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Surface Patterning of Uniform 2D Platelet Block Comicelles via Coronal Chain Collapse

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ABSTRACT

The formation of colloids with anisotropically patterned surfaces is of growing interest for the creation of hierarchical structures and the templating of nanoparticles. We have recently shown that well-defined two-dimensional platelets with low areal dispersities can be formed by the seeded growth of a blend of homopolymers and block copolymers. Herein we form rectangular platelets containing two block copolymers with different coronal chemistry. On addition of a solvent that is only able to solvate the corona of one block, we were able to form colloiddally stable micelles with patterned surfaces via coronal collapse. Scanning transmission electron microscopy-energy-dispersive X-ray spectroscopy and atomic force microscopy were employed to provide information on the structure and size of the patches decorating the micelle surfaces.

Despite the growing interest in 2D nanomaterials and their applications,^{1,2} access to uniform samples of colloidally stable 2D platelets with controlled dimensions from polymeric precursors has been a challenge. Block copolymers with amorphous core-forming segments rarely self-assemble into 2D platelets.³ In cases where the formation of planar assemblies might be anticipated, a closure process usually results in the generation of vesicles.³ In contrast, “Crystallization-Driven Self-Assembly” (CDSA) of block copolymers (BCPs) containing a crystallizable core-forming segment and a corona-forming block of comparable length has been well-developed as a route to 2D platelets.^{4–9} However, using the well-established self-assembly conditions, no control over their dimensions exists and the resulting assemblies are highly polydisperse. In contrast, “living CDSA”, in which unimers of polymeric amphiphiles are added to preformed seeds at or near ambient temperature, permits the reproducible formation of both 1D^{10–16} and 2D^{17–25} nanoparticles with predetermined dimensions and promising scalability. Recent advances include the use of these and related in situ methods at elevated temperature to prepare well-defined 2D platelets with applications as emulsifiers,²² components of adhesive gel nanocomposites,²⁶ and nanomotors and recyclable catalysts by means of nanoparticle attachment.^{27–29}

Control over the patterning of the surfaces of nanoparticles has gained significant interest in the past decade owing to the ability to produce anisotropic nanostructures. Such nanostructures can be employed as precursors to hierarchical assemblies.^{30–34} Spherical nanoparticles with surface patches have been shown to assemble into discrete aggregates,³⁵ polymeric structures^{34,36} and lattices.³⁷ In addition, one dimensional (1D) cylindrical micelles have been reported to form surface patches due to phase segregation of coronas into block regions^{38–42} or gradient

morphologies.⁴³ These patchy structures can incorporate functional materials into compartments^{44,45} and acts as templates for hybrid particle synthesis.⁴⁶

The creation of 2D platelets with surface patches is less developed. The formation of patterned 2D colloidal structures by the self-assembly of triblock terpolymers with amorphous core-forming segments has been reported, but without size control.⁴⁷ Platelet block comicelles with distinct spatial regions have been formed by the addition of BCP unimers to homopolymer crystals^{48,49} and via sequential addition of unimers with different corona-forming block chemistries to seeds using living CDSA methods.^{19–21,24} Herein, we report the formation of well-controlled rectangular platelets with spatially-defined zones by the seeded growth of a unimer blend of homopolymer and block copolymer. We then employ an alternative approach to form anisotropic 2D nanostructures, where we demonstrate control over the surface patterning of 2D platelet block comicelles via coronal chain collapse.

We targeted platelet micelles containing two spatially distinct spatial regions with different coronal chain chemistries and distinct polarities in order to form colloidally stable structures with patterned surfaces. In this proof-of-concept work we used block copolymers with a crystallizable poly(ferrocenyldimethylsilane) (PFS)⁵⁰ core-forming segment. Poly(2-vinylpyridine) (P2VP) and [poly(cobaltoceniumethylene)][bis(2-ethylhexyl) sulfosuccinate]_n ([PCE][AOT]_n) were chosen as the two corona-forming blocks. Both polymers are soluble in *iso*-propanol (*i*PrOH), which is important for formation of the block comicelles. However, in a 1:1 mixture of *i*PrOH:decane, only [PCE][AOT]_n remains soluble (Fig. S1), thereby allowing for the selective chain collapse of P2VP in the presence of [PCE][AOT]_n. The 3 materials **PFS**₂₃, **PFS**_x-**b**-**P2VP**_y, and **PFS**₄₂-**b**-**[PCE][AOT]**₇₅ (Fig. 1a) were synthesized according to previously published procedures.^{51,52} Seeds of **PFS**₅₀-**b**-**P2VP**₇₃₉ were formed by sequential self-nucleation, sonication, and unimer

addition procedures to form low-dispersity 1D micelles (Fig. S2a: $L_n = 631$ nm, $L_w/L_n = 1.03$; L_n = number-average contour length, L_w = weight-average contour length), from which platelet growth could be initiated.

Platelet block comicelles were initially formed in which the central region contained a [PCE][AOT]_n corona, and the outer zone a P2VP corona. To a solution of **PFS₅₀-*b*-P2VP₇₃₉** seeds in *i*PrOH was added a unimer blend of **PFS₂₃/PFS₄₂-*b*-[PCE][AOT]₇₅** (1:5 w/w) in THF and aged for 16 h. The 2D platelets that formed (Fig. S2b) were then further diluted in *i*PrOH and used as seeds, to which a unimer blend of **PFS₂₃/PFS₃₂-*b*-P2VP₇₆₀** (1:1 w/w) in THF was added and aged for 16 h.

Transmission electron microscopy (TEM) analysis of the sample, drop-cast from solution onto carbon-coated copper grids, revealed that rectangular block comicelles had been formed with a distinct and well-defined regionally distinct architecture. The coronal contrast was provided by the greater electron density of P2VP compared with that of [PCE][AOT]_n (Fig. 1c and d). This difference in electron density also allowed the seed micelle to be clearly visualized at the center of the platelet (Fig. 1d and f). The micelle lengths and widths were measured, and the areas calculated, demonstrating uniform rectangular structures with a number-average area of 2.25 μm^2 and low dispersities (Fig. S3). To induce the patterning of the outer platelet region through coronal chain collapse, decane, a poor solvent for P2VP, was added (Fig. 1b). After addition of this selective solvent, TEM image analysis showed the presence of distinct patches on the outer regions of the platelets (Fig. 1e and f). The patches appear to decrease in size, become less interconnected, and increase in number on traversing from the interface with the central region to the micelle periphery (Fig. 1f). The patch size is related to the surface density of the corona chains.

Figure 1. (a) Chemical structures of poly(ferrocenyldimethylsilane) (**PFS₂₃**), poly(ferrocenyldimethylsilane)-*block*-[poly(cobaltoceniumethylene)][bis(2-ethylhexyl)sulfosuccinate] (**PFS₄₂-*b*-[PCE][AOT]₇₅**) and poly(ferrocenyldimethylsilane)-*block*-poly(2-vinylpyridine) (**PFS₃₂-*b*-P2VP₇₆₀**), (b) Schematic of a rectangular 2D block comicelle before and after corona collapse on the outer spatial region, (c) low magnification TEM image and (d) high magnification TEM image of rectangular 2D block comicelles (central region = 1:5 w/w **PFS₂₃/PFS₄₂-*b*-[PCE][AOT]₇₅**, outer region = 1:1 w/w **PFS₂₃/PFS₃₂-*b*-P2VP₇₆₀**) in *i*PrOH, (e) low magnification TEM image and (f) high magnification TEM image of patchy rectangular 2D block comicelles (central region = 1:5 w/w **PFS₂₃/PFS₄₂-*b*-[PCE][AOT]₇₅**, outer region = 1:1 w/w **PFS₂₃/PFS₃₂-*b*-P2VP₇₆₀**) in 1:1 *i*PrOH:decane. P2VP = green, [PCE][AOT]_n = purple, PFS = yellow. Scale bars = 5000 nm, inset = 1000 nm.

Atomic force microscopy (AFM) was performed to gain further insight into the coronal patches (Fig. 2a-c). A height profile along the length of the platelet confirmed the trend of a decrease in the height of patches as the outer spatial region is traversed from the interface with the central block derived with a [PCE][AOT]_n corona (ca. 10 nm) to the periphery of the platelet (ca. 5 nm, Fig. 2a and b, blue trace). Additionally, this height profile showed that the cylindrical seed micelle produced a single patch that possessed a greater height (ca. 13 nm) than any of the patches in the outer spatial region, and that the central block containing a [PCE][AOT]_n corona possessed a relatively uniform surface. The greater height of the patch formed by the seed is attributed to two factors (i) the seed possessing a greater coronal density than is present in the surrounding regions, as it is produced from solely a BCP, rather than a blend of BCP and homopolymer, and (ii) the longer length of the PFS segment in the seed (degree of polymerization, DP_n = 50), which generates a crystalline core of greater height than that present in the outer regions of the platelet. Analysis of AFM height profiles taken across the width of the outer block region again show that patches at the interface with the central area with a [PCE][AOT] corona (ca. 10 nm high and ca. 55 nm wide, Fig. 2a and b, red trace) are higher and wider than at the periphery of the platelet (ca. 5 nm high and ca. 30 nm wide, Fig. 2a and b, green trace).

To characterize the spatial variations in coronal chemistry we used energy dispersive X-ray spectroscopy (EDX) in elemental mapping mode. Dark-field TEM was first used to locate platelets on the carbon-coated copper grid (Fig. 2d). The spectroscopy indicated that the patches consisted of higher densities of carbon and nitrogen than the regions without the patches, consistent with a P2VP composition (Fig. 2e and f). EDX mapping also revealed that there was a higher density of cobalt in the central region, owing to the [PCE][AOT]_n corona (Fig. 2f). Finally, iron was present

throughout the micelle structure (Fig. 2e and f) as a result of the presence of a crystalline PFS core in the seed and both the inner and outer block regions.

Figure 2. (a) AFM height image, (b) AFM height profiles, (c) 3D AFM image, (d) Dark-field TEM image, (e and f) EDX single element mapping images of patchy rectangular 2D block comicelles (central block region = 1:5 w/w **PFS₂₃/PFS₄₂-*b*-[PCE][AOT]₇₅**, outer block region = 1:1 w/w **PFS₂₃/PFS₃₂-*b*-P2VP₇₆₀**) in 1:1 *i*PrOH:decane. In (f) high magnification images taken from the white box highlighted in (d). Scale bars = (a, d and e) 1000 nm, (f) 250 nm.

The area of the outer block zone could be varied by changing the amount of **PFS₂₃/PFS₃₂-*b*-P2VP₇₆₀** unimer blend (1:1 w/w) added in the self-assembly process (Fig. S4). When the area of the outer block region was substantially greater than that of the central area, some platelet

aggregation could be detected after patch formation and drying for sample analysis (Fig. S4f). However, the micelles maintained colloidal stability and no precipitation was observed.

We explored whether the pattern and/or size of the patches on the surface of rectangular 2D block comicelles could be controlled. We found that control over the coronal patch density on the outer block region could be achieved by varying the ratio of PFS homopolymer to PFS-*b*-P2VP BCP in the unimer blend used to form this part of the platelet. As noted above, when a 1:1 w/w ratio of **PFS₂₃/PFS₃₂-*b*-P2VP₇₆₀** unimer was used, patches formed across the whole surface of the outer block region, with an average diameter of 57 nm (Fig. 3b, S5b and S6b). When the corona density was reduced, by using a 2:1 w/w ratio of **PFS₂₃/PFS₃₂-*b*-P2VP₇₆₀** unimer blend, patches of similar size to those for a 1:1 w/w blend were only observed close to the interface with the central block (Fig. 3a and S5a). However, the size of the patches decreased dramatically moving away from the interface and most of the outer block was covered by very small patches (ca. 22 nm wide, Fig. 3a and S6a). Increasing the corona density, by using a 1:2 w/w ratio of **PFS₂₃/PFS₃₂-*b*-P2VP₇₆₀** unimer blend, led to the outer block region being densely covered by interconnected patches, with a ring of high electron density at the edge of the platelet block comicelles (Fig. 3c and S5c). These results suggest that the deposition rates of the **PFS₂₃** homopolymer and **PFS₃₂-*b*-P2VP₇₆₀** block copolymer are relatively similar, presumably due to the lower degree of polymerization of PFS in the former compared to the latter which appears to mitigate the effect of the long solubilizing P2VP corona. Both homopolymer and block copolymer appear to epitaxially grow from the edge of the central block region concurrently, so that whichever species is present in a larger amount will be left to deposit on the periphery of the micelle.

In addition, the ratio of homopolymer to BCP in the unimer blend used to form the outer block region affected the size of the micelles, with an average area of 3.01 μm^2 , 2.24 μm^2 and 2.06 μm^2

for homopolymer/BCP blends of 2:1, 1:1 and 1:2 w/w respectively (Fig. 3a-c and S7). Blends with more homopolymer contained a larger amount of PFS by mass (as a reduced mass fraction comprised the corona-forming block), which led to the formation of larger micelles.

Figure 3. TEM images of patchy rectangular 2D block comicelles (central block region = 1:5 w/w **PFS₂₃/PFS₄₂-*b*-[PCE][AOT]₇₅**, outer block region = x: y w/w **PFS₂₃/PFS₃₂-*b*-P2VP₇₆₀**) in 1:1 *i*PrOH:decane. PFS/PFS-*b*-P2VP mass ratio = (a) 2:1, (b) 1:1, (c) 1:2. Insets showing higher magnification of patches at micelle tips. Scale bars = 1000 nm and 250 nm in insets.

The effect of varying the DP_n of the P2VP corona in the 1:1 w/w unimer blend of PFS/PFS-*b*-P2VP used to form the outer block region was also explored (Fig. S8). As the DP_n of the P2VP corona was reduced from 760 to 480, the size of patches decreased from an average of 57 nm to 24 nm (Fig. S6b, S6c, S8a and S8b). On further reduction of the P2VP length dense regions of interconnected patches and were observed only close to the interface with the central block region, rather than at the periphery of the outer block region (Fig. S8a-d). It is expected that BCP unimers with shorter P2VP coronas will be less-well solvated under the self-assembly conditions and deposit at a faster rate, which would lead to patch density being higher at the interface with the central block region. Additionally, defects were present in a majority of micelle formed using a

unimer blend containing the shortest P2VP corona investigated (**PFS₂₀-*b*-P2VP₁₁₆**, Fig. S8d). Rapid deposition is expected to increase the likelihood of defect formation.

Living CDSA is a powerful tool for forming architecturally diverse nanostructures. We also explored whether 2D surface-patterned platelets with other morphologies could be accessed via selective coronal collapse. Initially, we aimed to form inverted patchy platelets with the surface patterning restricted to the central block region. The order of addition of the unimer blends to the cylindrical **PFS₅₀-*b*-P2VP₇₃₉** seeds was reversed; first a unimer blend of **PFS₂₃/PFS₃₂-*b*-P2VP₇₆₀** (1:1 w/w) was added to seeds, followed by a unimer blend of **PFS₂₃/PFS₄₂-*b*-[PCE][AOT]₇₅** (1:5 w/w) to produce platelets with a P2VP corona decorating the central block region and a [PCE][AOT]_n corona on the outer area comprising the outer zone (Fig. S9). On addition of decane, these rectangular 2D block comicelles remained well-dispersed and displayed a patchy central block region surrounded by a periphery with uniform electron density (Fig. 4a).

More complex platelets with four concentric block regions were prepared by four sequential and alternate additions of **PFS₂₃/PFS₄₂-*b*-[PCE][AOT]₇₅** (1:5 w/w) and **PFS₂₃/PFS₃₂-*b*-P2VP₇₆₀** (1:1 w/w) unimer blends to cylindrical **PFS₅₀-*b*-P2VP₇₃₉** seeds in *i*PrOH. Extremely large rectangular 2D multiblock comicelles, over a micrometer wide and several micrometers long, were produced (Fig. S10). On addition of decane, well-dispersed micelles were observed that contained two patchy block regions possessing P2VP coronas separated by a zone possessing a [PCE][AOT]_n corona (Fig. 4b).

Finally, we wished to see if we could form colloiddally stable, surface patterned circular platelets. The platelets were produced by replacement of the cylindrical **PFS₅₀-*b*-P2VP₇₃₉** seeds with seeds prepared from the phosphonium-capped homopolymer [**PFS₂₀PPh₂Me**]**I** (Fig. S11a), as reported previously.²⁰ The sequential seeded growth of **PFS₂₃/PFS₄₂-*b*-[PCE][AOT]₇₅** (1:1 w/w) and

PFS₂₃/PFS₃₂-*b*-P2VP₇₆₀ (1:1 w/w) unimer blends produced circular 2D block comicelles with a [PCE][AOT]_n corona on the central block region and a P2VP corona on the outer block zone (Fig. S11c and d). A high proportion of the micelles displayed imperfections (Fig. S11d), as it is expected that the formation of rectangular crystals is thermodynamically favored over circular structures. Patch formation was again possible on the addition of decane (Fig. 4c). The pattern of patches resembled the pattern formed on rectangular 2D block comicelles (Fig. 1f), however the patches were more interconnected.

Figure 4. TEM images of (a) inverse patchy rectangular 2D block comicelles (central block region = 1:1 w/w **PFS₂₃/PFS₃₂-*b*-P2VP₇₆₀**, outer block region = 1:5 w/w **PFS₂₃/PFS₄₂-*b*-[PCE][AOT]₇₅**) in 1:1 w/w *i*PrOH:decane, (b) rectangular 2D block comicelles comprising of 4 concentric blocks (central block region = 1:5 w/w **PFS₂₃/PFS₄₂-*b*-[PCE][AOT]₇₅**, second block region = 1:1 w/w **PFS₂₃/PFS₃₂-*b*-P2VP₇₆₀**, third block region = 1:5 w/w **PFS₂₃/PFS₄₂-*b*-[PCE][AOT]₇₅**, outer block region = 1:1 w/w **PFS₂₃/PFS₃₂-*b*-P2VP₇₆₀**) in 1:1 w/w *i*PrOH:decane and (c) patchy circular 2D block comicelles (central block region = 1:1 w/w **PFS₂₃/PFS₄₂-*b*-[PCE][AOT]₇₅**, outer block region = 1:1 w/w **PFS₂₃/PFS₃₂-*b*-P2VP₇₆₀**) in 1:1 *i*PrOH:decane. Scale bars = (a) 5000 nm, (b) 2000 nm, (c) 1000 nm.

We have demonstrated the formation of 2D block comicelles, via living CDSA, which contain the same core-forming block (PFS) and differ in the corona-forming block (P2VP and [PCE][AOT]_n). On addition of a solvent that selectively solvates one corona, surface patterning occurred due to coronal collapse of the poorly solvated corona. Surface patterning was possible on the surface of a variety of 2D micelle architectures, including rectangular platelets containing 4 block regions and circular block comicelles.

EDX spectroscopy and AFM were used to study the chemistry and morphology of the patterned surfaces. These characterization techniques proved that the patches were indeed composed of P2VP corona chains that had collapsed onto the surface of the core of the micelle. The size of the patches is related to the density of the corona, and hence the size and distribution of the patches provided information on the locality of both homopolymer and block copolymer in the surface patterned block regions of the platelets. We demonstrated that it is possible to vary the size and number of patches that decorate the micelle surface by modulating both the ratio of homopolymer to BCP and the DP_n of the corona-forming block.

The ability to form patterns on discrete nanoscale surfaces may be of interest for a number of applications, such as data storage, the localization of functional materials within colloids to form novel hybrid materials, and to direct further assembly of nanoparticles into functional arrays for catalytic applications. Future work will aim to use the patterned structures formed herein to access such hybrid materials and also investigate whether reversible patch formation can be achieved by further modulation of solvent conditions.

ASSOCIATED CONTENT

Supporting Information. The following file is available free of charge containing details of the Materials and Equipment, description of self-assembly experiments and additional figures (PDF).

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REFERENCES

- (1) Zhuang, X.; Mai, Y.; Wu, D.; Zhang, F.; Feng, X. Two-Dimensional Soft Nanomaterials: A Fascinating World of Materials. *Adv. Mater.* **2015**, *27* (3), 403–427.
- (2) Boott, C. E.; Nazemi, A.; Manners, I. Synthetic Covalent and Non-Covalent 2D Materials. *Angew. Chemie - Int. Ed.* **2015**, *54* (47), 13876–13894.
- (3) Tritschler, U.; Pearce, S.; Gwyther, J.; Whittell, G. R.; Manners, I. 50th Anniversary Perspective: Functional Nanoparticles from the Solution Self-Assembly of Block Copolymers. *Macromolecules* **2017**, *50* (9), 3439–3463.
- (4) Lotz, B.; Kovacs, A. J.; Bassett, G. A.; Keller, A. Properties of Copolymers Composed of One Poly-Ethylene-Oxide and One Polystyrene Block - II. Morphology of Single Crystals. *Kolloid-Zeitschrift Zeitschrift für Polym.* **1966**, *209* (2), 115–128.
- (5) Gast, A. P.; Vinson, P. K.; Cogan-Farinas, K. A. An Intriguing Morphology in Crystallizable Block Copolymers. *Macromolecules* **1993**, *26* (7), 1774–1776.
- (6) Wang, J.; Zhu, W.; Peng, B.; Chen, Y. A Facile Way to Prepare Crystalline Platelets of Block Copolymers by Crystallization-Driven Self-Assembly. *Polymer (Guildf)*. **2013**, *54* (25), 6760–6767.
- (7) Su, M.; Huang, H.; Ma, X.; Wang, Q.; Su, Z. Poly(2-Vinylpyridine)- Block -Poly(ϵ - Caprolactone) Single Crystals in Micellar Solution. *Macromol. Rapid Commun.* **2013**, *34* (13), 1067–1071.
- (8) Wang, Z.; Cao, Y.; Song, J.; Xie, Z.; Wang, Y. Cooperation of Amphiphilicity and

- Crystallization for Regulating the Self-Assembly of Poly(Ethylene Glycol)-Block-Poly(Lactic Acid) Copolymers. *Langmuir* **2016**, *32* (37), 9633–9639.
- (9) Li, Z.; Liu, R.; Mai, B.; Wang, W.; Wu, Q.; Liang, G.; Gao, H.; Zhu, F. Temperature-Induced and Crystallization-Driven Self-Assembly of Polyethylene-*b*-Poly(Ethylene Oxide) in Solution. *Polymer (Guildf)*. **2013**, *54* (6), 1663–1670.
- (10) Wang, X.; Guerin, G.; Wang, H.; Wang, Y.; Manners, I.; Winnik, M. A. Cylindrical Block Copolymer Micelles and Co-Micelles of Controlled Length and Architecture. *Science* (80-.). **2007**, *317* (5838), 644–647.
- (11) Gilroy, J. B.; Gädt, T.; Whittell, G. R.; Chabanne, L.; Mitchels, J. M.; Richardson, R. M.; Winnik, M. A.; Manners, I. Monodisperse Cylindrical Micelles by Crystallization-Driven Living Self-Assembly. *Nat. Chem.* **2010**, *2* (7), 566–570.
- (12) Schmelz, J.; Schedl, A. E.; Steinlein, C.; Manners, I.; Schmalz, H. Length Control and Block-Type Architectures in Worm-like Micelles with Polyethylene Cores. *J. Am. Chem. Soc.* **2012**, *134* (34), 14217–14225.
- (13) Arno, M. C.; Inam, M.; Coe, Z.; Cambridge, G.; Macdougall, L. J.; Keogh, R.; Dove, A. P.; O'Reilly, R. K. Precision Epitaxy for Aqueous 1D and 2D Poly(ϵ -Caprolactone) Assemblies. *J. Am. Chem. Soc.* **2017**, *139* (46), 16980–16985.
- (14) Tao, D.; Feng, C.; Cui, Y.; Yang, X.; Manners, I.; Winnik, M. A.; Huang, X. Monodisperse Fiber-like Micelles of Controlled Length and Composition with an Oligo(*p*-Phenylenevinylene) Core via “Living” Crystallization-Driven Self-Assembly. *J. Am. Chem. Soc.* **2017**, *139* (21), 7136–7139.

- (15) Shin, S.; Menk, F.; Kim, Y.; Lim, J.; Char, K.; Zentel, R.; Choi, T. L. Living Light-Induced Crystallization-Driven Self-Assembly for Rapid Preparation of Semiconducting Nanofibers. *J. Am. Chem. Soc.* **2018**, *140* (19), 6088–6094.
- (16) Jin, B.; Sano, K.; Aya, S.; Ishida, Y.; Gianneschi, N.; Luo, Y.; Li, X. One-Pot Universal Initiation-Growth Methods from a Liquid Crystalline Block Copolymer. *Nat. Commun.* **2019**, *10* (1).
- (17) Hudson, Z. M.; Boott, C. E.; Robinson, M. E.; Rugar, P. A.; Winnik, M. A.; Manners, I. Tailored Hierarchical Micelle Architectures Using Living Crystallization-Driven Self-Assembly in Two Dimensions. *Nat. Chem.* **2014**, *6* (10), 893–898.
- (18) Yu, B.; Jiang, X.; Yin, J. Size-Tunable Nanosheets by the Crystallization-Driven 2D Self-Assembly of Hyperbranched Poly(Ether Amine) (HPEA). *Macromolecules* **2014**, *47* (14), 4761–4768.
- (19) Qiu, H.; Gao, Y.; Boott, C. E.; Gould, O. E. C.; Harniman, R. L.; Miles, M. J.; Webb, S. E. D.; Winnik, M. A.; Manners, I. Uniform Patchy and Hollow Rectangular Platelet Micelles from Crystallizable Polymer Blends. *Science (80-.)*. **2016**, *352* (6286), 697–702.
- (20) He, X.; Hsiao, M. S.; Boott, C. E.; Harniman, R. L.; Nazemi, A.; Li, X.; Winnik, M. A.; Manners, I. Two-Dimensional Assemblies from Crystallizable Homopolymers with Charged Termini. *Nat. Mater.* **2017**, *16* (4), 481–488.
- (21) He, X.; He, Y.; Hsiao, M. S.; Harniman, R. L.; Pearce, S.; Winnik, M. A.; Manners, I. Complex and Hierarchical 2D Assemblies via Crystallization-Driven Self-Assembly of Poly(l -Lactide) Homopolymers with Charged Termini. *J. Am. Chem. Soc.* **2017**, *139* (27),

9221–9228.

- (22) Inam, M.; Jones, J. R.; Pérez-Madrigal, M. M.; Arno, M. C.; Dove, A. P.; O'Reilly, R. K. Controlling the Size of Two-Dimensional Polymer Platelets for Water-in-Water Emulsifiers. *ACS Cent. Sci.* **2018**, *4* (1), 63–70.
- (23) Han, L.; Wang, M.; Jia, X.; Chen, W.; Qian, H.; He, F. Uniform Two-Dimensional Square Assemblies from Conjugated Block Copolymers Driven by π - π Interactions with Controllable Sizes. *Nat. Commun.* **2018**, *9* (1).
- (24) Pearce, S.; He, X.; Hsiao, M. S.; Harniman, R. L.; Macfarlane, L. R.; Manners, I. Uniform, High-Aspect-Ratio, and Patchy 2D Platelets by Living Crystallization-Driven Self-Assembly of Crystallizable Poly(Ferrocenyldimethylsilane)-Based Homopolymers with Hydrophilic Charged Termini. *Macromolecules* **2019**, *52* (16), 6068–6079.
- (25) Cha, Y.; Jarrett-Wilkins, C.; Rahman, M. A.; Zhu, T.; Sha, Y.; Manners, I.; Tang, C. Crystallization-Driven Self-Assembly of Metallo-Polyelectrolyte Block Copolymers with a Polycaprolactone Core-Forming Segment. *ACS Macro Lett.* **2019**, *8* (7), 835–840.
- (26) Arno, M. C.; Inam, M.; Weems, A. C.; Li, Z.; Binch, A. L. A.; Platt, C. I.; Richardson, S. M.; Hoyland, J. A.; Dove, A. P.; O'Reilly, R. K. Exploiting the Role of Nanoparticle Shape in Enhancing Hydrogel Adhesive and Mechanical Properties. *Nat. Commun.* **2020**, *11* (1), 1–9.
- (27) Dong, B.; Zhou, T.; Zhang, H.; Li, C. Y. Directed Self-Assembly of Nanoparticles for Nanomotors. *ACS Nano* **2013**, *7* (6), 5192–5198.

- (28) Dong, B.; Miller, D. L.; Li, C. Y. Polymer Single Crystal as Magnetically Recoverable Support for Nanocatalysts. *J. Phys. Chem. Lett.* **2012**, *3* (10), 1346–1350.
- (29) Mei, S.; Staub, M.; Li, C. Y. Directed Nanoparticle Assembly through Polymer Crystallization. *Chem. – A Eur. J.* **2020**, *26* (2), 349–361.
- (30) Glotzer, S. C.; Solomon, M. J. Anisotropy of Building Blocks and Their Assembly into Complex Structures. *Nat. Mater.* **2007**, *6* (8), 557–562.
- (31) Lunn, D. J.; Finnegan, J. R.; Manners, I. Self-Assembly of “Patchy” Nanoparticles: A Versatile Approach to Functional Hierarchical Materials. *Chem. Sci.* **2015**, *6* (7), 3663–3673.
- (32) Du, J.; O’Reilly, R. K. Anisotropic Particles with Patchy, Multicompartment and Janus Architectures: Preparation and Application. *Chem. Soc. Rev.* **2011**, *40* (5), 2402–2416.
- (33) Choueiri, R. M.; Galati, E.; Thérien-Aubin, H.; Klinkova, A.; Larin, E. M.; Querejeta-Fernández, A.; Han, L.; Xin, H. L.; Gang, O.; Zhulina, E. B.; et al. Surface Patterning of Nanoparticles with Polymer Patches. *Nature* **2016**, *538* (7623), 79–83.
- (34) Gröschel, A. H.; Walther, A.; Löbbling, T. I.; Schacher, F. H.; Schmalz, H.; Müller, A. H. E. Guided Hierarchical Co-Assembly of Soft Patchy Nanoparticles. *Nature* **2013**, *503* (7475), 247–251.
- (35) Wang, Y.; Wang, Y.; Breed, D. R.; Manoharan, V. N.; Feng, L.; Hollingsworth, A. D.; Weck, M.; Pine, D. J. Colloids with Valence and Specific Directional Bonding. *Nature* **2012**, *491* (7422), 51–55.

- (36) Cui, H.; Chen, Z.; Zhong, S.; Wooley, K. L.; Pochan, D. J. Block Copolymer Assembly via Kinetic Control. *Science* (80-.). **2007**, *317* (5838), 647–650.
- (37) Chen, Q.; Bae, S. C.; Granick, S. Directed Self-Assembly of a Colloidal Kagome Lattice. *Nature* **2011**, *469* (7330), 381–384.
- (38) Schmelz, J.; Karg, M.; Hellweg, T.; Schmalz, H. General Pathway toward Crystalline-Core Micelles with Tunable Morphology and Corona Segregation. *ACS Nano* **2011**, *5* (12), 9523–9534.
- (39) Schmalz, H.; Schmelz, J.; Drechsler, M.; Yuan, J.; Walther, A.; Schweimer, K.; Mihut, A. M. Thermo-Reversible Formation of Wormlike Micelles with a Microphase-Separated Corona from a Semicrystalline Triblock Terpolymer. *Macromolecules* **2008**, *41* (9), 3235–3242.
- (40) Nunns, A.; Whittell, G. R.; Winnik, M. A.; Manners, I. Crystallization-Driven Solution Self-Assembly of μ -ABC Miktoarm Star Terpolymers with Core-Forming Polyferrocenylsilane Blocks. *Macromolecules* **2014**, *47* (23), 8420–8428.
- (41) Cruz, M.; Xu, J.; Yu, Q.; Guerin, G.; Manners, I.; Winnik, M. A. Visualizing Nanoscale Coronal Segregation in Rod-Like Micelles Formed by Co-Assembly of Binary Block Copolymer Blends. *Macromol. Rapid Commun.* **2018**, *39* (22), 1800397.
- (42) Xu, J.; Zhou, H.; Yu, Q.; Guerin, G.; Manners, I.; Winnik, M. A. Synergistic Self-Seeding in One-Dimension: A Route to Patchy and Block Comicelles with Uniform and Controllable Length. *Chem. Sci.* **2019**, *10* (8), 2280–2284.

- (43) Finnegan, J. R.; Lunn, D. J.; Gould, O. E. C.; Hudson, Z. M.; Whittell, G. R.; Winnik, M. A.; Manners, I. Gradient Crystallization-Driven Self-Assembly: Cylindrical Micelles with “Patchy” Segmented Coronas via the Coassembly of Linear and Brush Block Copolymers. *J. Am. Chem. Soc.* **2014**, *136* (39), 13835–13844.
- (44) Wang, H.; Lin, W.; Fritz, K. P.; Scholes, G. D.; Winnik, M. A.; Manners, I. Cylindrical Block Co-Micelles with Spatially Selective Functionalization by Nanoparticles. *J. Am. Chem. Soc.* **2007**, *129* (43), 12924–12925.
- (45) Schöbel, J.; Burgard, M.; Hils, C.; Dersch, R.; Dulle, M.; Volk, K.; Karg, M.; Greiner, A.; Schmalz, H. Bottom-Up Meets Top-Down: Patchy Hybrid Nonwovens as an Efficient Catalysis Platform. *Angew. Chemie - Int. Ed.* **2017**, *56* (1), 405–408.
- (46) Chen, T.; Chen, G.; Xing, S.; Wu, T.; Chen, H. Scalable Routes to Janus Au-SiO₂ and Ternary Ag-Au-SiO₂ Nanoparticles. *Chem. Mater.* **2010**, *22* (13), 3826–3828.
- (47) Löbbling, T. I.; Borisov, O.; Haataja, J. S.; Ikkala, O.; Gröschel, A. H.; Müller, A. H. E. Rational Design of ABC Triblock Terpolymer Solution Nanostructures with Controlled Patch Morphology. *Nat. Commun.* **2016**, *7* (May).
- (48) Chen, W. Y.; Li, C. Y.; Zheng, J. X.; Huang, P.; Zhu, L.; Ge, Q.; Quirk, R. P.; Lotz, B.; Deng, L.; Wu, C.; et al. “Chemically Shielded” Poly(Ethylene Oxide) Single Crystal Growth and Construction of Channel-Wire Arrays with Chemical and Geometric Recognitions on a Submicrometer Scale. *Macromolecules* **2004**, *37* (14), 5292–5299.
- (49) Zheng, J. X.; Xiong, H.; Chen, W. Y.; Lee, K.; Van Horn, R. M.; Quirk, R. P.; Lotz, B.; Thomas, E. L.; Shi, A. C.; Cheng, S. Z. D. Onsets of Tethered Chain Overcrowding and

Highly Stretched Brush Regime via Crystalline - Amorphous Diblock Copolymers. *Macromolecules* **2006**, 39 (2), 641–650.

- (50) Hailes, R. L. N.; Oliver, A. M.; Gwyther, J.; Whittell, G. R.; Manners, I. Polyferrocenylsilanes: Synthesis, Properties, and Applications. *Chem. Soc. Rev.* **2016**, 45 (19), 5358–5407.
- (51) Jarrett-Wilkins, C. N.; Musgrave, R. A.; Hailes, R. L. N.; Harniman, R. L.; Faul, C. F. J.; Manners, I. Linear and Branched Fiber-like Micelles from the Crystallization-Driven Self-Assembly of Heterobimetallic Block Copolymer Polyelectrolyte/Surfactant Complexes. *Macromolecules* **2019**, 52 (19), 7289–7300.
- (52) Wang, H.; Winnik, M. A.; Manners, I. Synthesis and Self-Assembly of Poly(Ferrocenyldimethylsilane-*b*-2-Vinylpyridine) Diblock Copolymers. *Macromolecules* **2007**, 40 (10), 3784–3789.