Supporting Information

Effect of Chain Microstructure on Self-assembly and Emulsification of Amphiphilic Poly(acrylic acid)-polystyrene Copolymers

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Contents

Materials

Styrene (St) purchased from Sinopharm chemical reagent Co. Ltd (Shanghai, China) was dried with calcium hydride (CaH_2) for 24 h, and then distilled under reduced pressure. Acrylic acid (AA) purchased from purchased from Sinopharm chemical reagent Co. Ltd (Shanghai, China), and then distilled under reduced pressure. The purified St and AA were stored at 5 °C prior to use. 2,2'-Azobisobutyronitrile (AIBN) was purchased from Sinopharm chemical reagent Co. Ltd (Shanghai, China), and recrystallized twice from ethanol prior to use. 2-dodecylsulfanyl-thiocarbonylsulfanyl-2-methylpropinoic acid (DMP) was provided by Nanjing HDC trading Co. Ltd (Nanjing, China). 1,4-dioxane, petroleum ether, and other chemicals were purchased from Sinopharm chemical reagent Co. Ltd (Shanghai, China), and used without further purification.

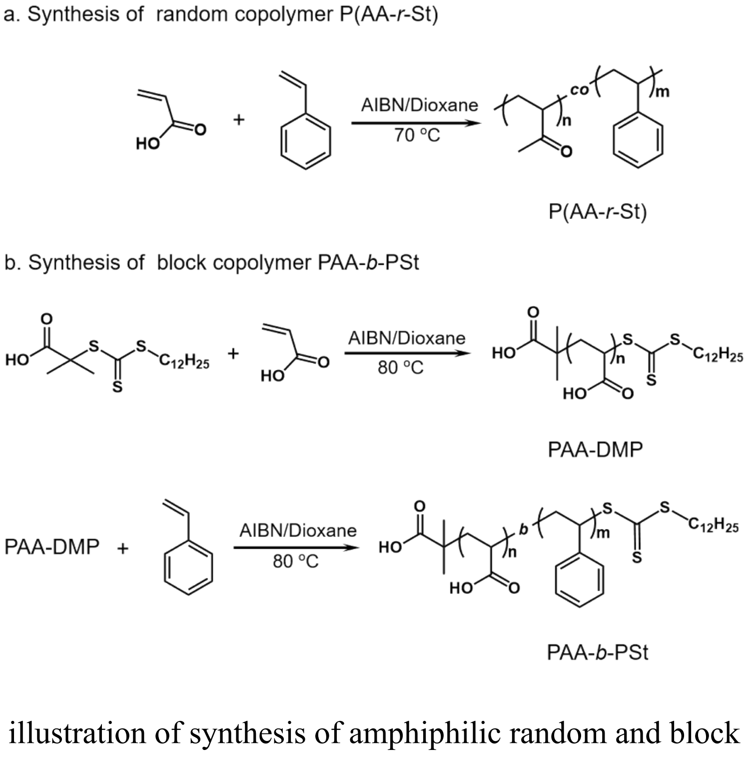


Figure S1. Schematic illustration of synthesis of amphiphilic random and block copolymer.

Synthesis of random copolymer P(AA-*r*-St)

P(AA-*r*-St) was synthesized through free radical copolymerization (Figure S1a) as reported in our previous study[1]. Briefly, calculated amount of St, AA monomer, 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 24 h.

Synthesis of block copolymer PAA-*b*-PSt

PAA-*b*-PSt was synthesized through reversible addition-fragmentation chain-transfer (RAFT) polymerization (Figure S1b) according to the previous report with slightly difference. First, PAA macro chain transfer agent DMP-terminated PAA (PAA-DMP) was prepared. Briefly, AA, DMP, AIBN with different molar ratio (1000:10:1, 2000:10:1, 3000:10:1, 4000:10:1 and 5000:10:1) were dissolved in 10 mL 1,4-dioxane, and then added 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. After stirring at 80 °C in an oil bath for 2 h, the reaction mixture was cooled to room temperature and precipitated into diethyl ether. The obtained PAA-DMP was further purified by repeating dissolution-precipitation process three times, and the finally products were dried under vacuum at room temperature for 24 h and stored in desiccator before further use.

The RAFT synthesis of PAA-*b*-PSt was then carried out. Into a 50 mL round bottom flask with a stirring bar, calculated amount of St, PAA-DMP, AIBN and 10 mL 1,4-dioxane were charged. The flask was degassed by three freeze-evacuate-thaw cycles and sealed under vacuum. The reaction was carried out at 80 °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 24 h.

Reference

1. Zhu, L. F.; Ma, C. F.; Li, X. J.; Chen, M. Q.; Yang, C.; Liu, X. Y. *Petrochem. Techno.* **2007**, *36*, 388-392.

Figure S2

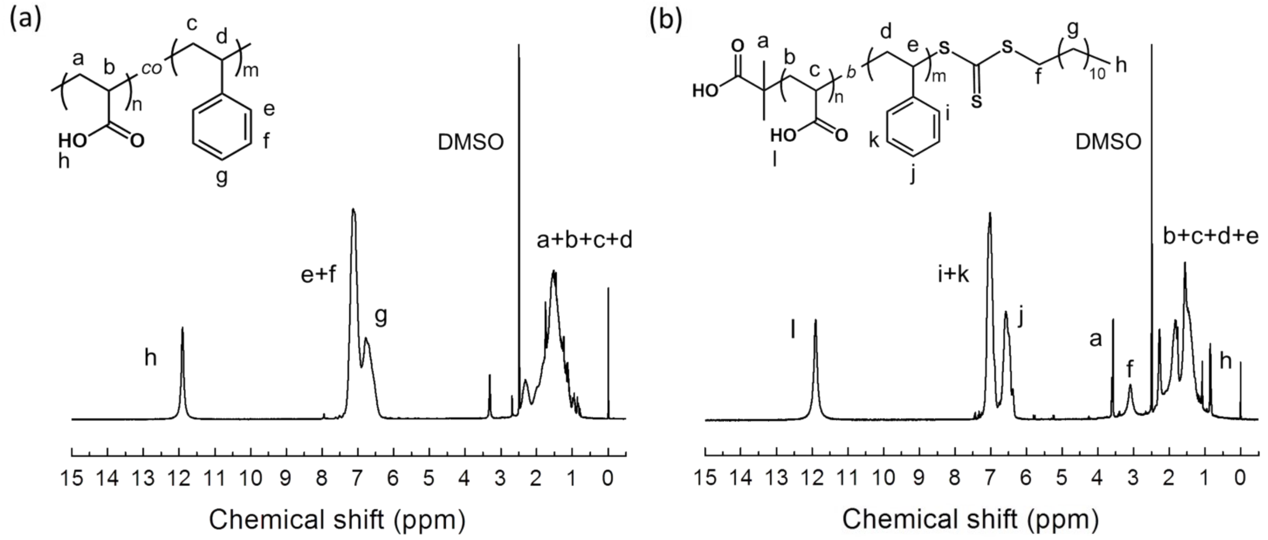


Figure S2. The ^{1}H-NMR spectra of (a) R49 and (b) B48 copolymers.

Figure S3

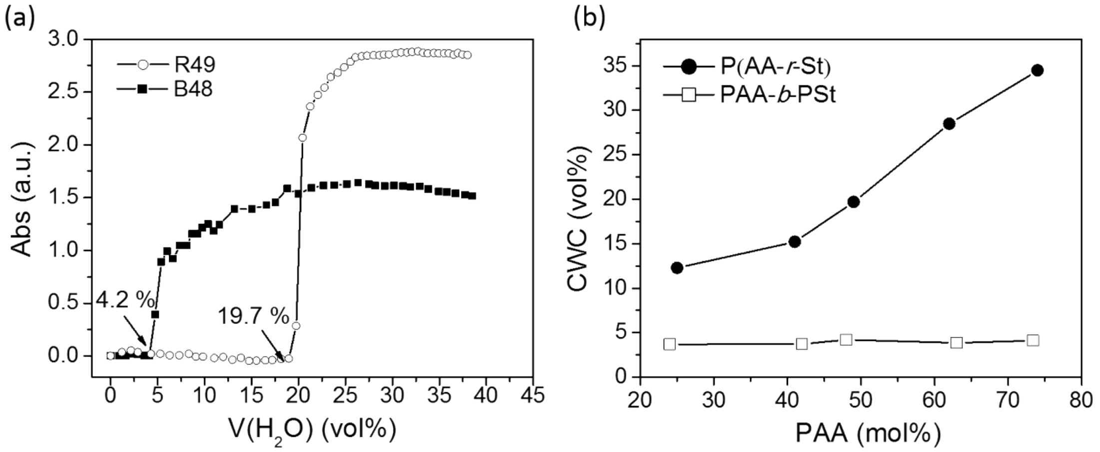
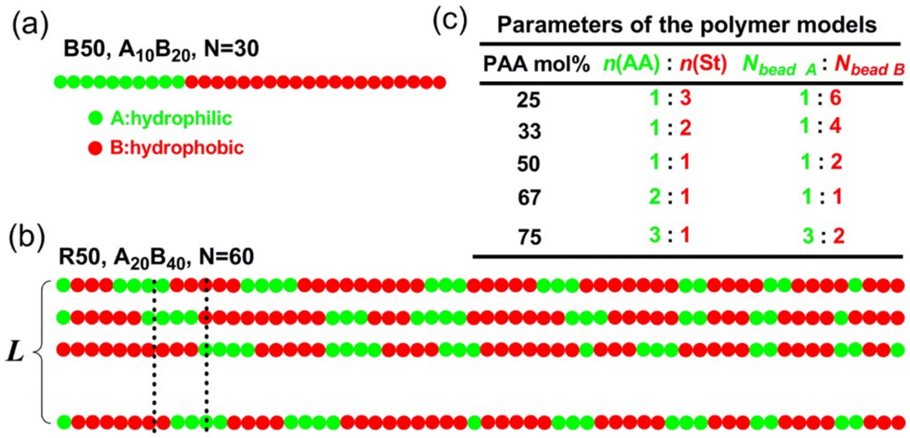


Figure S3. The self-assembly behavior of the amphiphilic copolymers in selective solvent DMF/H_2O. (a) UV trace the absorbance of the polymer solutions with water content increase; (b) Plots of the CWC of the random and block copolymers against the PAA molar content of the copolymers. All the initial concentration of copolymer solutions were 2 wt.% in DMF.

Figure S4



Parameters of the polymer models

PAA mol%	$n(AA) : n(St)$	$N_{bead\ A} : N_{bead\ B}$
25	1 : 3	1 : 6
33	1 : 2	1 : 4
50	1 : 1	1 : 2
67	2 : 1	1 : 1
75	3 : 1	3 : 2

Figure S4. The DPD model of (a) amphiphilic block copolymer B50, $A_{10}B_{20}$, and (b) amphiphilic random copolymer R50, $A_{20}B_{40}$. The A and B beads in each coarse-grained chain are referred to hydrophilic and hydrophobic particles, respectively. For random copolymers, the number of particles in per segment is a random number generated by the compute program in C language, and these coarse-grained chains are different from each other. (c) Table of the convertion of the chemical composite to the number ratio (*r*) of the hydrophilic DPD bead to the hydrophobic DPD bead.

Figure S5

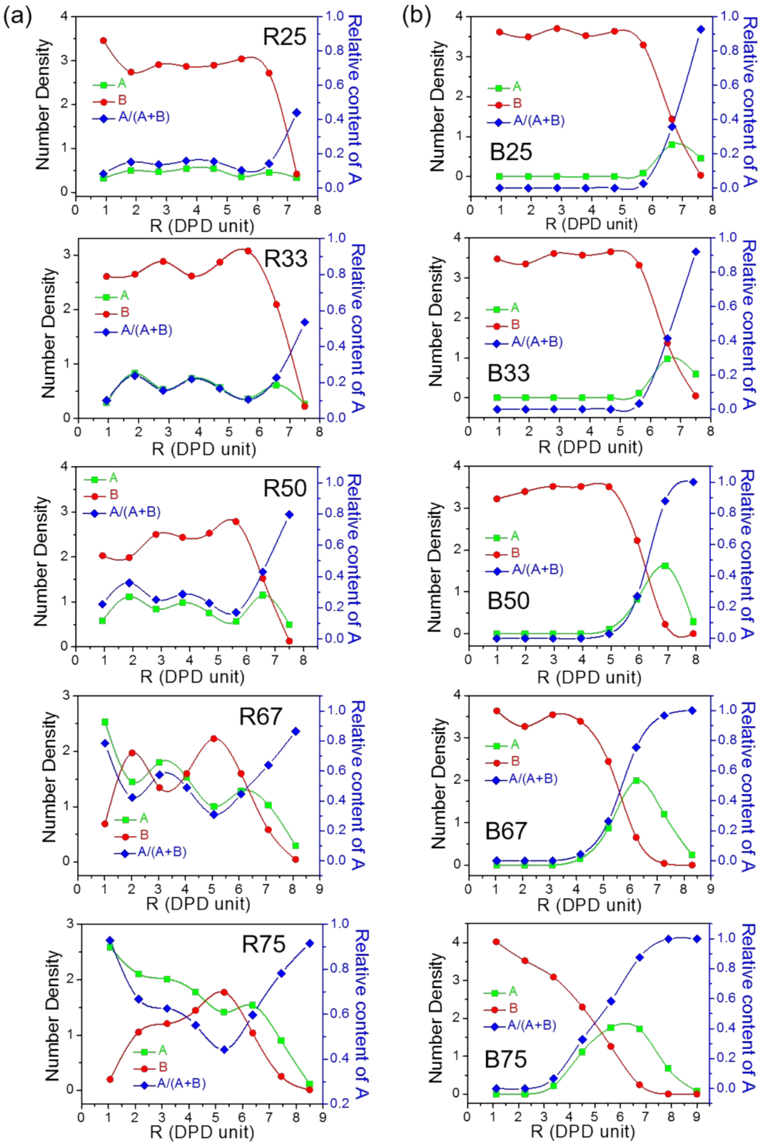


Figure S5. Density profile and relative content of hydrophilic beads in *R* direction of (a) random copolymer micelle and (b) block copolymer micelle simulated by DPD using coarse-grained models with different PAA mol%, where A/(A+B) is the relative content of hydrophilic beads in each layer of the spherical micelle.

Figure S6

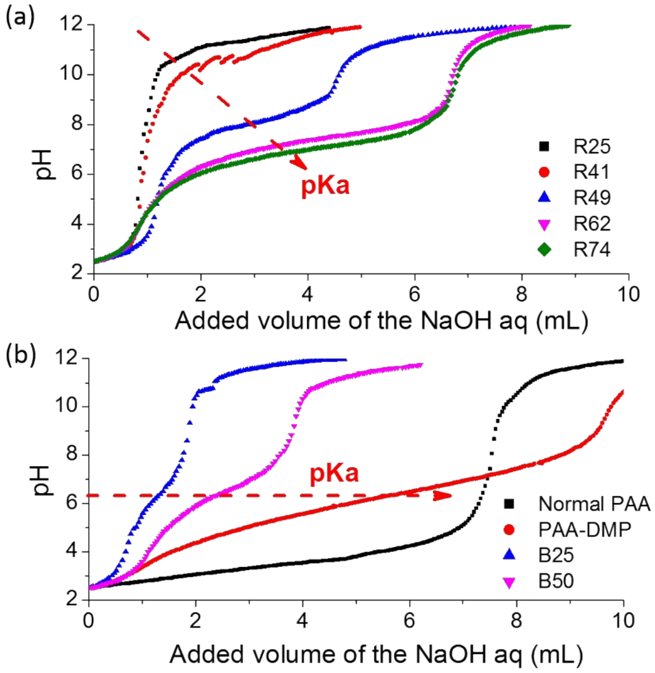


Figure S6. pH titration curves of micelles self-assembled from random and block copolymers with different PAA mol%.