCs produced by the traditional micelle**

## polymerization initiated by KPS with varied contents in DMF/H<sub>2</sub>O mixed solvent

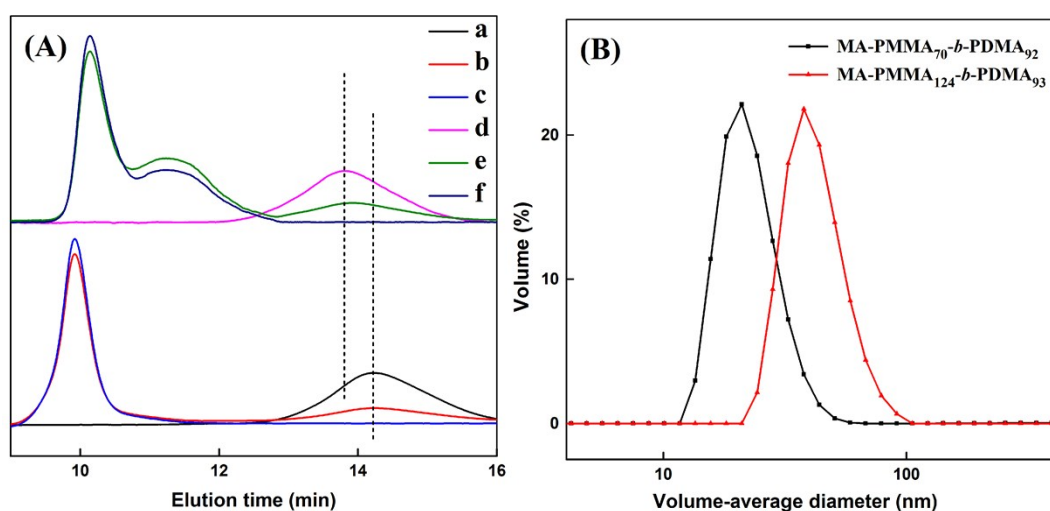
A typical procedure for the synthesis of PMA-*g*-PMMA/PDMA by the traditional micelle polymerization was as follows: macromonomer aqueous solution (6 mg/mL, 5 mL), KPS (0.9 mg) and 0.5 mL of fresh DMF were charged into a round bottom flask, and the flask was degassed by three freeze-pump-thaw cycles. The reaction flask was transferred to a preheated oil bath at 70 °C. After 10 h of polymerization, the reaction was stopped. The solvent was removed using rotary evaporator and the remaining polymer was dissolved into CH<sub>2</sub>Cl<sub>2</sub>, then precipitated into a large amount of ice diethyl ether. The precipitation and washing operations were repeated for three times, and the purified product was dried under vacuum at 25 °C. The volume fraction of DMF was 9.1%, and the amount of initiator from 0.5 wt% to 5.0 wt%. It was found that the optimal initiator content was 3 wt% versus the total weight of macromonomers, and the GPC peak at higher molecular weight region was observed after polymerization reaction (Fig. S5).



**Figure S5:** GPC traces of DBCs produced by the traditional micelle polymerization in

pure water, which were initiated by KPS with varied contents from 0.5 wt% to 5.0 wt%.

**S6: The effect of the length of PMMA block of macromonomer on the polymerization reaction at oil-water interface.**



**Figure S6:** (A) GPC curves for MA-PMMA<sub>70</sub>-b-PDMA<sub>92</sub> (a), DBCs of PMA-g-PMMA<sub>70</sub>/PDMA<sub>92</sub> before (b) and after fractionation (c), MA-PMMA<sub>124</sub>-b-PDMA<sub>93</sub> (d), DBCs of PMA-g-PMMA<sub>124</sub>/PDMA<sub>93</sub> before (e) and after fractionation (f); (B) Volume-average distribution of the hydrodynamic diameters of MA-PMMA<sub>70</sub>-b-PDMA<sub>92</sub> and MA-PMMA<sub>124</sub>-b-PDMA<sub>93</sub> macromonomer micelles in pure water.