Supporting Information

Inky flower-like supermicelles assembled from π -conjugated block copolymers

Meijing Wang, Yulin Zhu, Liang Han, Rui Qi and Feng He*

Polymer Synthesis

All of the air- or moisture-sensitive reactions were carried out in dried glassware under an argon pressure using Schlenk techniques or in a glove box under nitrogen atmosphere. The detailed procedure path of synthesis is illustrated in Scheme S1.



Scheme S1. Synthetic route for the preparation of dibock copolymers PPV-b-P2VP.

Synthesis of 2,5-bis(2-octyloxy)-4-methylbenzaldehyde (1). The compound (1) was synthesized referring to procedures described by articles. ¹ ¹H NMR (400 MHz, CDCl₃): δ 10.42 (s, 1H), 7.22 (s, 1H), 6.79 (s, 1H), 4.02 (t, 2H, 6), 3.95 (t, 2H, 6), 2.27 (s, 3H), 1.81-1.77 (m, 4H), 1.47-1.45 (m, 4H), 1.36-1.27 (br, 16H), 0.97-0.87 (m, 6H).



Figure S1. ¹H NMR spectra of 2,5-bis(2-octyloxy)-4-methylbenzaldehyde in CDCl₃

Synthesis of N-(2,5-bis(2-octyloxy)-4-methylbenzylidene) aniline (2). A mixture of 2,5-bis(2-octyloxy)-4-methylbenzaldehyde (compound 1, 5.7 g, 15.15 mmol) and aniline (3.08 g, 33.03 mmol) was stirred for 3 h at 60 °C under reduced pressure, then the temperature raised to 120 °C to remove redundant aniline. The yielded deep yellow viscous oil (compound 3, 6.56 g, 14.53 mmol, 95.91 %) needed to be stored at low temperature and under dark environment because it was easy to decompose. ¹H NMR (400 MHz, CDCl₃): δ 8.86 (s, 1H), 7.58 (s, 1H), 7.40-7.37 (m, 2H), 7.23-7.19 (m, 3H), 6.77 (s, 1H), 4.05-3.97 (m, 4H), 2.27 (s, 3H), 1.82-1.76 (m, 4H), 1.50-1.43 (m, 4H), 1.38-1.26 (br, 16H), 0.90-0.86 (m, 6H).



Figure S2. ¹H NMR spectra of N-(2,5-bis(2-octyloxy)-4-methylbenzylidene) aniline in CDCl₃.

Synthesis of Poly(2,5-di(2'-octyloxy)-1,4-phenylenevinylene)-aldehyde (3, PPV-CHO). In a round-bottom flask, potassium tert-butoxide (1.12 g, 9.97 mmol) was stirred in 120 mL anhydrous DMF at 50 °C. Maintaining temperature, a solution of N-(2,5-bis(2-octyloxy)-4-methylbenzylidene) aniline (compound **3**, 1.5 g, 3.32 mmol) in 20 mL anhydrous DMF was added into mixture. After stirring for 1 h, the mixture was poured into 250 mL 1M hydrochloric acid and stirred for 48 h. Then the reaction mixture was extracted with chloroform (3×50 mL), after that the organic phase was successively washed by aqueous NaHCO₃ and water followed by drying with MgSO₄ and rotary evaporating. Product with low dispersity was successively collected and fractionated using methanol, acetone, and hexane through Soxhlet extraction, and the fractionated product in hexane was precipitated into methanol. The value of $M_n = 2074$ and the number-average degree of polymerization n = 7 for PPV-CHO was determined by ¹H NMR. The polydispersity index was measured at 1.056 by GPC in THF. ¹H NMR (400 MHz, CDCl₃): δ 10.45 (s, 1H), 7.63-7.40 (m), 7.33-7.08 (m), 6.73 (s, 1H), 4.13-3.95 (m, 28H), 2.24 (s, 3H), 1.91-1.79 (m), 1.58-1.47 (m), 1.43-1.29 (m), 1.42-1.25 (m), 0.91-0.86 (m).



Figure S3. ¹H NMR spectra of PPV₇-CHO in CDCl₃.

Synthesis of Poly(2,5-di(2'-octyloxy)-1,4-phenylenevinylene)-block-poly (2-vinylpyridine) (PPV-*b*-P2VP). In a glovebox filled with N₂ at -78 °C, 86.9 µL of sec-BuLi (1.3 M in hexane) was quickly added to a stirring solution of dried LiCl (45.7 mg, 1.13 mmol) and 1,1-diphenylethylene (DPE, 20 µL, 0.113 mmol) in THF (2 mL). Then maintaining -78 °C, a certain amount of 2-vinylpyridine (2VP) in THF (2 mL) was added to the mixture. After the reaction went on running for 2 h at -78 °C, a solution of PPV₇-CHO (20 mg, 0.01 mmol) in benzene (2 mL) was quickly injected into the

reaction mixture to quench the anion polymerization. Then the reaction proceeded to room temperature and was stirred for additional 12 h. As the reaction stopped, the reaction mixture was poured into 25 mL chloroform and washed successively with aqueous HCl (pH = 3), water and aqueous NaHCO₃ 3 times, respectively. After rotary evaporating, the crude residue was purified by chromatography (silica gel, eluent was changed from chloroform to chloroform/Et3N 9:1), and finally orange solid was obtained. The block ratio of produced PPV₇-*b*-P2VP_n was determined by ¹H NMR and GPC.



Figure S4. ¹H NMR spectra of PPV₇-*b*-P2VP₁₀ in CD₂Cl₂.



Figure S5. ¹H NMR spectra of PPV_7 -*b*-P2VP₁₈ in CD_2Cl_2 .



Figure S6. ¹H NMR spectra of PPV₇-*b*-P2VP₂₅ in CD₂Cl₂.



Figure S7. GPC traces (UV-Vis) of PPV₇-CHO and BCPs PPV₇-*b*-P2VP_n.

Table S1. Summary data of ¹H NMR and GPC of PPV₇-*b*-P2VP_n.

	block ratio	Retention			Integral of fields of	Number of
BCPs	of	Time	$M_{\rm n}$	Đ	aromatic ring in ¹ H	P2VP calculated
	PPV/P2VP	(min)			NMR $(I_a)^{a)}$	by ¹ H NMR ^{b)}
PPV ₇ - <i>b</i> -P2VP ₁₀	1:1.4	8.973	3132	1.10	78.6	10.15
PPV ₇ - <i>b</i> -P2VP ₁₈	1:2.6	8.889	4021	1.13	109.8	17.95
PPV ₇ - <i>b</i> -P2VP ₂₅	1:3.6	8.802	4759	1.18	139.5	25.38

^{a)} the integral was calculated by using the integral of OCH₂ groups of PPV₇ as standard,

which was calibrated as 28; ^{b)} the number of P2VP was calculated by Eq. S1.

$$n = \frac{I_a - 28 - 10}{4}$$
(S1)



Figure S8. Inky flower-like supermicelles imaged by HIM.



Figure S9. Inky flower-like supermicelles imaged by LCSM.



Figure S10. TEM observation of micelles growth from PPV₇-*b*-P2VP₂₅ monitored at a) 70 °C; b) 60 °C; c) 40 °C and d) aging for 24 h.



Figure S11. TEM observation of micelles growth from PPV₇-*b*-P2VP₁₈ monitored at a) 70 °C; b) 60 °C; c) 40 °C and d) aging for 24 h.



Figure S12. TEM images (×6k) of micelles grown from PPV_7 -*b*- $P2VP_{25}$, PPV_7 -*b*- $P2VP_{18}$ and PPV_7 -*b*- $P2VP_{10}$ in various polar solvents. a), d), g) methanol; b), e), h) isopropanol and c), f), i) isobutanol.



Figure S13. TEM images (×15k) of micelles grown from PPV_7 -*b*-P2VP₂₅, PPV_7 -*b*-P2VP₁₈ and PPV_7 -*b*-P2VP₁₀ in various polar solvents. a), d), g) methanol; b), e), h) isopropanol and c), f), i) isobutanol.

Methods

Equipment and materials. One block of the BCPs poly(2,5-di(2'-octyl)-1,4-phenylenevinylene₇-aldehyde (PPV₇-CHO) homopolymer was prepared through the procedures described by the previous report,¹ then the fluorescent diblock copolymers PPV₇-*b*-P2VP_n used as building blocks of self-assembly were synthesized through quenching the anionic polymerization of P2VP with the PPV₇-CHO. The detailed procedures were described above. The anionic polymerization was carried out in a glove box filled with nitrogen atmosphere to avoid ambient oxygen and water. The block ratios of BCPs were determined by GPC and ¹H NMR spectroscopy. GPC measurements were operated on a Waters ACQUITY APC System equipped with a UV detector (Waters ACQUITY TUV) and 3 series connected chromatographic columns (ACQUITY APC XT 450, 200, 45, 4.6 × 150 mm). THF was used as the eluent, with a flow rate of 0.5 mL min⁻¹at 40 °C. Samples were dissolved in the eluent (1 mg mL⁻¹) and filtered with an organic phase filter (polytetrafluoroethylene membrane of 0.45 mm pore size) before analysis. Polystyrene standards (Aldrich) were used for calibration.**Preparation of self-assembly micelles.**PPV₇-*b*-P2VP_n were dissolved in spectrum

pure methanol, ethanol, isopropanol as well as mixed solvents of methanol and water at the concentration of 0.02 mg mL⁻¹ in the 20 mL sealed vial. Then, the prepared solutions were heated at 80 °C for 1 h, and then slowly cooling to room temperature (RT, 25 °C) followed by aging for 24 h, which was called the process of "heating–cooling–aging".

Characterizations

Transmission electron microscopy (TEM). TEM micrographs were captured on the Hitachi HT7700 microscope equipped with an AMF-5016 charge-coupled device camera under the voltage of 100 kV. Then the original images were analyzed by using DigitalMicrograph software package developed by the US Gatan company. TEM samples were prepared by dropping 10 μ L aliquot of the solution onto carbon-coated copper grids and followed by evaporation.

Cryo-Transmission electron microscopy (Cryo-TEM). The Cryogenic transmission electron microscopy (Cryo-TEM) experiments were performed on the Titan Krios G3i/CryoTitan Cryo-TEM with autoloader system (cryo-holder) operating at -170 °C under the voltage of 300 kV. The Titan Krios G3i is equipped with an XFG filament operating at 300 kV, and the images were recorded using a 4k × 4k Falcon 3EC camera. The CryoTitan is equipped with a field emission gun (FEG) operating at 300 kV. Images were recorded using a 4k × 4k Falcon CCD camera. Then the original images were analyzed through DigitalMicrograph software package developed by the US Gatan compony. The solution of scarf micelles was dropped on copper grid, after the evaporation of the solvent, the grids were put into autoloader system in liquid nitrogen bath for freezing to prepare the samples. SAED patterns of scarf micelles were also collected by Titan Krios G3i Cryo-TEM.

Atomic force microscopy (AFM). AFM analyses were performed under ambient conditions in Asylum Research AFM using AC air mode. The sensor cantilevers were silicon probe reflex coated with aluminum manufactured by Budgetsensors Company. Results were analyzed by Gwyddion software. The used samples were copper grids who had been used in the TEM characterization.

He-ion microscopy (HIM). HIM imaging was performed on the Zeiss ORION

11

NanoFab multi-ion beam system. The GFIS gun pressures were $\sim 2.6 \times e^{-6}$ Millibar, and the beam current was about 7.6 pA used for imaging experiments. The used samples were copper grids who had been used in the TEM characterization.

Laser scanning confocal microscopy (LSCM). LSCM photographs were obtained from Leica SP8 confocal attached to a Leica DMI6000 inverted epifluorescence microscope with $a \times 63$ (numerical aperture 1.4) oil-immersion objective lens. A drop of sample solution of scarf micelles was extracted and put on a clean slide followed by sealing with a cover slip, which was prepared for observing. The samples of formed scarf micelles in solution were excited using an argon laser operating at 405 nm, and the confocal images were obtained using digital detectors with observation windows of 530-630 nm.

UV-Vis absorption spectra. The UV-Vis absorption spectra were recorded by the SHMADZU UV-3600. A capped cuvette filled with the solution of PPV_7 -*b*-P2VP_n was placed in the holder of spectrophotometer which was linked with a temperature controller. The solution in cuvette was heated to 80 °C and kept for 1 h. Then the solution was gradually cooled to RT. The UV-Vis spectra and the real-time temperature of the solution was recorded every 5 °C during the cooling down process. After the sample solution was cooled to RT, the measurement was changed to be carried out every 30 min until aging for 24 h.

References

1 B. D.Olsen, R. A. Segalman, *Macromolecules* 2005, **38**, 10127-10137.