

Electronic Supplementary Information (ESI) for

A “green” method for preparing ABCBA penta-block elastomer by using RAFT emulsion polymerization

Zhi Qiao, Teng Qiu, Weiwei Liu, Liangdong Zhang, Jinqiang Tu, Longhai Guo*, Xiaoyu Li*

State Key Laboratory of Organic-Inorganic Composites, Key Laboratory of Carbon Fiber and Functional Polymers, Ministry of Education, Beijing Engineering Research Centre of Synthesis and Application of Waterborne Polymer, Beijing University of Chemical Technology, Beijing 100029, P. R. China

S-1

Synthesis of *S, S'*-bis (*R, R'*-Dimethyl-*R''*-acetic acid)-trithiocarbonate (BDAAT)

Carbon disulfide (27.4g, 0.36mol), chloroform (107.5g, 0.9mol), acetone (52.3g, 0.9mol) and tetrabutyl ammonium hydrogen sulfate (2.41g, 7.1mmol) were mixed with 120mL mineral spirits in a 2L jacketed reactor cooled with tap water under nitrogen. Sodium hydroxide (50%) (201.6g, 2.52mol) was added dropwise over 90 min, the temperature was kept below 25°C. The reaction was carried out overnight with stir. Then 900mL water was added to dissolve the solid, followed by 120mL concentrated HCl to acidify the aqueous layer. Stirred for another 30 min with nitrogen purge. Filter and rinse the solid thoroughly with water. Dry to constant weight, 41.3g sample was obtained, followed by further purified by recrystallizations from 60% acetone solution to obtain a yellow crystalline solid¹.

S-2

Synthesis of PAA₄₀-*b*-PTFEA₁₀ di-block copolymers for surface tension measurements

The polymerizations were conducted in 1,4-dioxane. AA monomer (3.6g, 0.05mol), the RAFT agent ((2-(((Butylsulfanyl) carbonothioyl) sulfanyl) propanoic acid, BCSPA, 320mg; 1.25mmol), the initiator of 4,4'-azobis (4-cyanovaleric acid) (V501; 70mg; 0.250mmol) and 1,4-dioxane (17.73g) simultaneously added into a 50mL round-bottom flask equipped with a magnetic bar. The mixture was deoxygenated by using nitrogen and then heated to 70°C using water bath to carry out the RAFT polymerization. After 2 h reaction, the TFEA monomer (1.93g; 0.0125mol) was added into the flask. The reaction was carried out for another 2 hours. The mole ratio of monomer/RAFT agent/initiator was 40/1/0.2 and the solid content was 25wt%. The products were collected by precipitation by hexane and dried under vacuum at 50°C until constant weight was reached.

Table S1. GPC characterization results of Synthesized AB and ABA polymeric surfactant

Exp	Molecule Structures ¹	Block(A) $M_{n,exp}^2$ (10^3 g/mol)	Block(A) Conv. ³ (%)	Block(B) $M_{n,exp}^2$ (10^3 g/mol)	Block(B) Conv. ³ (%)	Dispersity ⁴ (\bar{D})
SS-1	PAA ₄₀ - <i>b</i> -PTFEA ₁₀	3.97	97.2	4.49	96.7	1.29
SS-2	PAA ₃₀ - <i>b</i> -PTFEA ₂₀	2.37	99.1	5.08	95.2	1.20
SS-3	PAA ₂₅ - <i>b</i> -PTFEA ₂₅	2.24	97.2	4.57	96.8	1.23
SS-4	PAA ₂₀ - <i>b</i> -PTFEA ₁₀ - <i>b</i> -PAA ₂₀	2.22	94.4	4.38	92.4	1.40
SS-5	PAA ₁₅ - <i>b</i> -PTFEA ₂₀ - <i>b</i> -PAA ₁₅	2.01	95.1	4.49	98.1	1.35
SS-6	PAA _{12.5} - <i>b</i> -PTFEA ₂₅ - <i>b</i> -PAA _{12.5}	1.88	92.2	3.61	87.2	1.27
SS-7	PAA ₄₀ - <i>b</i> -PTFEA ₂₀ - <i>b</i> -PAA ₄₀	6.79	98.7	8.57	88.2	1.26
SS-8	PAA ₄₀ - <i>b</i> -PTFEA ₄₀ - <i>b</i> -PAA ₄₀	6.79	98.7	10.7	94.5	1.44
SS-9	PAA ₄₀ - <i>b</i> -PTFEA ₆₀ - <i>b</i> -PAA ₄₀	6.79	98.7	15.6	87.2	1.37

1. The subscript indicates the designed numbers of monomer

2. $M_{n,exp}$: experimental result of number-average molecular weight

3. Conv.: monomer conversion

4. Dispersity (\bar{D}): experimental result of the polydispersity index(M_w/M_n)

S-3 Every synthesis steps of Sample E-0 (PAA₅₀-*b*-PTFEA₂₅-*b*-PHFBA₄₀₀-*b*-PTFEA₂₅-*b*-PAA₅₀ penta-block terpolymer)

Synthesis of PAA₅₀-BDAAT-PAA₅₀

The polymerization was conducted in pure deionized water. AA monomer (3.6g, 0.05mol), the RAFT agent (BDAAT, 0.141g, 0.5mmol), the initiator of 4,4'-azobis (4-cyanovaleric acid) (V501, 35mg, 0.125mmol), and deionized water (14.93g) were simultaneously added into a 500mL round-bottom septum-sealed flask equipped with a magnetic bar, in which the mole ratio of monomer/RAFT agent/initiator was kept at 100/1/0.25 and the solid content was controlled at 20wt%. The mixture was deoxygenated by using nitrogen and then heated to 75 °C using water bath to carry out the RAFT polymerization for 2 hours.

Synthesis of PAA₅₀-*b*-PTFEA₅₀-*b*-PAA₅₀ by using synthesized PAA₅₀-BDAAT-PAA₅₀

PAA₅₀-BDAAT-PAA₅₀ water solution was synthesized firstly in the same method but different reaction time (1.5h). The initiator of 4,4'-azobis (4-cyanovaleric acid) (V501, 35mg, 0.125mmol), TFEA monomer (3.85g, 0.025mol) and additional deionized water (14.87g) were simultaneously added into the flask. The solid content was controlled at 20wt%. The mixture was deoxygenated by using nitrogen and then heated to 75 °C using water bath to carry out the RAFT polymerization for 2 hours.

Synthesis of PAA₅₀-*b*-PTFEA₂₅-*b*-PHFBA₄₀₀-*b*-PTFEA₂₅-*b*-PAA₅₀ by using synthesized PAA₅₀-*b*-PTFEA₅₀-*b*-PAA₅₀

PAA₅₀-*b*-PTFEA₅₀-*b*-PAA₅₀ water solution was synthesized firstly in the same method but different reaction time (1 h). The initiator of 4,4'-azobis (4-cyanovaleric acid) (V501, 35mg, 0.125mmol), HFBA monomer (47.2g, 0.2mol) and additional deionized water (188.08g) were simultaneously added into the flask. The solid content was controlled at 20wt%. The mixture was deoxygenated by using nitrogen and then heated to 75 °C using water bath to carry out the RAFT polymerization for 2 hours.

Table S2. GPC characterization results of synthesized ABCBA penta-block terpolymers

Exp	Block(A) $M_{n,exp}^1$ (10^3 g/mol)	Block(A) Conv. ² (%)	Block(B) $M_{n,exp}^1$ (10^4 g/mol)	Block(B) Conv. ² (%)	Block(C) $M_{n,exp}^1$ (10^4 g/mol)	Block(C) Conv. ² (%)	Dispersity ³ (\bar{D})	Particle Size (d.nm)
E-1	7.11	95.3	2.34	84.3	7.89	84.2	1.21	97
E-2	7.11	95.3	2.33	85.2	9.99	77.7	1.30	115
E-3	7.11	95.3	2.49	91.1	10.4	85.6	1.42	131
E-4	7.11	95.3	3.78	88.8	10.8	96.8	1.26	143
E-5	7.11	95.3	6.13	87.2	11.1	82.0	1.34	163

1. $M_{n,exp}$: experimental result of apparent number-average molecular weight

2. Conv.: monomer conversion

3. Dispersity (\bar{D}): experimental result of the polydispersity index(M_w/M_n)

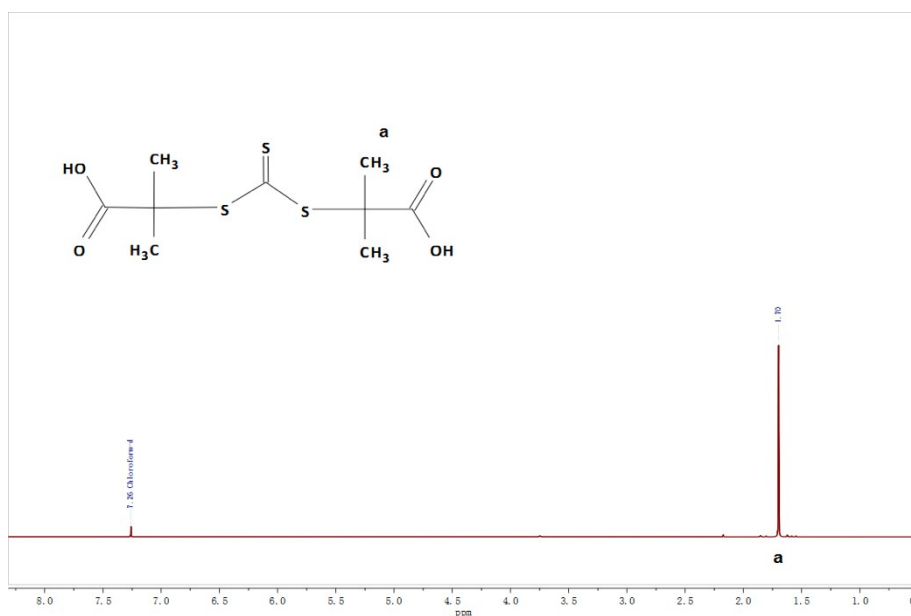


Fig.S1 ¹H NMR spectrum of BDAAT.

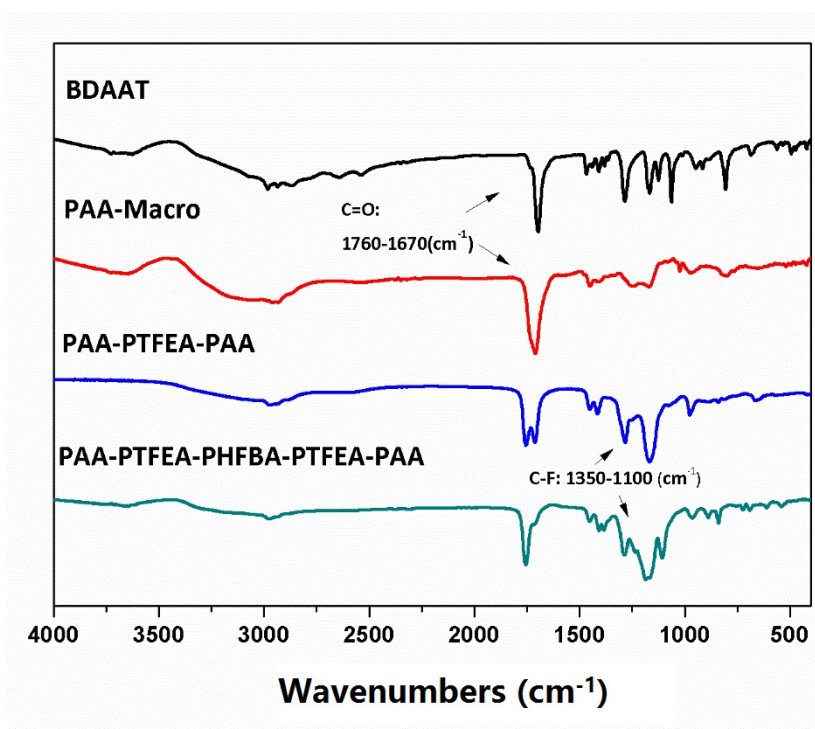


Fig.S2 FTIR spectra of sample E-0.

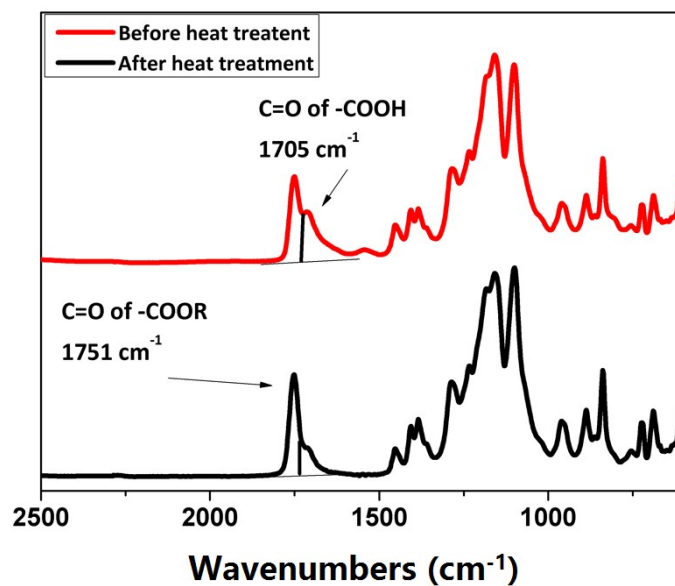


Fig.S3 ATR spectra of sample E-3 before and after heat treatment.

Table S3 T_g values of synthesized ABCBA penta-block terpolymers

Exp	Molecule Structures ¹	T_g-1^2 (°C)	T_g-2 (°C)
E-1	PAA ₅₀ - <i>b</i> -PTFEA ₆₅ - <i>b</i> -PHFBA ₂₀₀ - <i>b</i> -PTFEA ₆₅ - <i>b</i> -PAA ₅₀	-3	108
E-2	PAA ₅₀ - <i>b</i> -PTFEA ₆₅ - <i>b</i> -PHFBA ₄₀₀ - <i>b</i> -PTFEA ₆₅ - <i>b</i> -PAA ₅₀	-3	107
E-3	PAA ₅₀ - <i>b</i> -PTFEA ₆₅ - <i>b</i> -PHFBA ₆₀₀ - <i>b</i> -PTFEA ₆₅ - <i>b</i> -PAA ₅₀	-2	107
E-4	PAA ₅₀ - <i>b</i> -PTFEA ₁₁₅ - <i>b</i> -PHFBA ₄₀₀ - <i>b</i> -PTFEA ₁₁₅ - <i>b</i> -PAA ₅₀	0	106
E-5	PAA ₅₀ - <i>b</i> -PTFEA ₁₆₅ - <i>b</i> -PHFBA ₄₀₀ - <i>b</i> -PTFEA ₁₆₅ - <i>b</i> -PAA ₅₀	0	109

1. The subscript indicates the designed numbers of monomer
2. T_g values were determined via DMA method with T.A. Q800 dynamic mechanical analyser. Measurements were carried out from -30 to 150 °C at a scanning rate of 3 °C/min, a frequency of 1 Hz, and 20 μm of deformation amplitude in a single cantilever clamp. T_g values of samples were obtained from peak temperature of $\tan\delta$

REFERENCE

- 1 J. T. Lai, D. Filla and R. Shea, *Macromolecules*, 2002, **35**, 6754-6756.