

Facile Synthesis of Micron-Size Janus Particles by One-Pot Suspension Polymerization and Their Functional Modification

Tianai Tang,¹ Kai Tu,¹ Xiang Xu,¹ Jian Xie,² Duo Zhang,² Zexin Zhang,¹ Lifen Zhang,^{*1} and Zhenping Cheng^{*1}

¹State and Local Joint Engineering Laboratory for Novel Functional Polymeric Materials; Suzhou key Laboratory of Macromolecular Design and Precision Synthesis; College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou 215123, China.

²School for Radiological and Interdisciplinary Sciences (RAD-X) and Collaborative Innovation Center of Radiation Medicine of Jiangsu, Soochow University, Suzhou 215123, China.

E-mail: chengzhenping@suda.edu.cn (Z. P. Cheng) or zhanglifeng@suda.edu.cn (L. F. Zhang); Fax: 86-512-65882787

Synthesis of MS via ATRP

Synthesis of PMMA: The typical polymerization procedure with a molar ratio of $[MMA]_0/[EBPA]_0/[CuBr]_0/[PMDETA]_0 = 50/1/0.2/1$ is as follows. A homogeneous solution was obtained by adding MMA (10.0 mL, 93.9 mmol), EBPA (456.5 mg, 1.9 mmol), CuBr (53.9 mg, 0.4 mmol), and PMDETA (325.4 mg, 1.9 mmol) to a dried 25 mL round bottom flask, then the flask was sealed with a tee connector and degassed by three “freeze-pump-thaw” cycles to remove oxygen from the mixture. The flask was immersed in a water bath maintaining at 55 °C. After a prescribed time, the tee connector was opened and the reaction mixture was quenched by cool water to room temperature, diluted with tetrahydrofuran (THF) before it was passed through a Al_2O_3 column to remove the catalysts. PMMA was isolated as a white powder by precipitation from a large excess of petroleum ether and then dried under vacuum at 45 °C. Monomer conversion for MMA was determined by ¹H NMR using $CDCl_3$ as solvent. Molar mass of PMMA was determined by ¹H NMR using $DMSO-d_6$ as the solvent. The ¹H NMR spectrum of PMMA is shown in Figure S1.

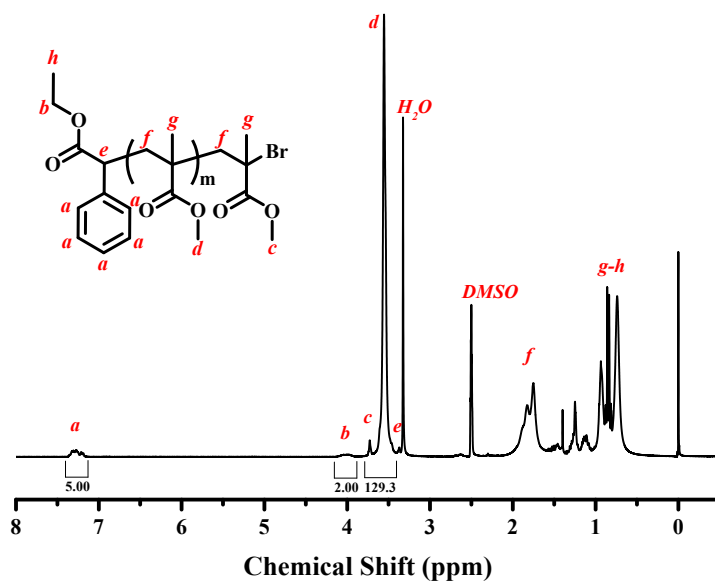


Figure S1. Typical ¹H NMR spectrum of PMMA.

Synthesis of MS: With the resultant PMMA above as the macroinitiator, the polymerization of PEGMA₅₀₀ was conducted in the same manner as MMA. The typical polymerization procedure with a molar ratio of $[PEGMA_{500}]_0/[PMMA]_0/[CuBr]_0/[PMDETA]_0 = 5.5/1/0.2/1$ is as follows. For sample 7# (Table 1) as an example, 0.4 mmol of PMMA ($M_{n,NMR} = 4600 \text{ g mol}^{-1}$) and 8.0 mL of toluene was added in a dried 25 mL round bottom flask. Then a homogeneous solution was obtained by adding PEGMA₅₀₀ (1.0 mL, 2.2 mmol), CuBr (11.4 mg, 0.08 mmol), and PMDETA (68.7 mg, 0.4 mmol), then the flask was sealed with a tee connector and degassed by three “freeze-pump-thaw” cycles to remove oxygen from the mixture. The flask was immersed in a water bath maintaining at 55 °C. After a prescribed time, the tee connector was opened and the reaction mixture was quenched by cool water to room temperature, diluted with tetrahydrofuran before it was passed through a Al_2O_3 column to remove the catalysts. Monomer conversion for PEGMA₅₀₀ was determined by ¹H NMR using $CDCl_3$ as solvent. Molar mass of MS was determined by ¹H

NMR using DMSO- d_6 as the solvent. The ^1H NMR spectrum of MS is shown in Figure S2.

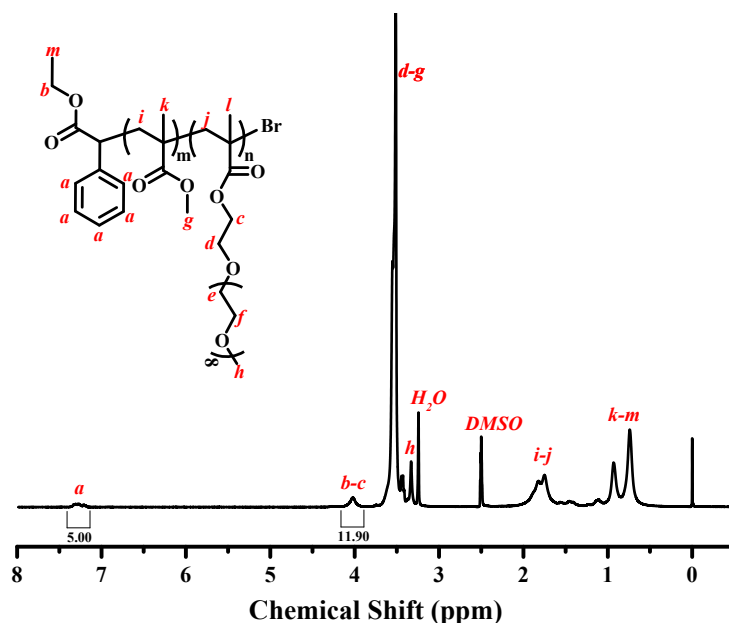


Figure S2. Typical ^1H NMR spectrum of MS.

The number average molar mass ($M_{n,\text{GPC}}$) and molar mass dispersity (D) values of the resultant polymers were determined using a TOSOH-HLC-8320 gel permeation chromatograph (GPC) equipped with a refractive index detector (Waters 2414) using TSK gel Super AWM-H columns (4.6 mm I.D. \times 15 cm \times 2) with measurable molar mass ranging from 10^3 to 10×10^5 g mol $^{-1}$. THF was used as the eluent at a flow rate of 0.35 mL min $^{-1}$ at 40 $^\circ\text{C}$. The GPC samples were injected using a TOSOH plus autosampler and were calibrated with PMMA standards obtained from TOSOH. The GPC traces are shown in Figure S3

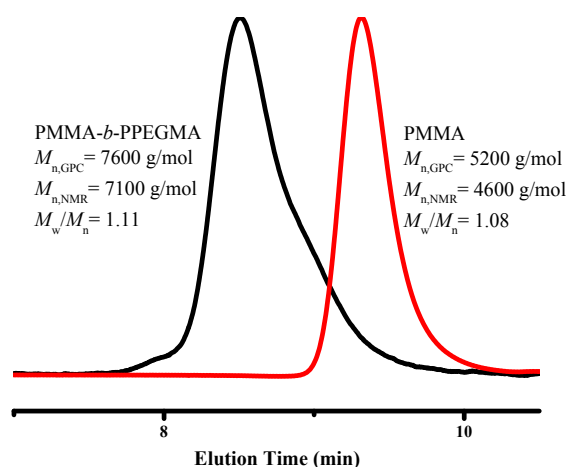


Figure S3. Typical GPC traces of PMMA and MS. (7#MS in Table 1)

Figure S4 shows the FTIR spectra of JPs, JPs-*g*-PPEGMA and JPs-*g*-PFMA. The spectrum of JPs presents four characteristic peaks at 530 cm $^{-1}$, 698 cm $^{-1}$, 1649 cm $^{-1}$ and 1730 cm $^{-1}$, which are attributed to C-Br, C-H, C=C and C=O stretching vibration,¹ respectively. These spectra exhibit some typical benzene adsorption peaks (698 cm $^{-1}$, 3000-3100 cm $^{-1}$). In addition, because the JPs-*g*-PPEGMA and JPs-*g*-PFMA were initiated on the surface of JPs, the peak intensity of C=O becomes larger while the matrix remains unchanged, and the C-Br still remains, indicating that the JPs can still be further functionally modified. The spectrum of JPs-*g*-PFMA presents two characteristic peaks at 650 cm $^{-1}$, 1144 cm $^{-1}$ (C-F)² and 1730 cm $^{-1}$ (C=O), which are attributed to C-F and C=O stretching vibration, respectively. These changes suggest that JPs, JPs-*g*-PPEGMA and JPs-*g*-PFMA was successfully synthesized.

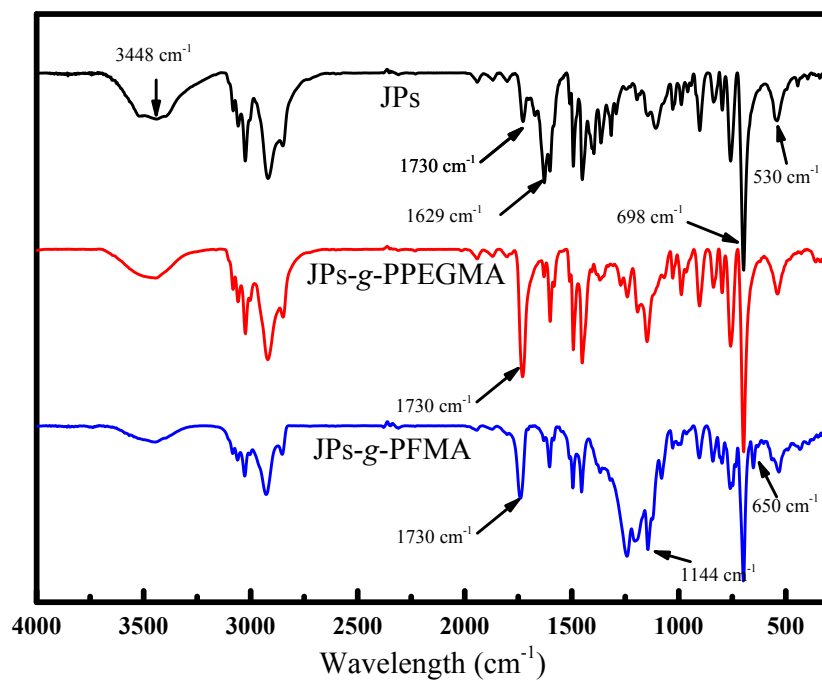


Figure S4. FTIR spectra of JPs, JPs-g-PPEGMA, JPs-g-PFMA.

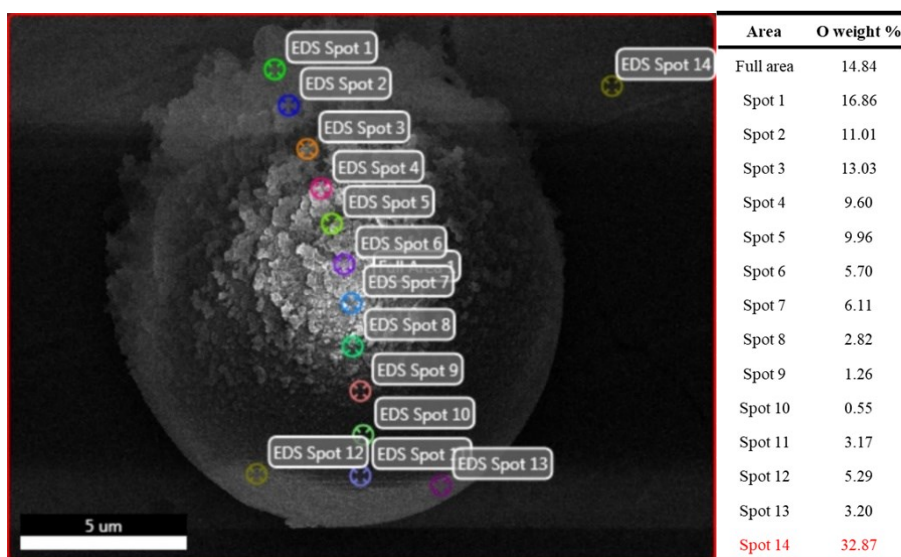


Figure S5. SEM image of EDS point analysis on the surface of JPs and the oxygen content of the corresponding point.

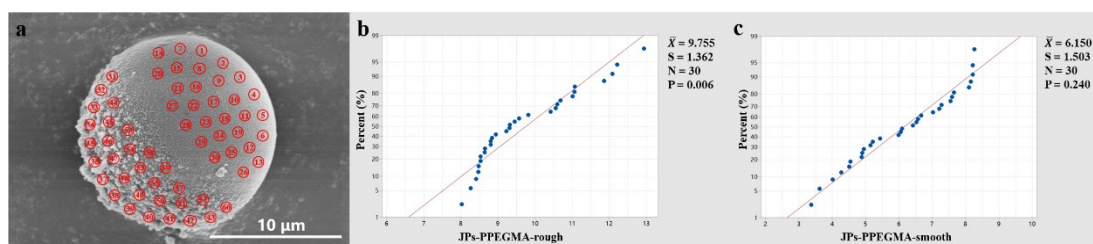


Figure S6. (a) Schematic diagram of the EDS point analysis scanning area on JPs-g-PPEGMA, (b-c) data simulation curves of the oxygen element on JPs-g-PPEGMA's (b) rough surface and (c) smooth surface.

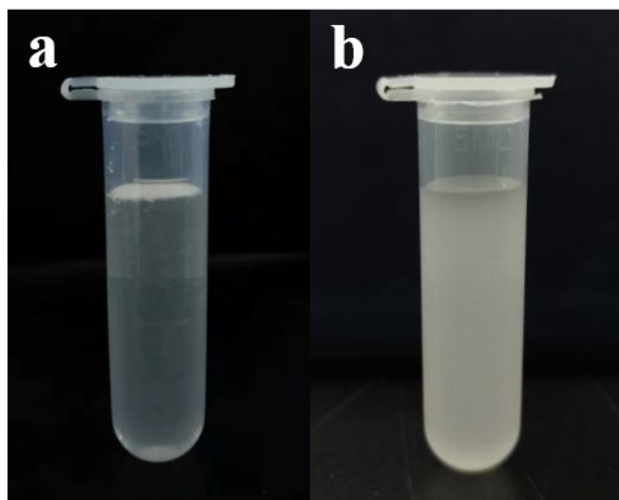


Figure S7. Optical images of (a) JPs and (b) JPs-g-PPEGMA dispersed in water.

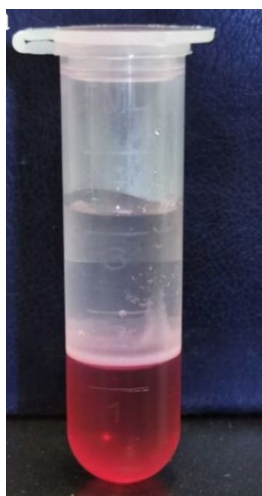


Figure S8. Optical image of the assembly of JPs-g-PPEGMA on the interface of water and trichloromethane.

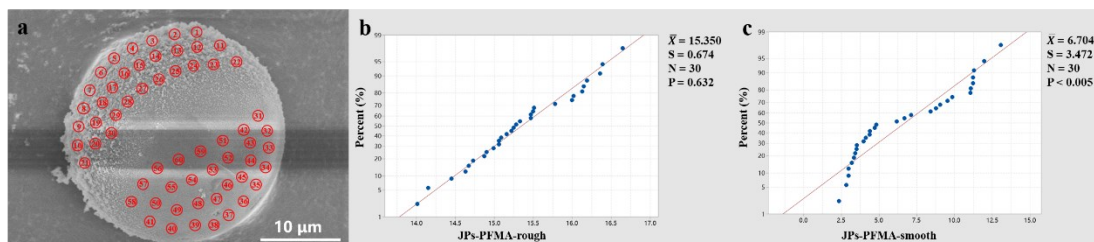


Figure S9. (a) Schematic diagram of the EDS point analysis scanning area on JPs-g-PFMA, (b-c) data simulation curves of the oxygen element on JPs-g-PFMA's (b) rough surface and (c) smooth surface.

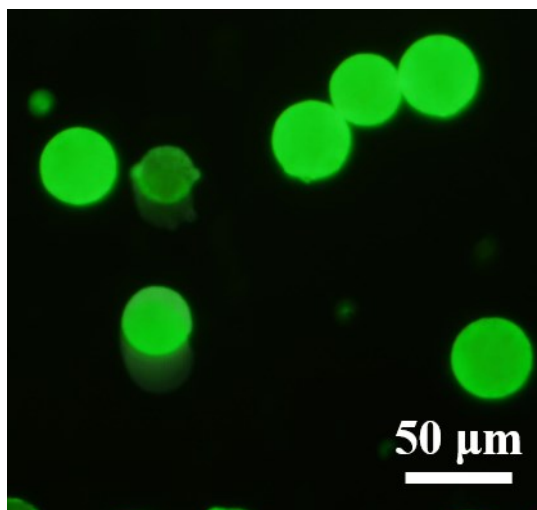


Figure S10. Fluorescence microscopy image of JP-g-PGMA-FITC which were produced by MS of HLB = 8.0.

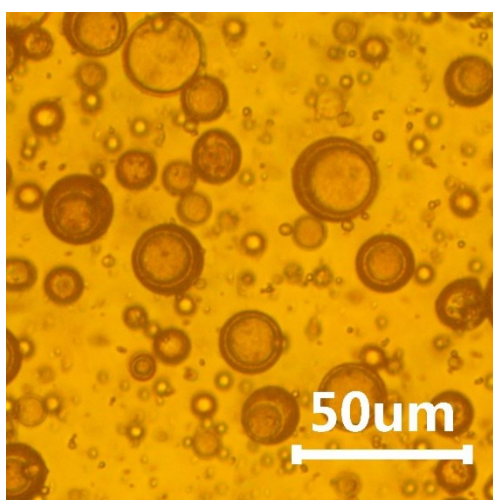


Figure S11. Optical image of particles. Polymerization conditions: oil phase: 0.75 g St, 0.25 g DVB, 0.04 g ABVN and 0.2 g 3# MS (Table 1); aqueous phase: 25.0 mL aqueous phase containing 1.0 wt. % of PVA, 0.01 wt. % of HQ, and 0.02 wt. % of Na₂SO₄, 5.0 mL of SDS aqueous solution (20.0 mg/mL); 45 °C for 1 h, 55 °C for 10 h.

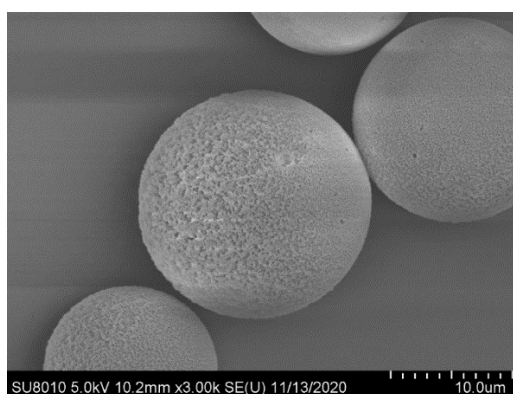


Figure S12. SEM image of the JPs prepared by 3#MS (Table 1) which was 10 wt.% of the monomer.

1. J. B. Qu, Y. Liu, J. Y. Liu, G. S. Huan, S. N. Wei, S. H. Li and J. G. Liu, *Macromolecules*, 2018, **51**, 4085-4093.
2. H. Tang, Y. Gou, Z. Yan, Q. Hu, F. Zhang, Q. Xiao, Y. Zhong and W. Zhu, *Microporous Mesoporous Mater.*, 2020, **305**, 110398.