

Supporting Information to

Polymeric Janus nanoparticles from triblock terpolymer micellar dimers

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Materials and Instrument

Isopropanol, acetone, acetonitrile and all other solvents were purchased from Shanghai Chemical Reagent Company and used as received. The mercury lamp (500 W) was purchased from Beijing Lighting Research Institute, used for UV-crosslinking of the PCEMA domains.

Formation of core-corona micelles

The PMMA-*b*-PCEMA-*b*-PDMAEMA terpolymers were dissolved in isopropanol/acetonitrile (3:1 v/v) 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 micellar dimers

To obtain the self-assembled micellar dimers, 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 micellar dimers, the solution was 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 acetone 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 method

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.

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 μ m. 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.

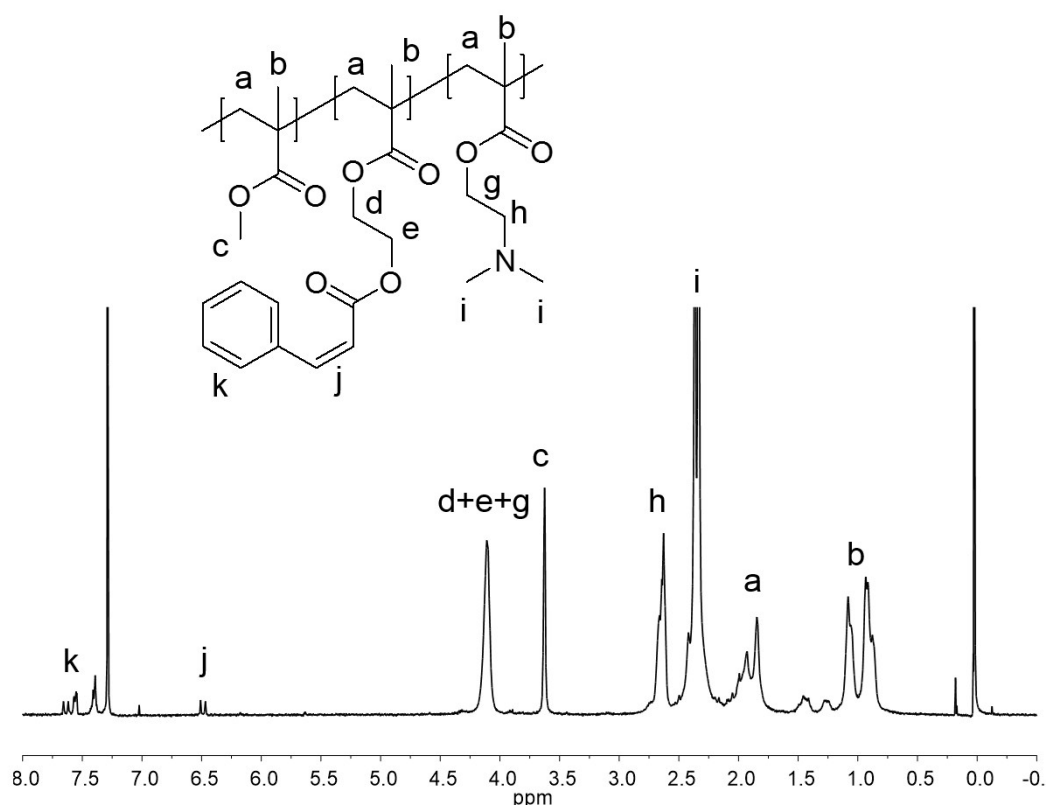


Figure S1. ¹H NMR spectrum PMMA-*b*-PCEMA-*b*-PDMAEMA.

Table S1. Important parameters of PMMA-*b*-CEMA-*b*-PDMAEMA triblock terpolymers and their precursors.

Polymer ^{a)}	Mn (g/mol) ^{b)}	PDI ^{c)}	Weight Fraction
M ₂₆₆	26,600	1.38	100
M ₂₆₆ H ₁₂₁	50,700	1.21	53:47
M ₂₆₆ H ₁₂₁ D ₂₆₉	92,900	1.21	29:26:45
M ₂₆₆ C ₁₂₁ D ₂₆₉	95,500	1.20	28:28:44

^{a)} M = poly(methyl methacrylate), H = poly(2-(trimethylsilyloxy)ethyl methacrylate), D = poly(2-(dimethylamino)ethyl methacrylate), C = poly(2-cinnamoyloxyethyl acrylate); the numbers in the subscript denote the degrees of polymerization.

- b) Mn was determined by GPC measurements with THF as eluent.
- c) PDI indicated the polydispersity index of the polymers (M_w/M_n), where weight-average molecular weight (M_w) and number-average molecular weight (M_n) were determined.

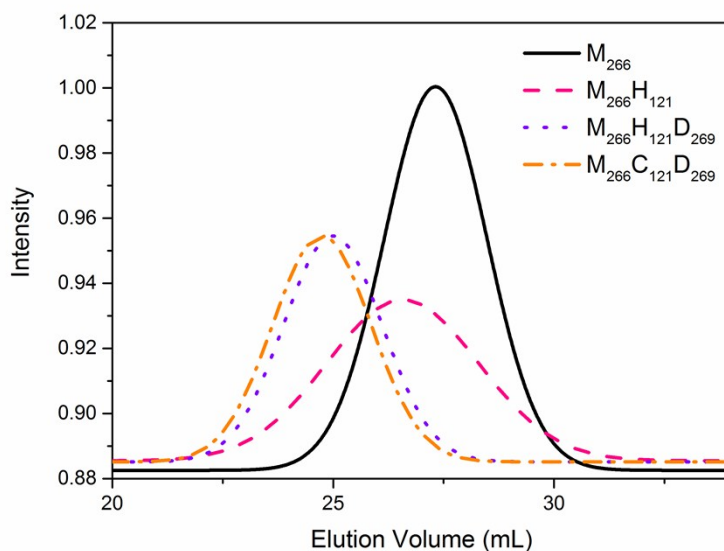


Figure S2. GPC traces of $PMMA_{266}$, $PMMA_{266}$ -b- $PHEMA_{121}$, $PMMA_{266}$ -b- $PHEMA_{121}$ -b- $PDMAEMA_{269}$, and $PMMA_{266}$ -b- $PCEMA_{121}$ -b- $PDMAEMA_{269}$.

Solubility test

Polymer solubility in different solvents was tested by observation method.[3] At the ambient temperature, 100 mg of the synthesized polymers were placed in the tubes separately and 3 mL of the solvent was then added. The solvents used in the solubility experiment include acetone, ethanol, isopropanol, tetrahydrofuran, acetonitrile, cyclohexane, dichloromethane and water. Polymers dissolved completely within 3 min were marked as readily soluble (+++), dissolved completely after being heated at 60 °C within 3 min were marked as soluble (++) , partially dissolved after being heated at 60 °C were marked as slightly soluble and those who were unable to be dissolved were marked as insoluble (-).

Table S2. Polymer solubility test results

Solvent	PMMA	PCEMA	PDMAEMA
Acetone	+++	+++	+++
Ethanol	-	-	+++
Tetrahydrofuran	+++	+++	+++
Cyclohexane	-	+++	-
Dichloromethane	+++	+++	+++
Isopropanol	+	-	+++
Acetonitrile	+++	+	+++
Isopropanol/Acetonitrile (3:1 v/v)	++	-	+++

Water	-	-	+++
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+++ Readily soluble, ++ soluble, + partially soluble, - insoluble

UV-crosslinking of PMMA-*b*-PCEMA-*b*-PDMAEMA micellar dimers

The degree of UV crosslinking was monitored by UV–Vis spectra and calculated with the equation $DC = 1 - A_t/A_0$ (A_0 and A_t are the initial absorbance and the absorbance at irradiation time).

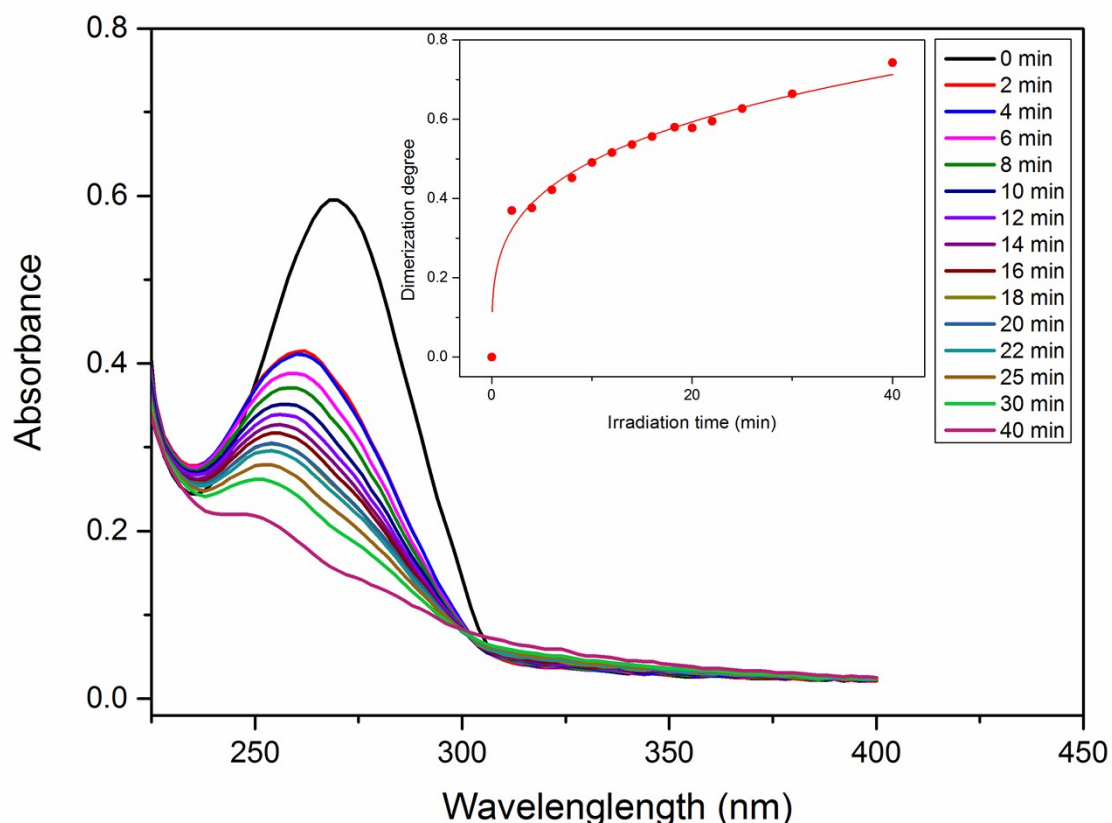


Figure S3. UV-crosslinking of micellar dimers traced by UV spectra with the micelle solution of 20 mL 1 g/L. Inset is the plot of the calculated crosslinking degree of micellar dimers against irradiation time.

1. Lu, Z., G. Liu, and F. Liu, *Block Copolymer Microspheres Containing Intricate Nanometer-Sized Segregation Patterns*. *Macromolecules*, 2001. **34**(25): p. 8814-8817.
2. Zheng, R., G. Liu, and X. Yan, *Polymer nano- and microspheres with bumpy and chain-segregated surfaces*. *J Am Chem Soc*, 2005. **127**(44): p. 15358-9.
3. Zhang, W., et al., *Preparation of multicompart ment micelles from amphiphilic linear triblock terpolymers by pH-responsive self-assembly*. *Colloid and Polymer Science*, 2015. **293**(10): p. 3013-3024.