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Monodisperse Fiber-Like Micelles of Controlled Length and Composition with an Oligo(*p*-phenylenevinylene) Core via “Living” Crystallization-Driven Self-Assembly

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Supporting Information Placeholder

ABSTRACT: We report the preparation of a series of fiber-like micelles of narrow length distribution with an oligo(*p*-phenylene vinylene) (OPV)-core and a poly(*N*-isopropyl acrylamide) (PNIPAM) corona via two different crystallization-driven self-assembly (CDSA) strategies. The average length L_n of these micelles can be varied up to 870 nm by varying the temperature in self-seeding experiments. In addition, seeded growth was employed not only to prepare uniform micelles of controlled length, but also to form fiber-like A-B-A triblock co-micelles with an OPV-core.

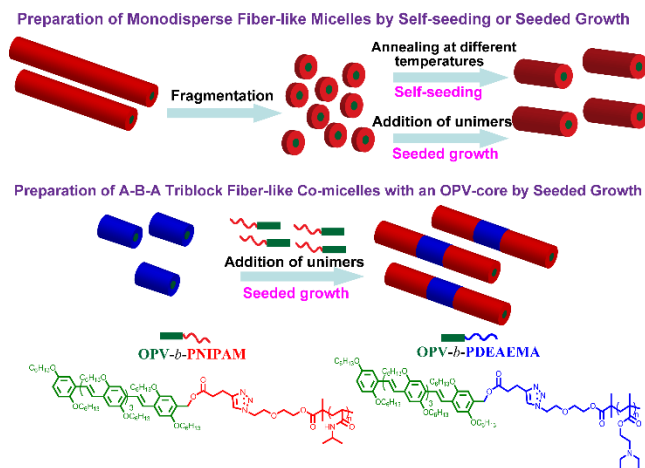
The preparation of functional and colloiddally stable one-dimensional (1D) or two-dimensional (2D) polymer nanostructures of uniform size remains a major challenge.¹ The way forward takes advantage of lessons from the field of polymer crystallization, where we know that spontaneous nucleation in solution leads to polymer crystals with a broad range of sizes.² In contrast, two special polymer crystallization techniques, “self-seeding”³ and seeded growth⁴ allow the preparation of 2D polymer crystals uniform in size. Self-seeding refers to a protocol where one heats a suspension of polymer crystals until all but a few micron-size crystallites persist.³ Upon cooling, they serve as nuclei, and all the crystals grow in parallel, leading to uniform structures. In seeded growth, one adds a solution of polymer in a good solvent to a suspension of tiny crystallites or uniform crystals in an appropriate solvent.⁴ If one can avoid homonucleation, all the polymer added grows epitaxially and uniformly onto the pre-formed seeds. Crystal growth resembles a living polymerization process.

Coil-crystalline block copolymers can self-assemble in solution to form low curvature structures (2D platelets, 1D fibers) with a semicrystalline core.¹ Over the past decade, a large number of these polymers have been investigated.¹⁻⁶ Polyferrocenyldimethylsilane (PFS) block copolymers are the classic example that have been shown to form uniform fiber-like micelles with control over length, both through self-seeding and seeded growth.^{3a-d,4a, 4b} Seeded growth also enables the formation of 1D block comicelles,^{4a,4b,6a} where a block copolymer with a common core-forming block but a different corona is grown uniformly off the ends of preformed micelles. Recently, successful control of the

length of rod-like poly(3-hexylthiophene) block copolymer micelles have been reported, both by self-seeding and by seeded growth, and seeded growth has been used to construct 1D block comicelles.⁵ It remains the only example of a coil-crystalline polymer with a π -conjugated core forming block where uniform structures can be formed by living CDSA. There is a compelling need to extend this capability to other block copolymers that assemble to form structures with a functional core.

Poly(*p*-phenylene vinylene) (PPV) or OPV is one of the best known π -conjugated materials with intriguing optical and electronic properties.⁷ Here we report preliminary results on the preparation of monodisperse fiber-like micelles with a crystalline OPV-core of different compositions and with controlled lengths up to *ca.* 870 nm by both self-seeding and seeded growth strategies. On the basis of our previous work on OPV-based fiber-like micelles,^{8a} we first prepared the diblock copolymer OPV₅-*b*-PNIPAM₄₉ (5 and 49 repeat units, respectively, $\bar{D} = 1.10$, see Supporting Information (SI) and Schemes S1- S4, Figures S1- S5 for details).

Scheme 1. Illustration of the preparation by CDSA of uniform fiber-like micelles and A-B-A triblock co-micelles with an OPV-core.



We examined CDSA of OPV₅-*b*-PNIPAM₄₉ in ethanol, a selective solvent for PNIPAM. A solution of OPV₅-*b*-PNIPAM₄₉ in ethanol (0.05 mg/mL) was heated at 80°C for 30 min followed by aging at room temperature (23°C) for 24 h. Transmission electron microscopy (TEM) images showed fiber-like micelles with lengths up to tens of micrometers and a width of about 22 nm (Figures 1A and S6). We also monitored the UV/vis absorption and fluorescence spectra of ethanol solutions of OPV₅-*b*-PNIPAM₄₉ at 23°C after heating at 80°C for 30 min. A blue shift of the maximum absorption from 441 nm to 430 nm with a decrease in absorption intensity from 0.51 to 0.38 and a redshift of the onset of absorbance were observed over the aging process (Figure 1B). The fluorescence intensity at 514 nm also decreased by 30% after 24 h, and then reached a plateau (Figure 1C). These phenomena are typical characteristics of H-aggregates of the OPV block.⁸ By dynamic light scattering (DLS), the apparent hydrodynamic diameter (D_h) of OPV₅-*b*-PNIPAM₄₉ in ethanol was 14 nm after heating at 80°C for 30 min and the size increased to 459 nm after aging for 24 h (Figure S7). All those observations suggest that OPV₅-*b*-PNIPAM₄₉ dissolved molecularly in ethanol after heating, and started to assemble into fiber-like micelles while aging at room temperature.

By AFM, the height of fiber-like micelles formed by OPV₅-*b*-PNIPAM₄₉ was about 6 nm (Figures 1D and 1E), slightly higher than the length of an OPV₅ molecule. The height of the fiber at “b” and “d” locations are about 3 nm and 2 nm, respectively, which are lower than that at location “a”. This observation suggests a twist in a ribbon-like structure, consistent with our previous report.^{8a} The crystallinity of OPV was also examined by wide-angle X-ray scattering (WAXS) on films of the micelles deposited on a silicon wafer (Figure S8). The micelles exhibited WAXS patterns with a strong diffraction at $2\theta = 6.2^\circ$ ($d = 1.43$ nm) and weak diffractions at $2\theta = 15.2^\circ$ ($d = 0.58$ nm) and 18.4° ($d = 0.48$ nm), consistent with previous reports on the crystalline properties of PPV-based copolymers with fiber-like features.⁹ These results suggest a face-to-face stacking mode of OPV₅ within the micelle core.

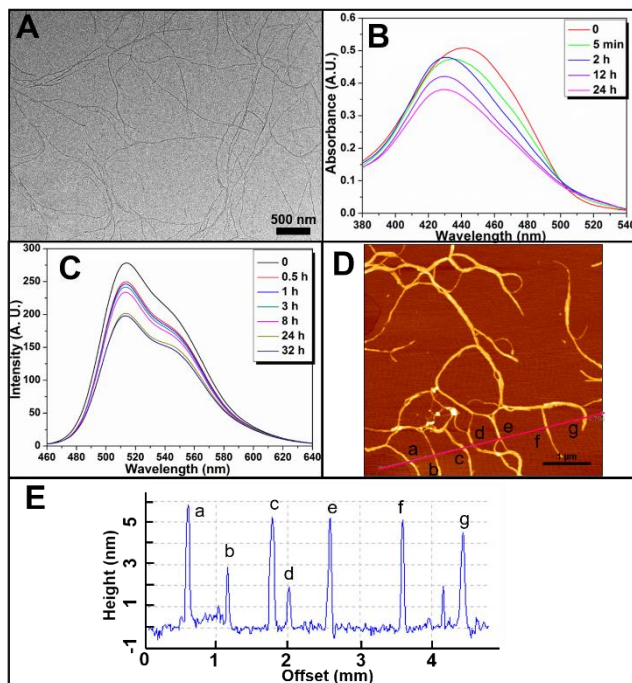


Figure 1. (A) TEM image of fiber-like micelles formed by OPV₅-*b*-PNIPAM₄₉ in ethanol (0.05 mg/mL); (B) UV/vis absorption and (C) fluorescent spectra of OPV₅-*b*-PNIPAM₄₉ in ethanol (0.05 mg/mL) over the aging process at 23°C after heating at 80°C for

30 min; (D) AFM height image of the micelles formed by OPV₅-*b*-PNIPAM₄₉ in ethanol, and (E) height profile along the red line shown in (D).

We first attempted to employ self-seeding to vary the length of the micelles (Scheme 1). Seed micelles were prepared by sonication (0°C, 30 min) of the as-prepared micellar solution (0.05 mg/mL). The seed micelles had a number-average length $L_n = 51$ nm (Figure 2A, $L_w = 53$ nm, $L_w/L_n = 1.05$, $\sigma/L_n = 0.24$). GPC analysis (Figure S9) showed that no degradation occurred upon sonication. Subsequently, aliquots of the seed micelle solution (0.05 mg/mL) were annealed for 30 min at temperatures ranging from 35°C to 60°C, and then were allowed to cool in air and aged at 23°C for 24 h. Figure 2B-2D show typical TEM images of fiber-like micelles after annealing at 40 °C, 57 °C, and 60 °C, with widths of 22 nm and average lengths of 143 nm, 556 nm, and 871 nm, respectively. The length of the OPV₅-*b*-PNIPAM₄₉ micelles increased gradually from 55 nm to 186 nm as the temperature was increased from 35°C to 47°C, but increased sharply from 311 nm to 871 nm as the temperature was elevated from 50°C to 60°C (Figure 2E, see details in Table S1, Figures S10 and S11). All of the micelles are uniform in length with values of L_w/L_n less than 1.10. The increase in length of the micelles with annealing temperature is consistent with the DLS results, where the apparent D_h of micelles also increased with the annealing temperature (Figure S12). On the basis of the initial length of the seeds and the final length of micelles formed in the temperature range from 35°C to 60°C, the percentage of surviving seeds of OPV₅-*b*-PNIPAM₄₉ at each annealing temperature can be estimated. It can be seen from Figure 2F that the percentage of surviving seeds of OPV₅-*b*-PNIPAM₄₉ decreased exponentially with the increase in annealing temperature (35°C to 60°C). This is a typical characteristic of the self-seeding process.³

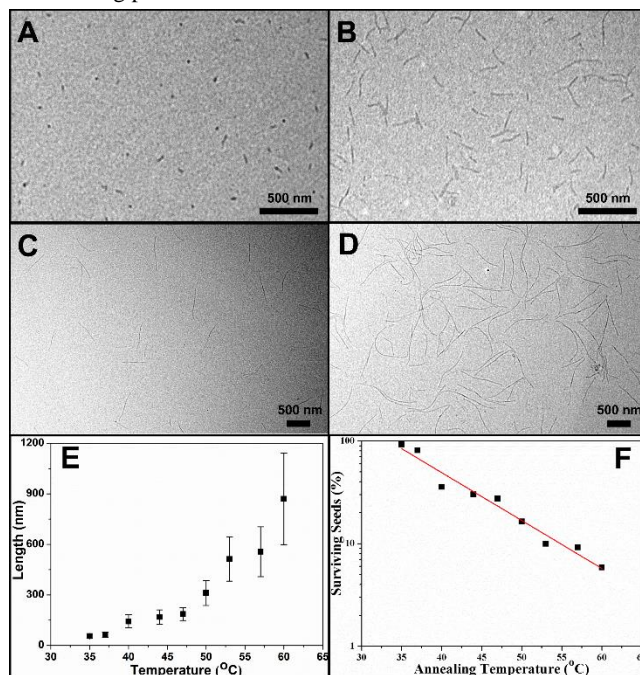


Figure 2. TEM images of (A) seeds, fiber-like micelles of OPV₅-*b*-PNIPAM₄₉ obtained by annealing the seeds in ethanol (0.05 mg/mL) at (B) 40°C, (C) 57°C, and (D) 60°C. (E) L_n values versus annealing temperature (The error bars represent the standard deviation σ of the length distribution). (F) Semi-logarithmic plot of the fraction of surviving seeds in solution versus annealing temperature.

In order to test if the ends of the fiber-like micelles with a crystalline OPV-core remain active for further growth, we attempted

to employ the seeded growth process to increase the length of the micelles (Scheme 1). Different aliquots (6.3, 12.5, 18.8, 25, 37.5, and 50 μL) of a concentrated solution of OPV₅-*b*-PNIPAM₄₉ in THF (6.0 mg/mL) were added under stirring to 3 mL of diluted seed solutions of OPV₅-*b*-PNIPAM₄₉ (0.01 mg/mL in ethanol, $L_n = 51$ nm, $L_w = 53$ nm, $L_w/L_n = 1.05$, $\sigma/L_n = 0.24$) at 23°C, respectively. Subsequently, the samples were stirred for another 10 s and then aged for 24 h. Experiments at 23 °C led to a broad size distribution (Figure S13), suggesting that self-nucleation had occurred. In order to minimize possible self-nucleation, we repeated the experiments at 30°C. Here, we obtained much better control over micelle length, with L_n values of 114, 175, 234, 290, 476, and 557 nm with narrow length distributions ($L_w/L_n = 1.04$ -1.08) for unimer-to-seed ratios of 1.25, 2.5, 3.75, 5.0, 7.5, and 10.0, respectively. (See details in Table S2, and in Figures 3A, 3B, 3C, S14, and S15). Figure 3D shows that L_n of the resulting micelles increased linearly with the unimer-to-seed ratio. These values are consistent with the predicted values for epitaxial deposition of all of the added polymer onto the ends of the seed (dashed line in Figure 3D) if the mass per unit length of the micelles remains constant. We conclude that seeded growth occurred without competing self-nucleation or micelle coupling.

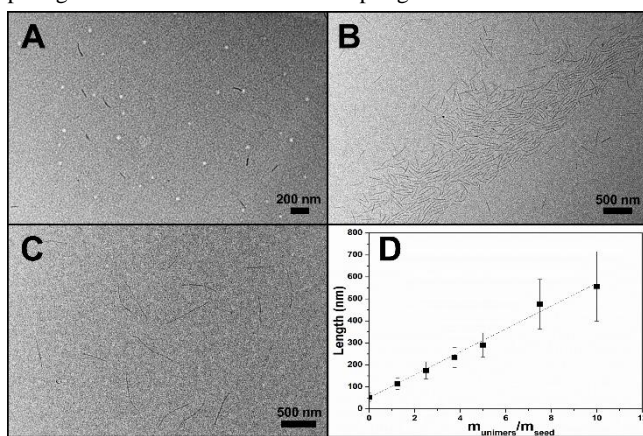


Figure 3. TEM images of fiber-like micelles of OPV₅-*b*-PNIPAM₄₉ obtained by adding (A) 1.25, (B) 3.75, and (C) 7.50 equivalent amounts of unimers (6 mg/mL in THF) to seed micelles in ethanol (3.0 mL, 0.01 mg/mL) at 30°C, followed by aging at 30°C for 24 h. (D) Linear dependence of micelle contour length on the unimer-to-seed ratio. The dashed line represents the theoretical value of L_n , assuming that all of the added unimers of OPV₅-*b*-PNIPAM₄₉ became attached to the ends of the pre-existing seeds without any competing self-nucleation.

The most attractive characteristic of the seeded-growth strategy of CDSA is its capacity to prepare well-defined multiple components of 1-D or 2D nanostructures by the virtue of the “living” seeded growth process of the crystalline segment.⁴ In order to establish the flexibility of the seeded growth process for fiber-like OPV block copolymer micelles, and to demonstrate the potential of OPV-based copolymer for the preparation of block co-micelles with desirable compositions, we attempted to prepare A-B-A type triblock co-micelles with a common crystalline OPV core, but a segmented corona. Thus, we synthesized a diblock copolymer containing OPV and poly(2-(diethylamino)ethyl methacrylate) segments (OPV₅-*b*-PDEAEMA₆₀, Scheme S5, Figure S16 and S17, for details). Then, uniform fiber-like OPV₅-*b*-PDEAEMA₆₀ micelles were prepared ($L_n = 126$ nm, $L_w/L_n = 1.04$, Figures 4A and 4D) by annealing of seed micelles ($L_n = 41$ nm, $L_w/L_n = 1.10$, Figure S18, see SI for details) at 53°C for 30 min, followed by aging at 23°C for 24 h.

Subsequently, these OPV₅-*b*-PDEAEMA₆₀ micelles were employed as seeds for further epitaxial growth. A THF solution of

OPV₅-*b*-PNIPAM₄₉ (12.5 μL , 6.0 mg/mL) was added to OPV₅-*b*-PDEAEMA₆₀ seed micelles ($L_n = 126$ nm, 0.01 mg/mL, 3.0 mL) at 30°C followed by aging at 30°C for 24 h (Scheme 1). TEM analysis showed that longer micelles ($L_n = 516$ nm, $L_w/L_n = 1.09$) formed (Figure 4B). We also observed some short fiber-like micelles of OPV₅-*b*-PNIPAM₄₉ (Figure S19), likely due to self-nucleation. In order to differentiate between the PDEAEMA and PNIPAM blocks in the elongated micelles, the sample was stained with an aqueous solution of phosphotungstic acid (1.0 mg/mL) prior to TEM analysis. Since the PDEAEMA block with its diethylamino groups is basic, it has a higher affinity for phosphotungstic acid than the PNIPAM segments. As expected, one can see that the central block of each micelle, with $L_n \approx 120$ nm ($L_w/L_n = 1.06$), is darker than the blocks at the two ends (Figure 4C). The length of the middle block is consistent with the L_n of the seed micelles of OPV₅-*b*-PDEAEMA₆₀ (126 nm) used for seeded growth (Figure 4D). This observation shows that the central block consists of OPV₅-*b*-PDEAEMA₆₀ micelles, whose exposed ends remained active toward the addition of OPV₅-*b*-PNIPAM₄₉ by epitaxial crystallization of the core-forming OPV₅ block.

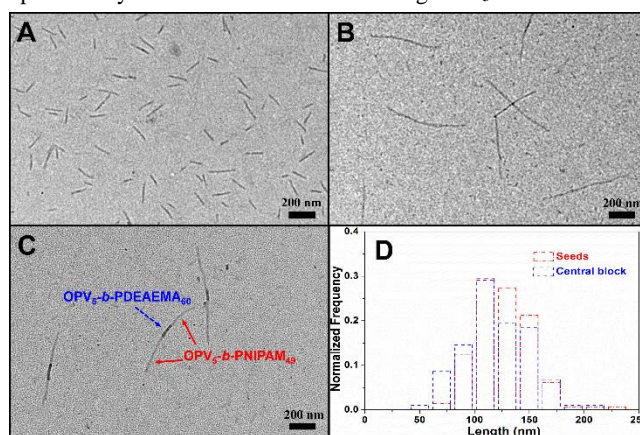


Figure 4. TEM images of (A) seed micelles of OPV₅-*b*-PDEAEMA₆₀ generated from shorter micelle fragments of OPV₅-*b*-PDEAEMA₆₀ ($L_n = 41$ nm, $L_w/L_n = 1.10$) by annealing at 53°C for 30 min, followed by aging at 23°C for 24 h, (B) and (C) A-B-A triblock co-micelles obtained by the addition of a THF solution of OPV₅-*b*-PNIPAM₄₉ (12.5 μL , 6.0 mg/mL) into the seed micelle solution of OPV₅-*b*-PDEAEMA₆₀ (0.01 mg/mL, 3.0 mL). TEM samples in (A) and (C) were stained with phosphotungstic acid. (D) Contour length distributions of seed micelles of OPV₅-*b*-PDEAEMA₆₀ and the central darker block of A-B-A triblock co-micelles.

In summary, by taking advantage of the crystalline property of the OPV segments, we were able to prepare monodisperse fiber-like micelles of uniform width (22 nm) and lengths ranging from 50 nm to 870 nm by self-seeding. Significantly, we also could employ the seeded growth strategy of “living” CDSA in ethanol to prepare uniform fiber-like micelles with lengths up to 560 nm. Here the mean micelle lengths were consistent with the predicted L_n values as a function of the unimer-added-to-seed ratio. The seeded growth route was successfully extended to the preparation of A-B-A triblock co-micelles containing an OPV core by the addition of OPV-*b*-PNIPAM unimers to seed micelles of OPV-*b*-PDEAEMA generated by self-seeding. We anticipate that the successful extension of seeded growth route to OPV-based copolymers should make feasible the formation of segmented block co-micelles with an OPV core, as well as other programmable architectures.

ASSOCIATED CONTENT

Supporting Information

Experimental procedures and additional comments on the synthesis and characterization of polymers and micelles. This materials is available free of charge via the internet at <http://pubs.acs.org>

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Notes

The authors declare no competing financial interests.

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Table of Contents

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