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JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
COMMUNICATION
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Cylindrical Micelles of Controlled Length with a π-Conjugated Polythiophene Core via Crystallization-Driven Self-Assembly

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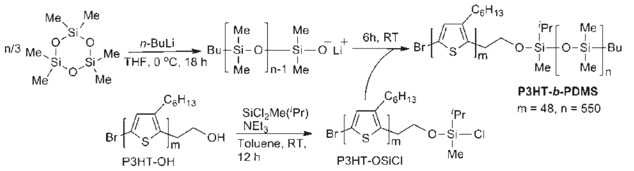
Supporting Information

ABSTRACT: Solution self-assembly of the regioregular polythiophene-based block copolymer poly(3-hexylthiophene)-*b*-poly(dimethylsiloxane) yields cylindrical micelles with a crystalline P3HT core. Monodisperse nanocylinders of controlled length have been prepared via crystallization-driven self-assembly using seed micelles as initiators.

The self-assembly of block copolymers in block-selective solvents gives rise to a range of core−shell structures such as spheres, cylinders, nanotubes, vesicles, and platelets and, more recently, a variety of more complex architectures.[1] A number of shape- and composition-dependent applications are currently under investigation for these interesting self-assembled nanomaterials, which can be rendered highly robust and stable with respect to dissociation by the use of core or corona cross-linking processes.[2] Cylindrical micelles are among the most attractive morphologies, with diverse potential uses in drug delivery, as additives for enhancing the toughness of epoxy resins, and as nanoscopic etch resists.[3] For many applications, the ability to access monodisperse structures with dimensional control is highly desirable.[4] However, solution self-assembly processes generally afford polydisperse samples and do not permit significant length control.

In our recent work on the solution self-assembly of metal-containing block copolymers,[5] we have demonstrated that diblock copolymers with a crystalline core-forming polyferrocenylsilane (PFS) metalloblock and a long corona-forming coblock self-assemble into cylindrical micelles in a solvent selective for the latter block.[6] Moreover, the exposed ends of the core of the cylindrical micelles remain active toward the further addition of PFS block-copolymer unimers (i.e., free diblock-copolymer chains in solution). This process, termed "crystallization-driven self-assembly" (CDSA), is mediated by the epitaxial crystallization of the core-forming PFS block and allows the micelle length to be increased by the addition of PFS block-copolymer unimers.[7] By using as initiators small, cylindrical seed micelles formed by sonication of longer structures, we have shown that monodisperse cylinders [length dispersity (L_w/L_n) <1.1] can be prepared with a length that can be controlled by the seed-to-unimer ratio.[8] This behavior is analogous to that of a living covalent polymerization. In principle, CDSA should be applicable to other crystalline-coil block copolymers.[9] The possible extension of this approach to block copolymers with π-conjugated core-forming blocks, which potentially could lead to conductive and emissive nanowire structures with controlled dimensions, is of considerable interest.[10] In this communication, we report our preliminary results on the successful extension of the potentially powerful CDSA approach to a regioregular polythiophene block copolymer.

Scheme 1. Synthesis of the P3HT-*b*-PDMS Diblock Copolymer



We prepared a regioregular poly(3-hexylthiophene)-*b*-poly(dimethylsiloxane) (P3HT-*b*-PDMS) rod−coil block copolymer (block ratio 1:11). The synthesis started with the preparation of a vinyl-terminated regioregular P3HT block by the Grignard metathesis (GRIM) route. Subsequent modifications to yield first hydroxyethyl-terminated P3HT−OH[11] and then P3HT−OSiMe(^{i}Pr)Cl enabled the target diblock copolymer to be furnished by coupling to living anionic PDMS (Scheme 1). The product was isolated as a purple, soft elastomeric material (72% yield) by precipitation into methanol. The P3HT-*b*-PDMS diblock copolymer and P3HT−OH homopolymer were characterized by gel permeation chromatography (GPC) and ^{1}H NMR spectroscopy (see Figures S1−S5 in the Supporting Information). The M_n and polydispersity index (PDI = M_w/M_n) of the P3HT−OH homopolymer were found by GPC analysis to be 8.40 kDa and 1.08, respectively. This corresponded to a number-average degree of polymerization (DP_n) of 48. For P3HT-*b*-PDMS, use of the DP_n value of 48 for the P3HT block along with the results of ^{1}H NMR integration indicated that DP_n = 550 for the PDMS block. This corresponds to a block ratio of 1:11. GPC analysis of P3HT-*b*-PDMS showed a narrow molecular weight distribution with a PDI of 1.05 (Figure S5). An M_n value of 49.15 kDa was calculated from a combination of GPC analysis of the P3HT−OH homopolymer and the ^{1}H NMR integration data.

Prior to the solution self-assembly studies, the electronic and photoluminescence (PL) spectra of P3HT-*b*-PDMS were collected in order to compare the degree of π conjugation of the rod block with that for the P3HT−OH homopolymer with the same chain length (DP_n = 48). The solution-state UV−vis spectra of

Received: March 16, 2011
Published: May 11, 2011

P3HT-*b*-PDMS and P3HT−OH in toluene (a good solvent for both P3HT and PDMS) showed similar absorption maxima (λ_{max}) at 450 nm ($\pi-\pi^*$ transition) characteristic of regioregular, π-conjugated P3HT (Figure S6).[12] In contrast, when thin films of these two materials were studied, the absorption maxima were red-shifted (P3HT-*b*-PDMS, λ_{max} = 505 nm; P3HT−OH, λ_{max} = 510 nm) (Figure S7). The red shift was indicative of a more planar and highly conjugated main-chain conformation than in solution. Each material also showed a shoulder at ~600 nm that is associated with crystalline order and results from strong intermolecular interactions among regioregular P3HT chains (Figure S7).[10b,12a,12b] PL measurements provided further evidence for increased π conjugation in the solid state. In toluene, P3HT-*b*-PDMS and P3HT−OH showed similar emission behavior (λ_{em} = 572 and 580 nm, respectively), whereas in the solid state, the values were significantly red-shifted (λ_{em} = 637 and 650 nm, respectively). The fluorescence intensity was also substantially reduced because of quenching, as found previously for crystalline P3HT aggregates (Figures S8 and S9).[13]

The crystallization of the P3HT-*b*-PDMS diblock copolymer in the solid state was also examined by differential scanning calorimetry (DSC) and wide-angle X-ray scattering (WAXS). DSC analysis of solid samples of both P3HT-*b*-PDMS and P3HT−OH (scan rate of 10 °C/min) indicated similar behavior during the heating scans, and each showed a melting transition (T_m) at 194 °C. However, whereas the cooling scan of the diblock copolymer revealed a crystallization peak at T_c = 142 °C, the T_c value for the homopolymer was 173 °C. The higher degree of hysteresis for the block copolymer is consistent with kinetic inhibition of the recrystallization of the P3HT by the PDMS block relative to the case for the P3HT−OH homopolymer (Figure S10). Moreover, the degree of crystallinity of P3HT-*b*-PDMS obtained from DSC measurements of melting enthalpies (~10%) was significantly lower than that of P3HT−OH (~45%). Thus, a WAXS pattern for P3HT-*b*-PDMS (measured on a film cast from chloroform solution in the 2θ interval from 5 to 30°) exhibited a peak at 2θ = 5.40° for the (100) reflection, which is characteristic of the interchain distance for interdigitated alkyl chains in P3HT (d = 1.61 nm). The (300) reflection was observed at 2θ = 16.55° (d = 0.54 nm), while the signal for the (200) reflection overlapped with the broad peak at 2θ = 11.79° corresponding to the PDMS block (Figure S11b). The signal at 2θ = 23.15° (d = 0.38 nm) corresponding to the (010) reflection is attributed to the stacking distance of successive thiophene rings between two polymer chains, suggesting a crystalline self-organized lamellar morphology with 3D ordering of the regioregular P3HT polymer chains.[12a]

In order to study solution self-assembly, the P3HT-*b*-PDMS diblock copolymer was dissolved in solvents selective for the PDMS block, namely, *n*-hexane and diethyl ether (0.30 mg/mL), to give clear orange solutions at room temperature (21 °C). After 2 days, the orange solution had turned red, and transmission electron microscopy (TEM) analysis showed the formation of small cylindrical micelles with various lengths (50−150 nm in *n*-hexane and 100−400 nm in Et_2O; see Figure S12). We also investigated micelle formation in mixed solvent systems. First, P3HT-*b*-PDMS was dissolved in toluene, a good solvent for both blocks. Et_2O was then added dropwise until the solution consisted of ~85% (v/v) Et_2O. This process was accompanied by a color change from orange to red (Figure 1a).

Bright-field TEM analysis revealed longer, well-defined cylindrical micelles of uniform width (~19 nm) but varied length (400−2000 nm) (Figure 1b; for atomic force microscopy images, see Figure S13). The enhanced solubility of the P3HT block provided by the common solvent (toluene) apparently reduces the number of nucleating sites, which favors the formation of longer cylinders. Analogous observations have been made for cylinders prepared from PFS-*b*-PDMS diblock copolymers.[6a] It is noteworthy that no staining of the samples was necessary to obtain sufficient contrast for the bright-field TEM images, presumably as a result of efficient packing of P3HT chains in the core involving π stacking of the thiophene rings.

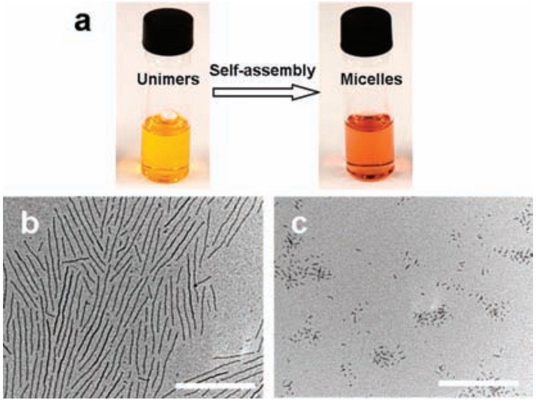


Figure 1. (a) Photographs of (left) P3HT-*b*-PDMS unimers in toluene and (right) cylindrical micelles in 85% (v/v) Et_2O/toluene. (b, c) Bright-field TEM images of (b) P3HT-*b*-PDMS cylindrical micelles formed in 85% (v/v) Et_2O/toluene and (c) seed micelles (L_n = 38 nm; L_w = 40 nm; L_w/L_n = 1.05) prepared by sonication of long cylindrical micelles. Scale bars: 500 nm.

The UV−vis absorption spectra of the micellar solutions showed significant red shifts in the absorption maxima (475−505 nm) relative to a solution of PHT-*b*-PDMS unimers. Moreover, the appearance of low-energy absorption bands in the 600−625 nm region (Figure S19) is indicative of a crystalline P3HT core on the basis of previous studies that assigned such peaks to crystalline aggregates in solution.[10b,12a,12b] As expected, the emission intensity was much lower than for unimers in solution (Figure S20) and typical of P3HT aggregates, for which fluorescence quenching has been well-established.[13]

In order to prepare small seed micelles for CDSA, the cylindrical micelles prepared in 85% (v/v) Et_2O in toluene were subjected to sonication at −5 °C for 2.5 h using a 50 W ultrasonic processor equipped with a titanium sonotrode. The average contour length (L_n = 38 nm; L_w = 40 nm; L_w/L_n = 1.05; σ/L_n = 0.22) of the resulting small cylinders was determined by TEM analysis (Figure 1c and Figure S14). The seeds were further characterized by dynamic light scattering (DLS) and showed an apparent hydrodynamic radius ($R_{H,app}$) of 44 nm, which, for comparison, was substantially greater than the value for P3HT-*b*-PDMS unimers in toluene ($R_{H,app}$ = 6.5 nm) (Figure S16).

To obtain monodisperse cylindrical micelles with controlled lengths, different amounts of P3HT-*b*-PDMS unimers (700, 1400, 2100, and 2800 μg) were added (as a 7 mg/mL toluene solution) to a slowly stirred solution containing 33 μg of the small P3HT-*b*-PDMS seeds [100 μL of a 0.33 mg/mL solution in 85% (v/v) Et_2O/toluene diluted with 1.5 mL of Et_2O]. The samples were stirred for 10 s and then aged for 2 days at 21 °C, during which time the color of the solutions changed from yellow to red-purple.[14] TEM analysis revealed that the average lengths

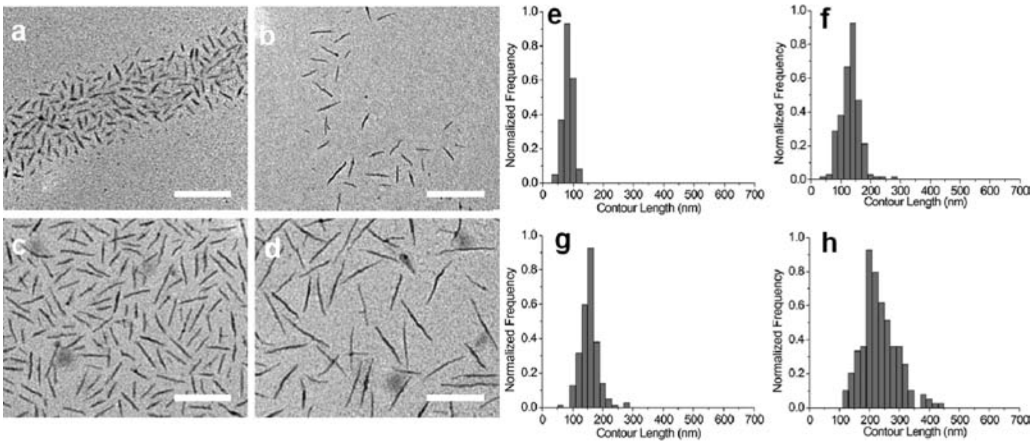


Figure 2. (a−d) Bright-field TEM micrographs of monodisperse cylindrical micelles of P3HT-*b*-PDMS obtained by adding (a) 700, (b) 1400, (c) 2100, and (d) 2800 μg of unimers (as 7 mg/mL solution in toluene) to 33 μg of seed micelles (L_n = 38 nm; Figure 1c) in 100 μL of an 85% (v/v) Et_2O/toluene mixture diluted by further addition of 1.5 mL of Et_2O. Scale bars: 200 nm. (e−h) Contour length distributions of samples (a)−(d), respectively.

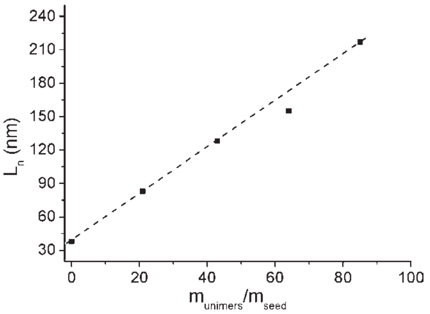


Figure 3. Linear dependence of the micelle contour length on the unimer-to-seed ratio.

(L_n) of the resulting cylindrical micelles were 83, 128, 155, and 217 nm, respectively, with narrow length dispersities (L_w/L_n = 1.05−1.08; σ/L_n = 0.22−0.28) (Figure 2). Contour length histograms of these cylindrical micelles were produced by measuring 220−250 micelles in images obtained from multiple locations on each TEM grid. Significantly, the length of the cylindrical micelles was found to be linearly dependent on the unimer-to-seed ratio, as shown in Figure 3. The growth of cylinders from the seeds (Figure 4) was similar to that previously observed for crystalline-coil PFS block copolymers, although in the latter, well-studied case cylinders of lengths up to ~2 μm could be prepared.[8,15]

A similar protocol was applied using the THF/*n*-hexane solvent system. Thus, 500, 1000, 2000, or 4000 μg of P3HT-*b*-PDMS unimers in THF was added to 25 μg [75 μL of a 0.33 mg/mL solution in 85% (v/v) *n*-hexane/THF] of P3HT-*b*-PDMS seed micelles (L_n = 41 nm; L_w = 43 nm; L_w/L_n = 1.05) that was diluted by further addition of 1.5 mL of *n*-hexane. This yielded cylindrical micelles with average lengths (L_n) of 72, 133, 215, and 320 nm, respectively, with even lower dispersities in length (L_w/L_n = 1.02−1.03; σ/L_n = 0.14−0.18) as revealed by TEM (Figure 5 left and Figures S17 and S18).[15] The cylindrical micelles with L_n = 320 nm were imaged by laser confocal fluorescence microscopy (LCFM) in THF/*n*-hexane, demonstrating the presence of the emissive P3HT core (Figure 5 right).

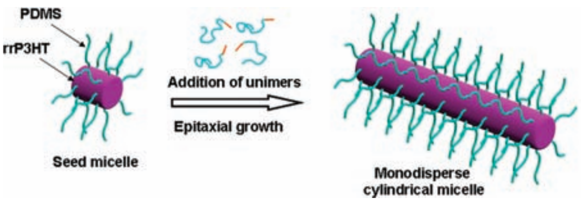


Figure 4. Schematic representation of the formation of monodisperse P3HT-*b*-PDMS cylindrical micelles via CDSA using small seed micelles as initiators.

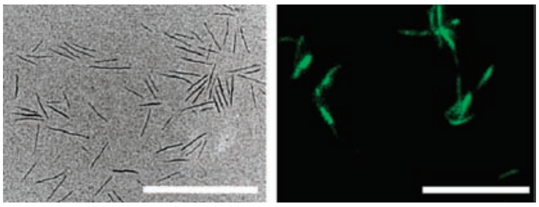


Figure 5. (left) Bright-field TEM image of monodisperse cylindrical micelles of P3HT-*b*-PDMS obtained by adding 4000 μg of unimers (as a 10 mg/mL THF solution) to 25 μg of seed micelles in 75 μL of a 85% (v/v) *n*-hexane/THF diluted with 1.5 mL of *n*-hexane. Scale bar: 500 nm. (right) LCFM image of the same sample in *n*-hexane/THF. Scale bar: 3 μm.

In summary, we have demonstrated the solution self-assembly of the regioregular polythiophene-based crystalline-coil block copolymer P3HT-*b*-PDMS to give cylindrical micelles with a P3HT core. The presence of the PDMS corona apparently provides colloidal stability and prevents the formation of the nanofibrillar aggregates characteristic of the P3HT homopolymer.[16] Moreover, in this preliminary work, monodisperse cylinders of controlled length between 40 and 320 nm have been prepared via crystallization-driven self-assembly, although much still needs to be understood for this new system.[15] These structures are of considerable interest, as P3HT is one of the most well-studied crystalline π-conjugated polymers and has been investigated as an active component of organic field-effect transistors, solar cells, and light-emitting diodes.[17] Significantly, we previously demonstrated that the sequential addition of different diblock copolymers with a crystalline core-forming metalloblock using CDSA yields segmented block comicelles as well as other complex hierarchical architectures. In particular, CDSA of block copolymers with different core-forming blocks can give rise to block comicelles with heterojunctions in the core via heteroepitaxial growth.[18] The formation of similar structures from block copolymers with core-forming π-conjugated blocks with different band gaps would be of considerable interest,[19,20] and this represents a key target of our future studies.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Experimental details and further characterization. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ ACKNOWLEDGMENT

This work was funded by the European Research Council (Advanced Investigator Grant to I.M.). S.K.P. and E.L.D. thank the EU for a Marie Curie Postdoctoral Fellowship and the Swiss National Science Foundation for a postdoctoral fellowship, respectively. D.J.L. thanks the EPSRC Bristol Chemical Synthesis Doctoral Training Centre for a Ph.D. studentship. We also thank Alan Leard (Wolfson Bioimaging Facility, U. Bristol) for the LCFM images and Prof. A. P. Davis for the use of a fluorescence spectrometer. M.A.W. thanks NSERC Canada for financial support.

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(14) Growth of the cylinders from seeds in solution was also supported by DLS data (see Figure S16).

(15) Preliminary attempts to generate monodisperse cylindrical micelles longer than ~350 nm in seeded-growth experiments by the further addition of P3HT-*b*-PDMS unimers were unsuccessful. TEM analysis after solvent evaporation led to the observation of presumably amorphous aggregates in addition to the pre-existing cylinders. The increased volume fraction of the common solvent existing under these conditions (due to the addition of more unimer solution in the common solvent) provides a likely explanation. However, other factors, such as an increase in the number of lattice defects in the crystalline core as the cylinder length increases, which would lower the efficiency of epitaxial growth, may also be significant.

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