

Supporting Information to

Controlled fabrication of polymeric Janus nanoparticles and their solution behaviors

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Materials and Instrument

Ethyl 2-bromoisobutyrate (EBriB, 98%, Sinopharm Chemical Reagent co., Ltd), N,N,N',N',N''-pentamethyldiethylenetriamine (PMDETA, 97%, Sinopharm Chemical Reagent co., Ltd), Cuprous bromide (CuBr, 97%, Sinopharm Chemical Reagent co., Ltd) were used as purchased. *Tert*-butyl methacrylate (*t*BMA, 99%, Sinopharm Chemical Reagent co., Ltd), 2-(trimethylsilyloxy)ethyl methacrylate (HEMA-TMS, 99%, Aldrich) and dimethylaminoethylmethacrylate (DMAEMA, 99%, Aldrich) were distilled under reduced pressure prior to polymerization. Anisole, isopropanol, tetrahydrofuran, and all other solvents were purchased from Shanghai Chemical Reagent Company and used as received. All reagents used were commercially available and at analytical grade. The mercury lamp (500 W) was purchased from Beijing Lighting Research Institute, used for UV-crosslinking of the PCEMA domains.

Synthesis of PtBMA-*b*-PCEMA-*b*-PDMAEMAs

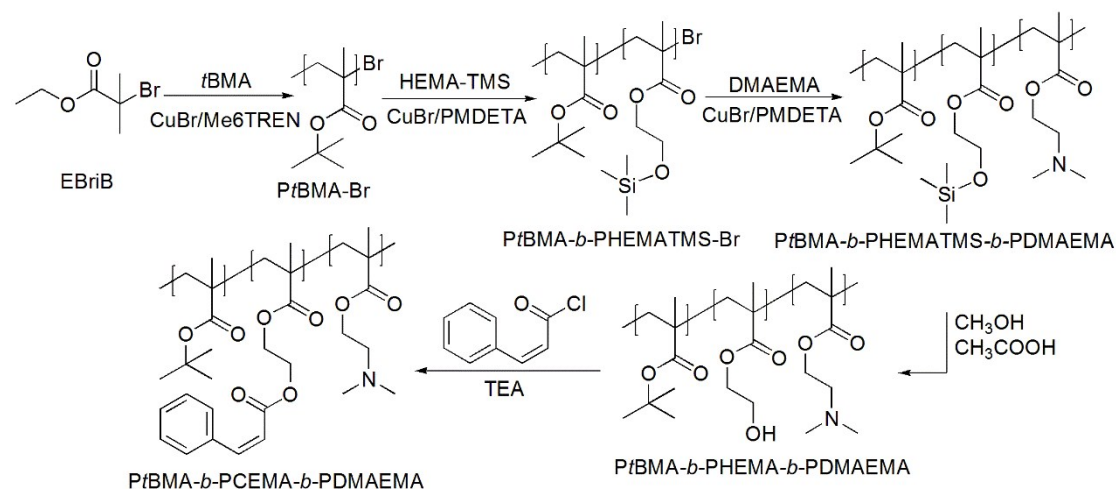


Figure S1 General Synthesis Route towards PtBMA-*b*-PCEMA-*b*-PDMAEMA

In the typical experiment, 10 mL (62.869 mmol) *t*BMA monomer was placed into a round-bottomed flask equipped with a magnetic stirrer, and 0.0601 g (0.419 mmol) CuBr, 321.4 μ L (1.257 mmol) Me₆TREN and 60.5 μ L (0.419 mmol) EBriB were added in sequence. After being subjected to three freeze-pump-thaw cycles to replace any dissolved oxygen with nitrogen, the flask was sealed and immersed in a thermostatic oil bath at 60 °C. The mixture turned dark green immediately and became viscous progressively as the reaction went on. After a prescribed time of the polymerization reaction, the mixture was exposed to air under stirring and diluted with acetone and passed through a column of neutral alumina to remove copper catalyst, then precipitated in excess methanol. The collected sample was then dried under vacuum overnight at 50°C to obtain the purified macro-initiator PtBMA-Br.

0.1 mmol of the *Pt*BMA-Br initiator was dissolved with 3 mL anisole in a round-bottomed flask, 0.1 mmol CuBr, 0.3 mmol PMDETA and a certain amount of HEMATMS monomer were added in sequence. After being subjected to three freeze-pump-thaw cycles to replace any dissolved oxygen with nitrogen, the flask was sealed and immersed in a thermostatic oil bath at 120 °C. After 24 h the polymerization was stopped by exposure to the air and the solution was diluted with acetone and passed through the column of neutral alumina then precipitated in excess petrol ether and dried under vacuum overnight at 50 °C to obtain diblock copolymer *Pt*BMA-PHEMATMS with a bromine end.

*Pt*BMA-*b*-PHEMATMS-*b*-PDMAEMA triblock terpolymers were synthesized from further chain extension from *Pt*BMA-*b*-PHEMATMS diblock copolymers with an -Br end as the macro-initiator. In the typical experiment, a typical 0.1 mmol of the *Pt*BMA-PEMATMS-Br initiator was dissolved with 4 mL anisole, addition of 0.1 mmol CuBr, 0.3 mmol PMDETA and a certain amount of DMAEMA monomer were carried out in sequence. After three freeze-pump-thaw cycles and being sealed, the reaction started at 120 °C. After a certain time the reaction was stopped by exposure to the air. The solution was diluted with acetone and passed through a column of neutral alumina to remove copper catalyst, then precipitated in excess petrol ether. The obtained solid *Pt*BMA-*b*-PHEMATMS-*b*-PDMAEMA was dried under vacuum overnight at 55 °C overnight.

Conversion of *Pt*BMA-*b*-PHEMATMS-*b*-PDMAEMA to *Pt*BMA-*b*-PCEMA-*b*-PDMAEMA was conducted by selective acidic hydrolysis of the TMS-groups on PCEMA blocks, followed by esterification with cinnamoyl chloride. For sufficient conversion, *Pt*BMA-*b*-PHEMATMS-*b*-PDMAEMA (0.5 g) was dissolved in a mixture of 10 mL THF and 10 mL methanol containing 1 mL acetic acid as catalyst. The mixture was stirred for 5 h at room temperature and quantitative removal of the TMS protective group was confirmed by ¹H-NMR analysis. The solvents were removed by evaporation and the newly formed hydroxyl groups of the PHEMA block were reacted with a 3 fold excess of cinnamoyl chloride in THF and TEA at room temperature overnight. The resultant *Pt*BMA-*b*-PCEMA-*b*-PDMAEMA was purified by dialysis against ethanol overnight then dialyzed against water and freeze-dried.

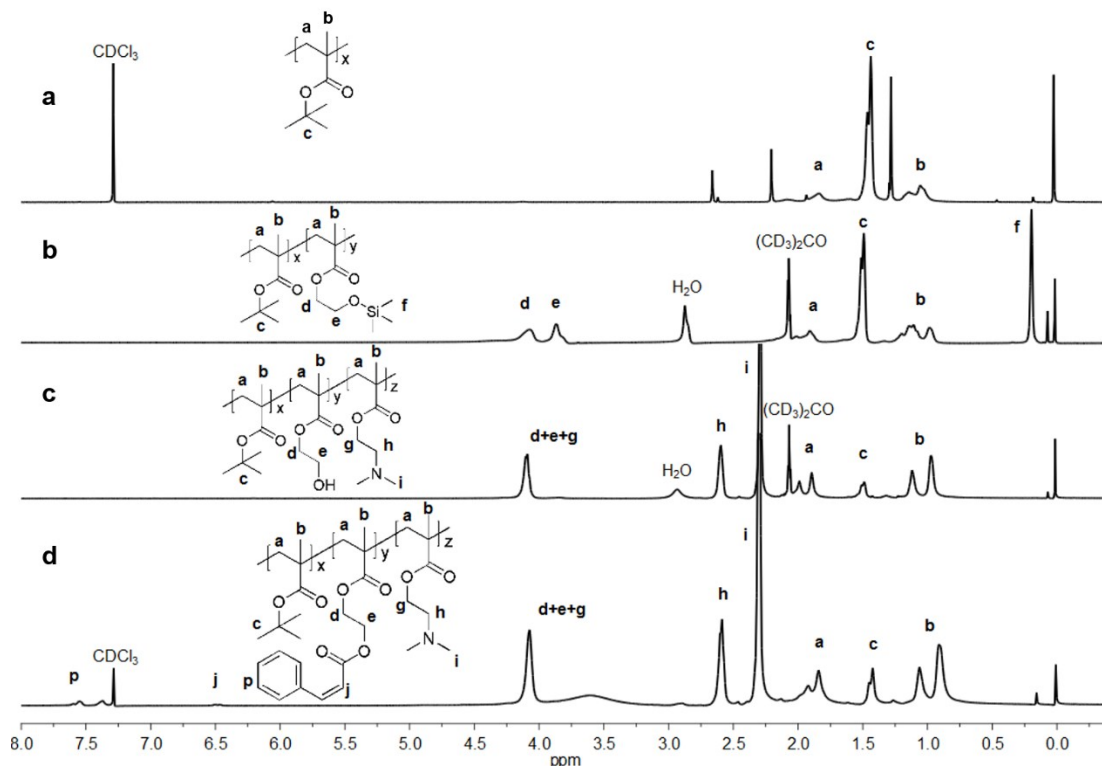


Figure S2 ^1H NMR spectra of (a) PtBMA in CDCl_3 , (b) PtBMA-*b*-PHEMATMS in $(\text{CD}_3)_2\text{CO}$, (c) PtBMA-*b*-PHEMA-*b*-PDMAEMA in $(\text{CD}_3)_2\text{CO}$, and (d) PtBMA-*b*-PCEMA-*b*-PDMAEMA in CDCl_3

Formation of core-corona micelles

The PtBMA-*b*-PCEMA-*b*-PDMAEMA terpolymers were dissolved in isopropanol and prepared at the concentration of 1 g/L. The as-prepared micellar solutions were annealed at 50 °C for 48 h to ensure an equilibrated system.

Formation of compartmentalized nanostructures

To obtain the self-assembled nanostructures, 20 mL of the as-prepared micellar solution were dialyzed against 2 L of ultrapure water which is the selective solvent for the PDMAEMA block.

Preparation of Janus particles

The cinnamoyl moieties of the PCEMA block provide an additive-free cross-linking chemistry, as they are able to polymerize under UV-irradiation.^{1,2} In order to permanently fix the phase-separated state of the compartmentalized nanostructures, the solutions were irradiated for 40 min using the mercury lamp that enabled UV-crosslinking of PCEMA domains. The irradiated solution was then dialyzed against 2 L of THF as a common solvent for all blocks, to yield the well-dispersed Janus particles. To further investigate the surface activity of the Janus particles, aqueous solutions were prepared at the concentration varied from 0.1 g/L to 1×10^{-5} g/L.

Characterization of the nanostructures and Janus nanoparticles

Transmission electron microscope (TEM) was performed in bright-field mode on JF2100 electron microscope operated at 200 kV. The samples were prepared by placing one drop of the polymer solution (0.05 g/L) onto carbon-coated copper grid. For selective staining, the TEM specimens were

exposed to RuO₄ vapor (stains PCEMA) for 20 min or I₂ vapor (stains PDMAEMA) for 2 h.

Dynamic laser scattering (DLS) measurements were performed at a scattering angle of 90° on Brookhaven BI-200SM with a laser operating at a wavelength of $\lambda = 532$ nm. Before light scattering measurements, all sample solutions were filtered through a polytetrafluoroethylene filter with a pore size of 0.22 μm . All the light scattering experiments were performed at 25 °C.

The equilibrium surface tension was measured at 25 °C by the Wilhelmy plate technique (Cahn Radian DCA 322 Analyzer, Thermo, USA), and the measurement was carried out until it deviated within ± 0.5 mN/m for the last two readings. To ensure equilibrium before the measurements, the solutions were placed in closed environment and stood overnight.

The dynamic surface tension was measured at 20 ± 1 °C by the maximum bubble pressure method with a Krüss BP100 bubble pressure tensiometer. Hydrophobically modified glass capillary with an inner diameter of 0.237 mm was used for the measurements, and the uncertainties in the measurements were ± 0.2 mN/m. Surface ages of the bubbles varied from 10 ms to 100000 ms.

References

1. Z. Lu, G. Liu and F. Liu, *Macromolecules*, 2001, **34**, 8814-8817.
2. R. Zheng, G. Liu and X. Yan, *Journal of the American Chemical Society*, 2005, **127**, 15358-15359.