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Uniform Patchy and Hollow Rectangular Platelet Micelles from Crystallizable Polymer Blends

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The preparation of colloidally stable, self-assembled materials with tailorable solid or hollow two-dimensional structures represents a major challenge. We describe the formation of uniform, monodisperse rectangular platelet micelles of controlled size by seeded-growth methods that involve the addition of blends of crystalline-coil block copolymers and the corresponding crystalline homopolymer to cylindrical micelle seeds. Sequential addition of different blends yields solid platelet block comicelles with concentric rectangular patches with distinct coronal chemistries. These complex nanoobjects can be subject to spatially-selective processing that allows their disassembly to form perforated platelets such as well-defined hollow rectangular rings. The solid and hollow 2D micelles provide a tunable platform for further functionalization and potential for a variety of applications.

Nanoscale two-dimensional (2D) materials, typified by graphene and metal chalcogenide or clay nanosheets, are of broad utility. In principle, the solution self-assembly of block copolymers (BCPs) provides a convenient route to analogous planar nanostructures derived from soft matter (*1, 2*). However, the formation of 2D platelet micelles is generally uncommon relative to other morphologies (*3, 4*). Moreover, although considerable control has recently been achieved over the structures of 1D BCP micelles, where fibers of tunable length and low dispersity (*5, 6*) with periodic patches (*7, 8*), block architectures (*9*), and amphiphilicity (*10*) are now accessible, progress with 2D assemblies is much more limited. Thus, the preparation of solid and hollow colloidally stable 2D micelles with similar fidelity and complexity remains a key challenge.

Self-assembly of BCPs with amorphous core-forming blocks in selective solvents provides a route to a diverse array of core-shell nanoparticles (micelles) with equilibrium or non-equilibrium morphologies of broad utility (*3, 4*). The most common morphologies formed are spheres, cylinders, and vesicles and colloidal stability is provided by the presence of the solvent swollen corona-forming block. The co-assembly or “blending” of different BCPs has recently been shown to provide a useful route to targeted conventional morphologies and also more complex nanostructures such as disk-sphere or disk-cylinder hybrid micelles (*11, 12*). As a result of their preference for the formation of rigid assemblies characterized by a core-corona interface with low mean curvature, BCPs with crystallizable core-forming blocks offer a promising route to planar micellar architectures (platelets) containing a core analogous to the well-studied, but colloidally unstable 2D lamellar single crystals formed by the solution crystallization of homopolymers (*2, 13*). Although platelet BCP micelles offer much promise as functional, colloidally-stable 2D nanoobjects, synthetic approaches that allow access to low dispersities, dimensional control, and spatial control of functionality are limited. Recent advances include the formation of platelets from end-functionalized, crystallizable linear polymers (*14, 15*) or hyperbranched analogs (*16*), which permits programmed nanoparticle attachment and patterning, and the creation of 2D assemblies from homopolymer crystals consisting of alternate rings of BCP and homopolymer (*17, 18*).

Lenticular platelet micelles can be formed by the growth of platelet-forming BCPs with a crystallizable poly(ferrocenyldimethylsilane) (PFS) core-forming block and a relatively short complementary corona-forming block (core : corona block ratio > 1:1) on addition to a solution containing cylindrical micelle seeds (*19*). Quantitative experiments demonstrated that the area of the resulting lenticular platelet micelles showed a linear dependence on the unimer to seed ratio.

The living nature of this crystallization-driven self-assembly (CDSA) process enabled the preparation of concentric lenticular platelet block comicelles with spatially segregated coronas by the sequential addition of PFS BCPs with different corona functionalities. However, the platelet formation was governed by a growth mechanism that gave the micelles a lenticular shape with irregular edges rather than a well-defined rectangular morphology (19). Moreover, as a direct result of the short coronal chain lengths for the BCPs used, the resulting platelets possess a low propensity for further processing. For example, poor colloidal stability above a size of ca. 1 μm leads to aggregation and effective corona-crosslinking (20) has not been possible.

In order to resolve these issues we have explored the analogous seeded growth of blends of PFS BCPs possessing much longer solubilizing corona-forming blocks together with the corresponding crystalline PFS homopolymer. We studied the seeded growth of the blends of PFS-*b*-PDMS with a long corona-forming PDMS block (PDMS = polydimethylsiloxane) and PFS homopolymer where the degrees of polymerization for the PFS block and homopolymer were relatively large (Fig S1A). Non-polar hexane was chosen as a selective solvent for the hydrophobic PDMS block but also as an only moderately poor solvent for PFS, which would therefore be expected to prevent the rapid precipitation of the PFS homopolymer. A mixture of PFS₄₉-*b*-PDMS₅₀₄ (core : corona block ratio ~1:10; the subscripts refer to the number-average degree of polymerization) and PFS₄₃ unimers in THF was added to colloidal solutions of the PFS₂₈-*b*-PDMS₅₆₀ cylindrical micelle seeds (number-average length $L_n = 50 \text{ nm} - 5.00 \mu\text{m}$, number-average core width $W_n = 13 \text{ nm}$ by TEM). This led to growth only from the seed termini to yield dumbbell-like micelles with a cylindrical central segment derived from the original seed, and two platelet-like or platelet-cylinder-like end segments arising from the blends for the cases of the 1:1 and 10:1 BCP : homopolymer mass ratios (mole ratio ~1:5 and ~2:1), respectively (fig. S2). In contrast, the use of blends with significantly shorter PFS blocks led to rectangular platelets that result from substantial growth from the seeds in both the terminal and lateral directions (figs. S3 and S4). Thus, when blends of PFS₂₈-*b*-PDMS₅₆₀ (block ratio 1:20) and PFS₂₀ (1:1 mass ratio, mole ratio ~1:10) were added to the cylindrical PFS₂₈-*b*-PDMS₅₆₀ seeds high aspect ratio, ribbon-like platelet micelles were formed with uniform but significantly broadened PFS cores ($W_n = \sim 50 \text{ nm}$ vs 13 nm in the seed, fig. S3). Moreover, the resulting micelles were of uniform size ($A_w/A_n = 1.02 - 1.08$, A_w and A_n are weight- and number-average area, respectively) and showed a linear dependence of area on the unimer to seed ratio consistent with a living CDSA process (fig. S3E).

To expand the generality of our approach to rectangular platelets that are dispersible in hydrophilic media we also explored the self-assembly of the blends derived from PFS₃₆-*b*-P2VP₅₀₂ (block ratio 1:14, P2VP = poly(2-vinylpyridine)), a BCP with a polar corona-forming P2VP block, and PFS₂₀ homopolymer. A mixture of hexane and isopropanol (iPrOH) was used to overcome the solubility issues (10, 21) and living CDSA could therefore be achieved for cylindrical micelle seeds with either a hydrophobic-corona (derived from PFS-*b*-PDMS) or a polar-corona (from PFS-*b*-P2VP). With a PFS₃₆-*b*-P2VP₅₀₂ to PFS₂₀ mass ratio of ~1:1 (mole ratio ~1:13) (fig. S5), the living CDSA using the same cylindrical PFS₂₈-*b*-PDMS₅₆₀ seeds in 1:3 (v/v) hexane/iPrOH (fig. S6) gave rise to low dispersity platelet micelles ($A_w/A_n < 1.01$) with regular rectangular morphologies (Fig. 1). These rectangular platelets were formed rapidly (ca. 5 min, fig. S7) and were characterized by a dual-trapezoid texture emanating from the central seed, with a differential in contrast by TEM and of height by AFM analyses (~18 nm for the higher, more electron dense regions vs. ~12 nm for the lower regions) (Fig. 1B). The TEM and AFM data suggest that the growth process leads to a significantly higher density of BCP with P2VP coronal chains lateral to the seed and for homopolymer in the terminal regions. The length, width, area, and aspect ratio of these platelets could be precisely controlled by the unimer to seed ratio and the length of the cylindrical micelle seeds (fig. S8). Giant rectangular platelets with dimensions of 60 $\mu\text{m} \times 10 \mu\text{m}$ (fig. S9) could be created without any obvious defects utilizing a slow growth process in a mixture of hexane and methanol (1:3, v/v) and nevertheless retained their high colloidal stability. We attributed this to the relatively high volume fraction of the corona-forming block (core : corona ratio ~ 3:5 vs. > 1:1 for the lenticular platelet-forming PFS BCPs used in ref. 19).

Fig. 1. Rectangular platelet micelles by living CDSA of PFS₃₆-*b*-P2VP₅₀₂/PFS₂₀ blends. Low dispersity rectangular platelet micelles can be formed by living CDSA of the PFS₃₆-*b*-P2VP₅₀₂/PFS₂₀ blends initiated by the cylindrical micelle seeds of PFS₂₈-*b*-PDMS₅₆₀ in a mixture of hexane and iPrOH. **(A)** Schematic diagram illustrating this process. **(B)** TEM images and AFM height images and profiles of a representative sample of the rectangular platelet micelles formed by the addition of a mixture of the PFS₃₆-*b*-P2VP₅₀₂ and PFS₂₀ unimers (1:1 mass ratio) in a small amount of THF to a solution of the PFS₂₈-*b*-PDMS₅₆₀ cylindrical micelle seeds ($L_n = 590$ nm) in a mixture of hexane and iPrOH (1:3, v/v) at 45 °C. **(C)** Analogous images for perforated rectangular platelets formed after crosslinking of the P2VP coronas via coordination of the pyridyl groups on P2VP to small Pt nanoparticles and subsequent redispersal in THF to remove the PFS₂₈-*b*-PDMS₅₆₀ cylindrical micelle seeds.

To explore the location of the P2VP corona-forming block in the rectangular platelets corona-crosslinking was achieved via coordination of the pyridyl groups on P2VP with small (diameter ca. 2 nm) Pt nanoparticles (NPs) (22). After redispersal for 24 h in THF (a good solvent for both PFS and P2VP), the rectangular platelets retained their integrity except for a perforated channel in the

center corresponding to the previous location of the uncrosslinked seed (Fig. 1C, fig. S10). The dual-trapezoid texture became more apparent by TEM after corona-crosslinking as a result of the increase in electron density contrast due to the presence of Pt NPs (identified by energy dispersive X-ray (EDX) spectroscopy, Fig. S11). Moreover, AFM demonstrated that, relative to the corresponding values before crosslinking (Fig. 1B), the height of the central region at the side of the channel and also the platelet edges was increased by ~ 30 nm compared to ~ 5 nm near the platelet ends (Fig. 1C). This is consistent with the presence of a higher density of incorporated Pt NPs in the former regions due to a higher concentration of P2VP corona chains. These results therefore also indicate that, although P2VP corona chains are distributed over the whole rectangular platelet, their concentration is significantly higher in the central regions lateral to the seed. The seeded assembly of the BCP – homopolymer blend to form uniform rectangular platelets therefore appears to be a cooperative growth process as, in the absence of seeds, irregular platelets or other morphologies were formed (see fig. S5). Moreover, monitoring of the growth process demonstrated that the mechanism of formation differs from that for lenticular platelet micelles where only a BCP is added to the seed. Thus, the rectangular platelets form by simultaneous growth in both the terminal and lateral directions relative to the seed (fig. S7) whereas in the lenticular case, growth proceeds initially from the ends of the cylindrical micelle seed termini followed by a gradual enveloping process (19).

The difference in micellar morphology formed by the seeded growth of PFS₂₈-*b*-PDMS₅₆₀/PFS₂₀ blends in hexane (higher aspect ratio, ribbon-like) and the PFS₃₆-*b*-P2VP₅₀₂/PFS₂₀ blends in 1:3 hexane/iPrOH (lower aspect ratio, rectangular) indicated a significant influence of the coronal chemistry and/or solvent composition on the living CDSA process. Indeed, the formation of rectangular platelets by the PFS₃₆-*b*-P2VP₅₀₂/PFS₂₀ blends was favored in iPrOH-dominated hexane/iPrOH mixtures but not in hexane-dominated systems (fig. S6A). For the PFS₂₈-*b*-PDMS₅₆₀/PFS₂₀ blends, the resulting micellar morphology changed from ribbon-like platelets for hexane : iPrOH > 1:1 (v/v) to rectangular platelets at hexane : iPrOH < 1:2 (v/v) (fig. S6B). These studies indicate that the use of relatively short crystallizable segments in the BCP/homopolymer blends and a careful choice of solvent composition should permit the formation of rectangular platelets from BCPs with a broad range of corona chemistries.

We targeted patchy rectangular platelet multiblock comicelles by the seeded growth of sequentially added PFS₂₈-*b*-PDMS₅₆₀/PFS₂₀ and PFS₃₆-*b*-P2VP₅₀₂/PFS₂₀ blends (Fig S1B). For

example, concentric rectangular platelet triblock comicelles were prepared by the addition of the PFS₂₈-*b*-PDMS₅₆₀/PFS₂₀ (1:1 mass ratio) blend unimers in THF to a solution of the rectangular platelets derived from the PFS₃₆-*b*-P2VP₅₀₂/PFS₂₀ blends, followed by a further addition of the PFS₃₆-*b*-P2VP₅₀₂/PFS₂₀ (1:1 mass ratio) blend unimers in THF after 10 min (Fig. 2A). TEM and AFM analyses indicated that the P2VP corona regions were darker (more electron rich) and of greater height than the PDMS corona regions (Fig. 2B), favoring an easy identification of the segmented structures. The dimensions of the P2VP- and PDMS-corona regions were precisely controllable by the amount of the respective blend added.

Although self-assembled hollow structures such as nanotubes (23), toroids (24), dynamic tubules (25), and nanocapsules (26) are of intense interest, well-defined and monodisperse rectangular 2D structures are unknown. Based on the triblock platelet comicelle structure we envisaged that crosslinking of the P2VP coronas followed by the addition of a good solvent for the PFS core and coronas should lead to disassembly to generate a perforated architecture. The P2VP coronas were once again heavily crosslinked via coordination with Pt nanoparticles (22) (Fig. 2C) and subsequent redispersal in THF led to the formation of a mixture of perforated rectangular platelets and well-defined hollow rectangular rings with relatively broader ends and narrower rims along the long axis (Figs. 2D and E and fig. S11). Similarly, the concentric rectangular platelet diblock comicelle precursors were prepared by the sequential addition of the PFS₂₈-*b*-PDMS₅₆₀/PFS₂₀ and PFS₃₆-*b*-P2VP₅₀₂/PFS₂₀ blends in THF to a solution of the PFS₂₈-*b*-PDMS₅₆₀ cylindrical micelle seeds and pure ring-like structures were obtained after shell-crosslinking and redispersal in THF (fig. S12). The size, aspect ratio and rim thickness of the rectangular rings can be readily tailored by the seed length and the unimer to seed ratio applied to each unimer addition (fig. S12C). The excellent dimensional stability and sharp edges of the hollow rectangular rings are attributed to the high crosslinking density present. The living nature of this CDSA process also allowed the formation of more complex multiblock comicelles (for example, heptablock comicelles, fig. S13A) using further steps involving dissolved blends. Moreover, with the additional use of the PFS₃₆-*b*-PnBMA₇₅₆/PFS₂₀ (PnBMA = poly(*n*-butylmethacrylate)) blends, rectangular platelet block comicelles with even more complex and tunable segmented 2D structures were also fabricated (fig. S13B).

Fig. 2. Concentric rectangular and hollow platelet block comicelles. Concentric rectangular platelet block comicelles can be prepared through the sequential, alternate addition of $\text{PFS}_{36}\text{-}b\text{-P2VP}_{502}/\text{PFS}_{20}$ and $\text{PFS}_{28}\text{-}b\text{-PDMS}_{560}/\text{PFS}_{20}$ blend unimers. (A) Schematic diagram illustrating this process. (B) TEM, AFM height and AFM 3D images of triblock comicelles formed by sequential addition of the $\text{PFS}_{36}\text{-}b\text{-P2VP}_{502}/\text{PFS}_{20}$, $\text{PFS}_{28}\text{-}b\text{-PDMS}_{560}/\text{PFS}_{20}$ and $\text{PFS}_{36}\text{-}b\text{-P2VP}_{502}/\text{PFS}_{20}$ blend unimers (BCP : homopolymer = 1:1 mass ratio) to a solution of the $\text{PFS}_{28}\text{-}b\text{-PDMS}_{560}$ cylindrical micelle seeds ($L_n = 810$ nm) in a hexane : iPrOH (1:3, v/v) at 45 °C. As P2VP has a higher T_g and a larger volume repeat unit than PDMS, for similar degrees of polymerization, the P2VP regions are higher in AFM height images and, as the path length is longer for electrons, darker by TEM. (C) TEM image of rectangular platelets after crosslinking of the P2VP coronas. (D and E) TEM and AFM height images of a mixture of perforated rectangular platelets and well-defined hollow rectangular rings formed after redispersal in THF.

The rectangular platelet micelles and block comicelles offer a tunable 2D platform for the fabrication of functional materials. For a proof-of-concept demonstration, we synthesized a series of fluorescent PFS-*b*-PDMS BCPs, namely, PFS₂₉-*b*-(PDMS₆₅₂-*r*-R₁₉), PFS₂₉-*b*-(PDMS₆₅₂-*r*-G₁₉) and PFS₂₉-*b*-(PDMS₆₅₂-*r*-B₁₉), in which the PDMS block was functionalized with red (R), green (G) and blue (B) dyes, respectively (27). and then blended them with the. Living CDSA of their blends with PFS₂₀ homopolymer, together with the non-fluorescent PFS₃₆-*b*-P2VP₅₀₂/PFS₂₀ blends, yielded fluorescent concentric rectangular platelet block comicelles with multiple and variable fluorescence for the selected segments as confirmed by confocal laser scanning microscopy (CLSM) and structured illumination microscopy (SIM) analyses (Fig. 3A). Further functionalization was also feasible utilizing the spatially defined coronal chemistries. For example, silica nanoparticles (average diameter 70 nm) could be selectively deposited onto the P2VP coronas as a result of the hydrogen bonding (28), allowing the controlled patterning in the form of solid rectangles and/or rings (Fig. 3B).

In summary, we demonstrate a versatile method for the formation of well-defined, low dispersity rectangular platelet micelles with tunable dimensions based on a new conceptual approach that involves seeded growth of crystallizable polymer blends of BCPs and homopolymers. Multiblock platelet comicelles are accessible by the sequential addition of different blends and crosslinking/dissolution strategies allow the formation of well-defined hollow rectangular micelles. The resulting solid and hollow platelets exhibit excellent colloidal stability due to the substantial volume fraction of coronal chains and are sufficiently robust to be manipulated in solution, including by optical tweezers (fig. S14). The introduction of diverse functions can be envisaged by the use of various other polymers such as π -conjugated materials as the crystallizable component (29-31) and also by facile coronal functionalization. Moreover, the segmented planar solid and hollow 2D structures open possible avenues to customizable platforms for future applications in fluorescent imaging, sensing, electronics, and catalysis, and as liquid crystals, motile nano/micro machines, or therapeutic carriers.

Fig. 3. Spatially-selective functionalization of rectangular platelets. The coronas of the rectangular platelet micelles and block comicelles can be selectively functionalized using a series of fluorescent PFS BCPs or via association with nanoparticles. **(A)** Schematic representations, CLSM and SIM images of typical rectangular platelet block comicelles with segregated regions comprised of non-fluorescent P2VP coronas and multiple dye-functionalized fluorescent PDMS coronas. The PDMS coronas with red, green and blue fluorescence were denoted as PDMS-R, PDMS-G and PDMS-B, respectively. For the images in column 4 the rapid photobleaching of the blue dye required the use of low excitation laser power and rapid scans which significantly limited resolution. **(B)** Schematic representations and TEM images of rectangular platelet micelles and block comicelles with silica nanoparticles selectively deposited on the P2VP coronas.

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AUTHOR CONTRIBUTIONS

H.Q. and I.M. conceived the project. H.Q. and Y.G. performed the self-assembly experiments. C.E.B. synthesized the fluorescent polymers. H.Q., C.E.B. and S.E.D.W. performed the CLSM and SIM imaging and H.Q. and R.L.H. performed the AFM analysis. O.E.C.G. performed the manipulation experiments using optical tweezers and the corresponding analyses. H.Q. and I.M. prepared the manuscript with input from all the other authors. The project was supervised by I.M.

SUPPLEMENTARY MATERIALS

Materials and Methods

Figures S1 to S14

References (32-39)