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Supplementary Information

Customized 2D Assemblies from Crystallizable Homopolymers with Charged Termini

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Methods

Materials

All reactions were carried out in an MBraun MB150B-G glove box under argon or using standard Schlenk line techniques. All chemicals were purchased from Aldrich and were used as received unless otherwise stated. *L*-lactide was recrystallized twice from dry toluene and stored in the glove box. PFS₂₅-*b*-P2VP₂₅₀ and PFS₂₅-*b*-P2VP₃₃₀, PFS₂₀-*b*-P2VP₁₄₀, PFS₅₁-*b*-P2VP₇₃₁ and PFS₂₅-*b*-PMVS₁₇₀ BCPs were prepared by literature procedure.¹⁻³ Detailed synthesis for the newly reported polymers PFS_mPPh₂ (*m* = 20 or 61), PFS_m[PPh₂Me]I (*m* = 20 or 61), PI₂₅-*b*-PFS₂₂PPh₂, PI₂₅-*b*-PFS₂₂[PPh₂Me]I, PFS₂₂-G, PLLA_mPPh₂ (*m* = 24 or 34), PLLA_m[PPh₂Me]I (*m* = 24 or 34), PLLA₂₁-G, PLLA₂₁-R are described in supplementary information. Photoirradiation experiments were carried out with Pyrex-glass filtered emission from a 125 W medium-pressure mercury lamp (Photochemical Reactors Ltd). Tetrahydrofuran (THF) for living anionic polymerizations was pre-dried with sodium and distilled off sodium/benzophenone prior to use. All of the self-assembly experiments were performed in HPLC grade solvents that were acquired from Fisher. ¹H, ¹³C and ³¹P NMR spectra were recorded using Jeol Eclipse 400 MHz or Varian VNMR 400 MHz and 500 MHz spectrometers.

Polymer characterization

The molecular weights of the PFS and PLLA homopolymers were determined from matrix-assisted laser desorption/ionization time of flight (MALDI-TOF) mass spectrometry measurements. For BCPs, the molecular weights were determined by combining the *M_n* of PFS homopolymers with the block ratio obtained by ¹H NMR integration. MALDI-TOF mass spectrometry measurements of PFS and PLLA homopolymers were performed using a Bruker Ultraflex extreme running in linear mode. Samples were prepared using a *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile matrix (20 mg/mL in THF) and the polymer sample (2 mg/mL in THF), mixed in a 10:1 (v/v) ratio. Approximately 1 μL of the mixed solution was deposited onto a stainless steel sample plate and allowed to dry in air.

Polydispersity indices (PDI = *M_w*/*M_n*) of all the polymers were obtained by Gel Permeation Chromatography (GPC) using a Viscotek VE 2001 Triple-Detector Gel Permeation Chromatograph equipped with automatic sampler, pump, injector, inline degasser, column oven (30 °C), styrene/divinylbenzene columns (pore sizes of between 500 Å and 100,000 Å), VE 3580 refractometer, four-capillary differential viscometer, VE 3210 UV/Vis detector (λ = 450 nm) and VE 270 dual angle laser light scattering detector (7° and 90°). THF stabilized with 0.025% butylated hydroxytoluene (Fisher) was used as the chromatography eluent, at a flow rate of 1.0 mL·min⁻¹. Samples were dissolved in the eluent (2 mg/mL) and filtered (PTFE membrane with 0.45 μm pore size) before analysis. Calibration of the detectors was performed using polystyrene standards (Viscotek).

Transmission electron microscopy (TEM)

Copper grids from Agar Scientific, mesh 400, were coated with a carbon film. Carbon coating was done using an Agar TEM Turbo Carbon Coater in which carbon was sputtered onto mica sheets before

deposition on the grids via flotation on water. The samples for electron microscopy were prepared by drop-casting one drop (~10 µl) of the micelle colloidal solution onto a carbon-coated copper grid. Bright-field transmission electron microscopy (TEM) micrographs were obtained on a JEOL1200EX II microscope operating at 120 kV and equipped with an SIS MegaViewIII digital camera. As the micelles reported here are trapped kinetically because of crystallization of the core block, the morphologies observed from dried samples by TEM are anticipated to match closely those observed in solution, as previously shown for 1D systems.

Selected area electron diffraction (SAED) patterns for PFS based platelet micelle and comicelles were collected by Philips CM200 LaB6 TEM equipped with 4 pi imaging system with spot size of 8 nm at 200 kV (the diameter of selected area aperture is 200 nm). The d-spacings of SAED patterns were calibrated using gold nanoparticles standard. Elemental mapping from images of quasi-hexagonal disk-like platelet micelles and comicelles was performed on the FEI Talos F200X FEG TEM operating at 200 kV in STEM mode with spot size of 6.

Micelle area and length distributions were determined using the software program ImageJ from the National Institutes of Health. For the statistical analyses, more than 200 micelles in several images were traced by the software in order to obtain the area or length information. The number average micelle length (L_n) and weight average micelle length (L_w) (for 1D cylindrical micelles) or number average micelle area (A_n) and weight average micelle area (A_w) (for 2D platelets) were calculated as shown below (L , length of object; N , number; A , area of object).

$$\begin{aligned}
 (1) \quad L_n &= \frac{\sum_{i=1}^n N_i L_i}{\sum_{i=1}^n N_i} & (2) \quad L_w &= \frac{\sum_{i=1}^n N_i L_i^2}{\sum_{i=1}^n N_i L_i} \\
 (3) \quad A_n &= \frac{\sum_{i=1}^n N_i A_i}{\sum_{i=1}^n N_i} & (4) \quad A_w &= \frac{\sum_{i=1}^n N_i A_i^2}{\sum_{i=1}^n N_i A_i}
 \end{aligned}$$

The standard deviations (σ) of the measured lengths were calculated directly from the data set.

Atomic force microscopy (AFM)

Samples for AFM were prepared by drop-casting 8 µL of the micelle solution onto a freshly cleaved mica substrate or carbon-coated mica substrate. Imaging was conducted under ambient conditions using a Bruker Multimode VIII atomic force microscope equipped with a ScanAsyst-HR fast scanning module and a ScanAsyst-Air-HR probe (tip radius, 2 nm), utilizing peak force feedback control. Images were analyzed using Gwyddion or Nanoscope Analysis software program.

Laser Scanning Confocal Microscope (LSCM)

LSCM imaging were obtained using a Leica SP8 AOBS confocal laser scanning microscope, which was attached to a Leica DM I6000 inverted epifluorescent microscope with adaptive focus control to correct focus drift during time-courses and a 100 × oil immersion objective lenses (numerical aperture, NA = 1.44).

Seeded growth of PFS₂₀[PPh₂Me]I from 1D PFS-*b*-P2VP cylindrical seed in *i*PrOH

To a 1mL solution of 1D cylindrical micelles (0.0125 mg/mL in *i*PrOH) derived from PFS₂₅-*b*-P2VP₂₅₀ or PFS₂₅-*b*-P2VP₃₃₀ (in *i*PrOH), was added a certain amount of unimer PFS₂₀[PPh₂Me]I in THF (10 mg/mL). The solution was manually shaken for 10 s and aged at room temperature for 24 h. Uniform rectangular platelets are observed under different concentrations of PFS₂₀[PPh₂Me]I unimer (Supplementary Fig. 1 and 6). As a control experiment, the neutral analogue PFS₂₀PPh₂ was used instead of PFS₂₀[PPh₂Me]I, and only irregular 2D plate structures formed with uncontrolled aggregation (Supplementary Fig. 5).

Effect of mismatches in the degrees of polymerization of the PFS segments in the unimer and seed in the self-assembly

Crystalline lattice matching has been found to be very important for a successful epitaxial growth in living CDSA. Variation of the relative length of PFS core-forming block in the unimer and seed is one of the approach to investigate the effect of crystalline lattice matching. Addition of PFS₂₀[PPh₂Me]I to PFS₅₁-*b*-P2VP₇₃₁ seed in *i*PrOH similarly produced rectangular platelets. On the other hand, we prepared a PFS₆₁[PPh₂Me]I polymer with a long PFS chain length, using the similar synthetic approach to PFS₂₀[PPh₂Me]I. Successful formation of 2D platelets were also observed by CDSA of PFS₆₁[PPh₂Me]I from PFS₂₅-*b*-P2VP₃₃₀ seed, but a higher % of good solvent was required (30% THF in *i*PrOH). In pure *i*PrOH, considerable numbers of spherical micelles were observed. See Supplementary Fig. 7.

Counter-anion exchange of PFS₂₀[PPh₂Me]I and its effect on self assembly

Anion exchange could be easily realized by metathesis reactions. Typically, 30 mg PFS₂₀[PPh₂Me]I was dissolved in 1 mL THF, and excess of a selected salt (sodium *p*-toluenesulfonate, sodium tetraphenylborate or sodium perchlorate; 200 eq.) in 4 mL MeOH was added. A precipitate formed rapidly and the solution was subsequently stirred for 1 h. The precipitate was collected by centrifuge and wash with excess MeOH (3 times) to obtain the desired product. In a control experiment, to a PFS₂₀[PPh₂Me]I solution (30 mg/mL) in THF was added 4 mL of pure MeOH as solvent. The resulting solution was still clear and no precipitation was noted. This result indicated that anion exchange (from I⁻ to OTs⁻, BPh₄⁻ and ClO₄⁻) decreased the polarity of the polymer. Because of characteristic ¹H NMR signal of OTs⁻ and BPh₄⁻ anions, the integration analysis based on the ratio of

PFS₂₀[PPh₂Me]X from and aromatic signal of OTs⁻ and BPh₄⁻ anions confirmed complete anion exchange (see below).

The effect of the counter-anion on the self-assembly behavior was also investigated. Switching the counter-anion from I⁻ to other anions, such as tosylate (OTs⁻) or tetraphenylborate (BPh₄⁻) anions also led to the formation of rectangular platelets in *i*PrOH. Due to the very hydrophobic nature of BPh₄⁻, a certain degree of spherical micelles formation was noted in that case. See Supplementary Fig. 8.

Self-nucleation of PFS₂₀[PPh₂Me]I in MeOH

To 4 mL MeOH (in a 7 mL screw-up vial) was added 400 μL unimer of PFS₂₀[PPh₂Me]I as a 1 mg/mL THF solution. The solution was manually shaken for 10 s and aged for 12 h. 2D disk-like aggregates formed (Supplementary Fig. 11).

Preparation of 2D Seed_{HD} and Seed_{R1} of PFS₂₀[PPh₂Me]I

In brief, 2D Seed_{HD} and Seed_{R1} refer to the 2D seeds that can form quasi-hexagonal disk-like and rectangular platelet micelles using seeded growth, respectively.

(a) 2D Seed_{HD}: 2D disk-like aggregates of PFS₂₀[PPh₂Me]I were firstly prepared from the self nucleation in MeOH using the above procedure. Then the disk-like platelet solution (0.1 mg/mL, MeOH/THF = 10:1) was sonicated at 23 °C for 2 h (four 30-min periods) using an ultrasonic bath to get the desired 2D Seed_{HD} (Supplementary Fig. 12).

(b) 2D Seed_{R1}: Firstly, large rectangular platelets were prepared by seeded growth of PFS₂₀[PPh₂Me]I from PFS₂₅-*b*-P2VP₂₅₀ cylindrical micelles. To 4 mL MeOH was added 8 μ L of 1D cylindrical micelles (0.5 mg/mL in *i*PrOH) derived from PFS₂₅-*b*-P2VP₂₅₀. After a gentle shaking, 400 μ L unimer of PFS₂₀[PPh₂Me]I as a 1 mg/mL THF solution was added to the seed solution. The solution was manually shaken for 10 s and aged at room temperature for 24 h. The unimer-to-seed mass ratio is 100. Then this platelet solution (0.1 mg/mL, MeOH/THF = 10:1) was sonicated at 23 °C for 2 h (four 30-min periods) using an ultrasonic bath to get the desired 2D Seed_{R1} (Supplementary Fig. 15).

Seeded growth of PFS₂₀[PPh₂Me]I from 2D Seed_{HD} and Seed_R

To 1 mL MeOH/THF (100:5) solution (in a 7 mL screw-up vial) was added 20 μ L of 2D Seed_{HD} or Seed_R (0.1 mg/mL, MeOH/THF = 10:1) derived from PFS₂₀[PPh₂Me]I. After a gentle shaking, a certain amount of unimer PFS₂₀[PPh₂Me]I as a 2.5 mg/mL THF solution. The solution was manually shaken for 10 s and aged for 24 h at 23 °C. 2D quasi-hexagonal disk-like and rectangular platelets could be prepared by choosing 2D Seed_{HD}, or Seed_{R1} or Seed_{R2}, respectively (Supplementary Fig. 13, 16, 17). Based on the absence of unimer detectable as a film on the TEM grids the seeded growth processes were complete within 6 h.

Formation of concentric 2D platelet block comicelles

Firstly, different 2D platelets of PFS₂₀[PPh₂Me]I (rectangular platelet, quasi-hexagonal disk-like platelet) were diluted in 1:3 hexane/*i*PrOH (or MeOH) solution with the final concentration of 0.01 mg/mL. Then specified amounts of the PFS₂₀-*b*-P2VP₂₅₀/PFS₂₅ blend unimers (1:1 mass ratio) were added as 5 mg/mL (overall concentration) THF solutions. The solution was manually shaken for 10 s and aged for 24 hours at 23 °C to obtain the desired diblock comicelles (Fig. 3). For the preparation of multiple platelet block comicelles (e.g. tetrablock comicelles, Supplementary Fig. 19), specific amounts of PFS₂₀[PPh₂Me]I (2.5 mg/mL in THF) and PFS₂₀-*b*-P2VP₂₅₀/PFS₂₅ blend unimers (1:1 mass ratio, overall concentration of 5 mg/mL in THF) were further subsequently added.

For the preparation of fluorescent platelet block comicelles, PFS₂₀-*b*-P2VP₂₅₀/PFS₂₅ blend unimers was replaced with PFS₂₀[PPh₂Me]I/PFS₂₂-G (10:1, mass ratio). The seeded growth process can be carried out in MeOH (without hexane). Typically, different 2D platelets of PFS₂₀[PPh₂Me]I (rectangular platelet, quasi-hexagonal disk-like platelet) were firstly diluted in MeOH solution with the final concentration of 0.01 mg/mL. Then specified amounts of the PFS₂₀[PPh₂Me]I/PFS₂₂-G (10:1) blend unimers (10:1 mass ratio) were added as 2.5 mg/mL (overall concentration) THF solutions. The solution was manually shaken for 10 s and aged for 24 hours at 23 °C (Supplementary Fig. 22).

Self-nucleation of PLLA₂₄[PPh₂Me]I and PLLA₃₄[PPh₂Me]I

To 4 mL *i*PrOH or MeOH was added 400 μ L of PLLA_{*n*}[PPh₂Me]I (*n* = 24 or 34) unimer as a 1 mg/mL CHCl₃ solution. The total solvent composition is *i*PrOH(or MeOH)/CHCl₃ (10:1). The solution was manually shaken for 10 s and aged for 24 h at 23 °C. Under this condition, formation of aggregates

of 2D diamond-shape platelet of variable size (final $c = 0.1$ mg/mL) was observed based on TEM analysis (Supplementary Fig. 26).

In order to investigate the effect of solvent composition on the self-nucleation, higher concentration of unimer (5 mg/mL) was used. Similarly, to a 4 mL solution of *i*PrOH was added 80 μ L of PLLA₃₄[PPh₂Me]I unimer as a 5 mg/mL CHCl₃ solution. The total solvent composition is *i*PrOH/CHCl₃ (100:2). The solution was manually shaken for 10 s and aged for 24 h at 23 °C. Under this condition, more spherical micelles were observed (Supplementary Fig. 26b), kinetically trapping the unimer state. Annealing (65 °C for 30 min) induced a transformation from spherical micelles to large 2D platelets (Supplementary Fig. 26b). However, this spontaneous nucleation process led to non-uniform 2D materials.

Preparation of seed of PLLA₂₄[PPh₂Me]I and PLLA₃₄[PPh₂Me]I

Large 2D diamond-shape platelet aggregates from self-nucleation of PLLA₂₄[PPh₂Me]I and PLLA₃₄[PPh₂Me]I (0.1 mg/mL) in *i*PrOH/CHCl₃ (10:1) were firstly prepared using the above procedure. Then the platelet aggregates were fragmentized by sonication at 23 °C for 90 min (three 30-min periods) using an ultrasonic bath. Sonication of 2D platelet of PLLA₂₄[PPh₂Me]I (0.1 mg/mL) in *i*PrOH/CHCl₃ (10:1) produced relatively small, almost 1D platelet fragments of low dispersity that function as seeds ($L_n = 200$ nm, $L_w/L_n = 1.09$; Supplementary Fig. 27).

However, under the same conditions sonication of the 2D platelet of PLLA₃₄[PPh₂Me]I in *i*PrOH/CHCl₃ (10:1) gave 2D seeds with large size and high polydispersity ($A_n = 13,980$ nm², $A_w/A_n = 1.75$). By using MeOH/CHCl₃ (10:1), relatively small, lower dispersity 2D seeds of PLLA₃₄[PPh₂Me]I ($A_n = 6542$ nm², $A_w/A_n = 1.38$; Supplementary Fig. 28) were successfully obtained. The 2D seeds of PLLA₃₄[PPh₂Me]I were further characterized by dynamic light scattering (DLS), with apparent hydrodynamic radius ($R_{H,app}$) of 398 nm (in *i*PrOH) and 124 nm (in MeOH), respectively, consistent with the size trend measured by TEM.

Seeded growth of PLLA_n[PPh₂Me]I ($n = 24$ or 34) in *i*PrOH

To 1 mL *i*PrOH solution was added 25 μ L seed (0.1 mg/mL) of PLLA₂₄[PPh₂Me]I in *i*PrOH/CHCl₃ (10:1). Then a certain amount of concentrated unimer PLLA₂₄[PPh₂Me]I as a 5 mg/mL CHCl₃ solution was added to the dilute seed solution. The solution was manually shaken for 10 s and aged for 24 h at 23 °C. Highly uniform 2D diamond platelets with controlled size were observed.

Seeded growth of PLLA₃₄[PPh₂Me]I from 2D seeds of PLLA₃₄[PPh₂Me]I was carried out using similar procedure. PLLA₃₄[PPh₂Me]I seeds and unimer were used instead of PLLA₂₄[PPh₂Me]I seeds and unimer. Formation of 2D diamond platelets also occurred (Supplementary Fig. 29). Because of relatively high polydispersity and large area of the 2D seeds of PLLA₃₄[PPh₂Me]I compare to the 1D seeds of PLLA₂₄[PPh₂Me]I, the resulting 2D diamond-shaped platelets were not very regular and monodisperse until the addition of a large amount of unimer had taken place. This is similar to the formation of 2D platelets from 2D seed_{HD} of PFS₂₀[PPh₂Me]I. Based on the absence of unimer detectable as a film on the

TEM grids the seeded growth processes were complete within 6 h.

During seeded growth we did not observe screw dislocations and crystal stacking, which have been previously observed for block copolymer crystals involving a PLLA core.⁴⁻⁶ Although the reasons for this observation are not clear at this stage, this may reflect both the presence of charge repulsions involving the terminal phosphonium groups, which could hinder crystal stacking, and also the controlled nature of the seeded growth of the PLLA_m[PPh₂Me]I ($m = 24$ or 34) materials under the conditions used. The growth appears to proceed in a highly defect-free manner, which may be the result of the absence of bulky corona that could hinder core-crystallization. We have previously attributed defect formation in 2D platelets to corona effects.⁷

Formation of fluorescent concentric 2D diamond platelet block comicelles by seeded growth

To a 1mL solution of 2D diamond non-fluorescent platelets (0.01 mg/mL in MeOH) of PLLA₂₄[PPh₂Me]I, was added a certain amount of unimer blend PLLA₂₄[PPh₂Me]I/PLLA₂₁-G (10:1 mass ratio) as a 5 mg/mL (overall concentration) CHCl₃ solution. The solution was manually shaken for 10 s and aged for 24 h at 23 °C, and non/green concentric diblock micelles could be generated (Fig. 5j). By further sequential adding PLLA₂₄[PPh₂Me]I and blend of PLLA₂₄[PPh₂Me]I/PLLA₂₁-R (10:1 mass ratio), tetrablock micelles non/green/non/red, coded with two fluorescent colors could be obtained (Fig. 5k).

Additional discussion on loading and patterning SiO₂ NPs

2D platelets nanostructures have potential application as platforms for nanoparticles to generate highly organized structures.⁸⁻¹⁰

In our case, since the positive charges are located on the surface of the platelets, it is anticipated that using electrostatic interactions, these platelet micelles could be a useful platform for loading negatively charged nanostructures. To test this idea we chose silica nanoparticles (SiO₂ NPs), due to their easily tunable size and characteristic negative charge. One size of positive platelet ($L_n = 1595$ nm, $W_n = 175$ nm), and two different sizes of negative SiO₂ NPs ($D = 150$ nm and 55 nm) were chosen. Based on the size selection, we can control the loading array of SiO₂ NPs on the surface of platelets. Initially, we mixed the positive platelets and negative SiO₂ NPs in *i*PrOH, followed by measuring the interaction by TEM. Only large bundles of aggregates were found on the TEM grids. It is difficult to control the interaction by a simple mixing procedure. In order to control the specific loading, we carried out the layer-by-layer approach. Platelet micelles were drop-cast on carbon-coated TEM grids. These grids were immersed in the ethanol solution of SiO₂ NPs for 30 min. Then *i*PrOH was used to wash out the free SiO₂ NPs on the grids after the incubation. Supplementary Fig. 4 shows the TEM images of platelet micelles loaded with different size of SiO₂ NPs. All of the platelets were loaded with SiO₂ NPs. For larger SiO₂ NPs which the diameter matches with width of the platelets, they are arrayed along the length of platelets one by one. In contrast, the diameter of smaller SiO₂ NPs is about one third of the width, and they are organized two by two. It is important to note that neither free positive platelets nor negative SiO₂ NPs were found in the TEM grid, indicating the specific loading due to the mutual electrostatic interaction.

Additional discussion on selected area electron diffraction (SAED)

In principle, the shape of a polymer single crystal is determined by the slowest growing crystallographic planes because the faster growing planes are exhausted first during crystal growth.¹¹ As shown in Fig. 4c-d, rectangular platelet micelle formation is attributed to the slight difference in growth rate of both the (100) and (010) planes, but the (110) planes were exhausted first due to their fast growth rate during growth of the crystalline PFS core (Fig. 4c). Formation of disk-like quasi-hexagonal platelets was attributed to approximately equal growth rate of six growth fronts because of a similar nucleation barrier for the two crystalline habits with a single crystalline PFS core. The (010) planes were exhausted first due to its fast growth rate, followed by approximately equal growth rate of the (100) and (110) crystalline fronts (Fig. 4d).

Additional discussion on the 2D seeds and their use in seeded growth

We have previously shown that sonication of cylindrical micelles with a crystalline PFS core leads to fracture by Gaussian scission along the long direction of cylindrical micelles, to yield shorter cylinders with low dispersity.¹² In the case of sonication of 2D platelet, it is difficult to produce uniform 2D seeds, probably because the fragmentation occurs in two dimensions. Nevertheless, because of the seeds are very small relative to the size of the 2D structures ultimately grown from them, the non-uniform dimensions of the seed become insignificant. Thus, the area dispersity is a function of the dispersity of the seed made through sonication (generally high) and the relative size of the platelet formed by seeded growth relative to the seed.

Seeded growth proceeded for 2 – 6 h in each experiment and after this time no further change in dimensions was detected and no remaining added unimer was observed as a film by TEM. This indicated that the unimer conversion was 100 % within the detection limit in our experiments. No change in dimensions or area dispersity were detected after several months in solution indicating that 2D micelles derived from PFS or PLLA BCPs are kinetically-trapped as a result of the crystalline core as found previously with 1D systems i.e. there is no significant unimer-micelle exchange under the growth conditions used as this would increase the very low area dispersities.

Based on the 100 % conversion of added unimer and the absence of significant unimer exchange between micelles, and also the fact that initiation from the seeds is expected to be fast relative to self-nucleation (that would form platelets without seed initiation, which was not detected), and given a homogeneous solution and a clean 2D (rather than 3D or 1D) growth process, a linear relationship between the platelet area and $m_{\text{unimer}}/m_{\text{seed}}$ together with a low area dispersity would be anticipated. This was observed in every case.

For the 2D platelets formed by seeded growth the standard deviation of measured areas was found to increase as the $m_{\text{unimer}}/m_{\text{seed}}$ increased (Figures 2 and 5h, Supplementary Figures 6g, 9e, 13h, 16h, 17f and 29f). This has a mathematical explanation. As the numerical value of a sample increases so will the numerical value of the standard deviation, but this doesn't mean the variance has increased, just that the absolute numerical value has increased. We have therefore reported the value of the standard deviation divided by the mean area as in Supplementary Tables S1-5 as this provides a relative value that can be compared between samples of different area.

Additional discussion on the “memory” effect

Xu et al reported that polymer single crystals can maintain the same shape using the self-seeding approach, where the formed 2D structures maintain the same orientation inherited from an initial single crystal (or seed).¹³ In the present study the use of different seeds (2D seed_{HD} and 2D seed_R) from the same polymer but from precursor platelets of different shape is shown to induce the formation of 2D platelets of different shape via seeded growth in solution. It appears that the fragments or seeds generated by sonication of different shaped platelets possess a “memory” of the relative growth rates of different crystal faces from the original platelet. At this stage, the mechanism for such a difference in crystal growth is not completely understood. The SAED data for the quasi-hexagonal disk-like and rectangular platelets (Fig. 4 and Supplementary Fig 20) are near identical but very subtle differences in the former case from the hexagonal pattern for the latter suggest slightly different packing. This may explain the “memory” effect. We also note that 2D seed_{HD} appear slightly less axial than 2D seed_R, as might be expected based on their formation by sonication of 2D precursors of different shape. Indeed, although substantially smaller than their precursor platelets, all of the 2D seeds used possess a significant area and therefore represent a significant portion of the original platelet. That they form similar shapes to their precursors on seeded growth is therefore perhaps not surprising. However, to provide a complete explanation for the “memory” effect will require further detailed experiments.

Polymer Synthesis and Characterization

Note – Key MALDI-TOF and NMR data shown in Supplementary Data Figures 30 – 35.

Synthesis of PFS₂₀PPh₂

The synthesis was adapted from the reported procedure.¹⁴ In a N₂-filled glovebox at room temperature, dimethylsila[1]ferrocenophane (400 mg, 1.65 mmol) was dissolved in 5 mL of THF, to which was added 52 μ L (0.083 mmol) of *n*-BuLi (1.6 M solution in hexanes) quickly. The polymerization was allowed to proceed for 45 min, during which time the colour of the solution changed from red to amber. The polymerization was terminated by the addition of an excess of ClPPh₂ (300 μ L, 1.67 mmol) and stirred for 90 min. Subsequent precipitation of the polymer solution by adding degassed methanol, followed by washing with degassed methanol for 3 times. The precipitate was dried under vacuum to afford the polymer as a red-orange solid. Yield: 80 %. PDI = 1.06. MALDI-MS: m/z 5105 [M⁺O]⁺ (oxidized form of PFS₂₀-PPh₂), 5127 [M⁺O + Na]⁺. ³¹P NMR (162 MHz, CDCl₃): δ (ppm) = -16.1. ¹H NMR (400 MHz, CDCl₃): δ (ppm) = 7.36-7.28 (m, 10 H, PPh₂), 4.20 (m, 80 H, CpH), 3.99 (m, 80 H, CpH), 0.44 (s, 120 H, SiCH₃).

Synthesis of PFS₂₀[PPh₂Me]I

To a solution of PFS₂₀PPh₂ (100 mg) in THF 1 mL, was added excess MeI (100 μ L) and the mixture was stirred for 3 hours. Subsequent precipitation of the solution by adding degassed hexane gave the desired product. Yield 90 %. PDI = 1.10. MALDI-MS: m/z 5104 [M]⁺. ³¹P NMR (162 MHz, CDCl₃): δ (ppm) = + 24.5. ¹H NMR (400 MHz, CDCl₃): δ (ppm) = 7.75-7.60 (m, 10 H, PPh₂), 4.20 (m, 80 H, CpH), 4.00 (m, 80 H, CpH), 3.04 (d, J = 12 Hz, 3 H, P-CH₃), 0.45 (s, 120 H, SiCH₃).

Synthesis of PFS₆₁[PPh₂Me]I

The synthetic procedure is similar to that of PFS₂₀[PPh₂Me]I. Yield: 90 %. PDI = 1.10. MALDI-MS: m/z 15030 [M]⁺. ³¹P NMR (162 MHz, CDCl₃): δ (ppm) = + 29.3. ¹H NMR (400 MHz, CDCl₃): δ

(ppm) = 7.80-7.60 (m, 10 H, PPh_2), 4.20 (m, 244 H, CpH), 3.99 (m, 244 H, CpH), 3.00 (d, $J = 12$ Hz, 3 H, $P-CH_3$), 0.45 (s, 366 H, $SiCH_3$).

Synthesis of $PI_{25}-b-PFS_{22}PPh_2$

This polymer was synthesized according to a modified procedure for $PI-b-PFS$ which was terminated by $ClPPh_2$.¹⁵ In a N_2 -filled glovebox, 56 mg of isoprene (0.83 mmol) was dissolved in 1 mL THF, and the solution was cooled to 0 °C. 24 μ L of sec -BuLi (1.4 M in cyclohexane, 0.034 mmol) was added quickly, and the reaction was stirred for 2 h at 0 °C. Then a solution of dimethylsila[1]ferrocenophane (200 mg, 0.83 mmol) in THF (2 mL) was added, and the reaction mixture was allowed to warm to room temperature for 1 h. The polymerization was terminated by the addition of an excess of $ClPPh_2$ (300 μ L, 1.67 mmol) and stirred for 90 min. Subsequent precipitation of the polymer solution by adding degassed methanol, followed by washing with degassed methanol for 3 times. Yield: 70 %. $M_n = 9413$, $M_w = 9572$, $PDI = 1.02$. ^{31}P NMR (162 MHz, $CDCl_3$): δ (ppm) = - 16.4. 1H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.40-7.28 (m, 10 H, PPh_2), 6.00-4.50 (br, 75 H, vinyl), 4.24 (m, 88 H, CpH), 4.03 (m, 88 H, CpH), 2.30-0.80 (br, 150 H, vinyl), 0.45 (s, 132 H, $SiCH_3$).

Synthesis of $PI_{25}-b-PFS_{22}[PPh_2Me]I$

The synthetic procedure is similar to that of $PFS_{20}[PPh_2Me]I$. Yield: 70%. $M_n = 7540$, $M_w = 9048$, $PDI = 1.20$. ^{31}P NMR (162 MHz, $CDCl_3$): δ (ppm) = + 23.9. 1H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.85-7.60 (m, 10 H, PPh_2), 6.00-4.50 (br, 75 H, vinyl), 4.24 (m, 88 H, Cp), 4.03 (m, 88 H, CpH), 2.74 (d, $J = 16$ Hz, 3 H, $P-CH_3$), 2.30-0.80 (br, 150 H, vinyl), 0.45 (s, 132 H, $SiCH_3$).

Synthesis of $PFS_{22}-G$

This compound was prepared according to our previous reported procedure.¹⁶ To a 7 mL screw-cap vial with stir bar was added amine-functionalized PFS₂₂ (25 mg, 4.4 x 10⁻³ mmol), Fluorescein isocyanate (4.0 mg, 10.0 x 10⁻³ mmol, 2.2 equiv.) and 4 mL dry THF. The reaction was stirred under an argon atmosphere at room temperature for 72 h, precipitated fourteen times into methanol, and the resulting solid dried *in vacuo* at 40°C to afford the pure polymer. Yield: 50 %. PDI = 1.26. ¹H NMR (400 MHz; CDCl₃): δ (ppm) = 7.10-6.00 (br, ArH, fluorescein moiety), 4.24 (s, 92 H, CpH), 4.03 (s, 92 H, CpH), 3.50-2.50 (m, 6 H, CH₂SCH₂CH₂N), 0.90 (br, 2 H, SiCH₂CH₂S), 0.48 (s, 138 H, FcSi(CH₃)₂), 0.23 (s, 6H, Si(CH₃)₂).

Synthesis of PLLA_mPPh₂ (m = 24 or 34)

PLLA₂₄PPh₂ (m = 24) PLLA₃₄PPh₂ (m = 34)

Poly(L-lactide) were synthesized according to a modified literature procedure.^{17,18} Typically, for DP = 24, in an Ar-filled glovebox at room temperature, initiator [4-(diphenylphosphanyl)phenyl]methanol (55 mg, 0.18 mmol) and (-)-sparteine (33 μ L, 0.14 mmol) were combined in one vial with L-lactide (0.52 g, 3.6 mmol) and 1-(3,5 bis(trifluoromethyl)phenyl)-3-cyclohexyl-thiourea (101 mg, 0.27 mmol) in another. Dry dichloromethane (2 mL and 4 mL for each vial respectively) was then added to each of the vials, and then the initiator solution was quickly injected into another one. The mixture was stirred at room temperature for 3 h. The product was precipitated in *n*-hexane three times before filtration and drying *in vacuo* to yield a white solid. Yield: 90 %.

Characterization of PLLA₂₄PPh₂: PDI = 1.06. MALDI-MS: m/z 3785 [M]⁺. ³¹P NMR (162 MHz, CDCl₃): δ (ppm) = -5.19. ¹H NMR (400 MHz, CDCl₃): δ (ppm) = 7.34-7.26 (m, 14 H; ArH), 5.15 (q, J = 8.0 Hz, 48 H; PLLA backbone CHCH₃), 1.57 (d, J = 8.0 Hz, 144 H; PLLA backbone CHCH₃).

Characterization of PLLA₃₄PPh₂: PDI = 1.05. MALDI-MS: m/z 5085. ³¹P NMR (162 MHz, CDCl₃): δ (ppm) = - 5.19. ¹H NMR (400 MHz, CDCl₃): δ (ppm) = 7.34-7.26 (m, 14 H; ArH), 5.15 (q, J = 8.0 Hz, 68 H; PLLA backbone CHCH₃), 1.57 (d, J = 8.0 Hz, 204 H; PLLA backbone CHCH₃).

Synthesis of PLLA_m[PPh₂Me]I (m = 24 or 34)

PLLA₂₄PMeI (m = 24) PLLA₃₄PMeI (m = 34)

To a 8 mL THF solution of PLLA₂₄PPh₂ or PLLA₃₄PPh₂ (400 mg) was added excess MeI (0.4 mL), and the resulting mixture was allowed to stir for 2 hours at room temperature. The product was precipitated into *n*-hexane three times from THF before filtration and drying *in vacuo* to yield a white solid. Yield: 92 %.

Characterization of PLLA₂₄[PPh₂Me]I: PDI = 1.07. MALDI-MS: m/z 3617 [M]⁺. ³¹P NMR (162 MHz, CDCl₃): δ (ppm) = + 22.38. ¹H NMR (400 MHz, CDCl₃): δ (ppm) = 7.83-7.60 (m, 14 H; ArH), 5.15 (q, J = 8.0 Hz, 48 H; PLLA backbone CHCH₃), 3.25 (d, J = 12 Hz, 3 H; CH₃), 1.56 (d, J = 8.0 Hz, 144 H; PLLA backbone CHCH₃).

Characterization of PLLA₃₄[PPh₂Me]I: PDI = 1.05. MALDI-MS: m/z 5060 [M]⁺. ³¹P NMR (162 MHz, CDCl₃): δ (ppm) = + 22.39. ¹H NMR (400 MHz, CDCl₃): δ (ppm) = 7.83-7.60 (m, 14 H; ArH), 5.15 (q, J = 8.0 Hz, 68 H; PLLA backbone CHCH₃), 3.25 (d, J = 12 Hz, 3 H; PCH₃), 1.56 (d, J = 8.0 Hz, 204 H; PLLA backbone CHCH₃).

Synthesis of PLLA₂₁-alkyne

The synthesis of PLLA₂₁-alkyne was similar to that of PLLA_mPPh₂ (m = 24 or 34). In an Ar-filled glovebox at room temperature, initiator, propargyl alcohol (13 mg, 13.5 μ L, 0.21 mmol) and (-)-sparteine (24.2 μ L, 0.11 mmol) were combined in one vial with *L*-lactide (0.60 g, 4.2 mmol) and 1-(3,5 bis(trifluoromethyl)phenyl)-3-cyclohexyl-thiourea (74 mg, 0.20 mmol) in another. Dry dichloromethane (2 mL and 4 mL for each vial respectively) was then added to each of the vials, and then the initiator solution was quickly injected into another one. The mixture was stirred at room temperature for 3 h. The product was isolated by precipitation into *n*-hexane three times before filtration and drying *in vacuo* to yield a white solid. Yield: 93 %. PDI = 1.10. MALDI-MS: m/z 2958 [M]⁺. ¹H NMR (400 MHz, CDCl₃): δ (ppm) = 5.17 (q, J = 8.0 Hz, 42 H; PLLA backbone CHCH₃), 4.37 (m, 2 H; HC≡CCH₂O), 2.50 (t, J = 4.0 Hz, 1 H; alkynyl C≡CH), 1.59 (d, J = 8.0 Hz, 126 H; PLLA backbone CHCH₃).

Synthesis of PLLA₂₁-NH₂

To a solution of PLLA₂₁-CC (100 mg, 0.032 mmol) in dry THF/*i*PrOH (6 mL; 2:1, v/v) was added 2,2-dimethoxy-2-phenylacetophenone (4 mg, 10 mol%) and 2-mercaptomethylamine hydrochloride (38 mg, 3.2 mmol, 10 equiv.) under a nitrogen atmosphere. The reaction mixture was sealed in a glass vial and irradiated 3 cm away from a mercury lamp for 2 h. The solution was precipitated twice in methanol (with 5 % trimethylamine), and the product dried *in vacuo* to afford a

white solid. Yield: 94%. PDI = 1.15. ^1H NMR (400 MHz, CDCl_3): δ (ppm) = 5.18 (q, J = 8.0 Hz, 42 H; PLLA backbone CHCH_3), 4.37 (m, 2 H; CH_2O), 2.90-2.58 (m, 11 H; $\text{NH}_2\text{CH}_2\text{CH}_2\text{S}$ and SCH_2CHS), 1.59 (d, J = 8.0 Hz, 126 H; PLLA backbone CHCH_3).

Synthesis of PLLA₂₁-G

To a 7 mL screw-cap vial with stir bar was added amine-functionalized PLLA₂₁-NH₂ (20 mg, 6.3×10^{-3} mmol), fluorescein isothiocyanate (10 mg, 4 equiv.) and 3 mL dry THF. The reaction was stirred under an argon atmosphere at room temperature for 72 hours, then precipitated 3 times into methanol. The product was dried *in vacuo* at 40°C (9 mg, 40 %). ^1H NMR analysis showed quantitative functionalization of the amine functional groups with fluorescein dye. Yield = 30 %. PDI = 1.20. ^1H NMR (500 MHz, CD_2Cl_2): δ (ppm) = 8.05 (s, 2 H; NH), 7.75 (s, 2 H; NH), 7.50-6.50 (m, 18 H; Fluorescein ArH), 5.20 (q, J = 8.0 Hz, 42 H; PLLA backbone CHCH_3), 3.00-2.50 (m, 11 H; $\text{NH}_2\text{CH}_2\text{CH}_2\text{S}$ and SCH_2CHS), 1.59 (d, J = 8.0 Hz, 126 H; PLLA backbone CHCH_3).

Synthesis of PLLA₂₁-R

The synthesis of PLLA₂₁-R is synthesized similar to compound PLLA₂₁-G. Fluorescein isocyanate were used instead of BODIPY 630/650-X. Yield: 40 %. PDI = 1.19. ^1H NMR (500 MHz, CD_2Cl_2): δ (ppm) = 8.19-7.67 (m, 28 H; ArH), 5.20 (q, J = 8.0 Hz, 42 H; PLLA backbone CHCH_3), 3.10-2.50 (m, 11 H; $\text{NH}_2\text{CH}_2\text{CH}_2\text{S}$ and SCH_2CHS), 1.59 (d, J = 8.0 Hz, 126 H; PLLA backbone CHCH_3).

Supplementary Scheme 1 | Synthetic route to PFS building blocks.

Supplementary Scheme 2 | Synthetic route to PLLA building blocks.

Supplementary Figure 1 | Uniform rectangular platelet micelles of controlled area prepared by seeded growth of $\text{PFS}_{20}[\text{PPh}_2\text{Me}]\text{I}$ using a 1D cylindrical seed. **a**, Schematic representation of the formation of 2D rectangular platelets through seeded growth of $\text{PFS}_{20}[\text{PPh}_2\text{Me}]\text{I}$ from 1D cylindrical seeds. **b**, AFM topography image of a rectangular platelet micelle formed from a 20:1 unimer:seed mass ratio ($m_{\text{unimer}}/m_{\text{seed}}$). **c**, AFM height profile of the rectangular platelet. **d-g**, TEM images of uniform 2D rectangular platelet micelles prepared by the seeded growth of unimer $\text{PFS}_{20}[\text{PPh}_2\text{Me}]\text{I}$ in THF from $\text{PFS}_{25}\text{-}b\text{-P2VP}_{250}$ seed micelles ($L_n = 840$ nm, $L_w / L_n = 1.03$) in $i\text{PrOH}$. $m_{\text{unimer}}/m_{\text{seed}}$ of 4:1 (d), 12:1 (e), 20:1 (f), 32:1 (g). **h-j**, Dependence of micelle length L_n (h), width W_n (i), and aspect ratio L_n/W_n (j) on the $m_{\text{unimer}}/m_{\text{seed}}$. Error bars in h and i, represent the standard deviation in the measured length and width, respectively.

Supplementary Figure 2 | Contour area distributions of rectangular platelet micelles. These rectangular platelet micelles were prepared by seeded growth of unimer PFS₂₀[PPH₂Me]I in THF from 1D PFS₂₅-*b*-P2VP₂₅₀ seed micelles ($L_n = 840$ nm, $L_w / L_n = 1.03$) in *i*PrOH at 23 °C.

Supplementary Figure 3 | Zeta potential result for rectangular 2D platelet micelles ($L_n = 1955$ nm, $W_n = 348$ nm) derived from PFS₂₀[PPh₂Me]I in *i*PrOH. These rectangular platelet micelles were prepared by seeded growth of unimer PFS₂₀[PPh₂Me]I in THF from 1D PFS₂₅-*b*-P2VP₂₅₀ seed micelles ($L_n = 840$ nm, $L_w / L_n = 1.03$) in *i*PrOH at 23 °C.

Supplementary Figure 4 | Application of PFS positive platelets in NPs loading. a-b, TEM images showing the specific loading of negatively-charged SiO₂ NPs with different sizes (diameter of SiO₂ NPs: (a) 150 nm, (b) 55 nm) on the positive platelets. The rectangular platelet micelles were prepared by seeded growth of unimer PFS₂₀[PPh₂Me]I in THF from 1D PFS₂₅-*b*-P2VP₂₅₀ seed micelles ($L_n = 840$ nm, $L_w / L_n = 1.03$) with $m_{\text{unimer}}/m_{\text{seed}}$ of 8 in *i*PrOH at 23 °C. Detailed procedure for SiO₂ NP loading: i) Rectangular platelet micelles in *i*PrOH were firstly drop-cast on carbon-coated TEM grid and dried for 30 min under air; ii) The grid was immersed in the ethanol solution of SiO₂ NPs for 30 min; iii) Then *i*PrOH or EtOH was used to wash out the free SiO₂ NPs on the grid after the incubation.

Supplementary Figure 5 | Control experiment using neutral polymer PFS₂₀PPh₂ as unimer. TEM images of control experiment by adding neutral unimer PFS₂₀PPh₂ in THF to PFS₂₅-*b*-P2VP₂₅₀ cylindrical seed micelles in *i*PrOH with $m_{\text{unimer}}/m_{\text{seed}}$ of 12.

Supplementary Figure 6 | Formation of rectangular platelet micelles of controlled area prepared by seeded growth of PFS₂₀[PPh₂Me]I using a 1D cylindrical PFS₂₅-*b*-P2VP₃₃₀ seed. a, TEM image of PFS₂₅-*b*-P2VP₃₃₀ seed ($L_n = 58 \text{ nm}$, $L_w/L_n = 1.02$). **b-f**, TEM images of uniform 2D rectangular platelet micelles prepared by the seeded growth of unimer PFS₂₀[PPh₂Me]I in THF from PFS₂₅-*b*-P2VP₃₃₀ seeds in *i*PrOH at 23 °C. $m_{\text{unimer}}/m_{\text{seed}}$ of 4:1 (b), 8:1 (c), 12:1 (d), 16:1 (e), 20:1 (f). **g**, Linear dependence of micelle area on the $m_{\text{unimer}}/m_{\text{seed}}$. Error bars, standard deviation of measured areas. **h**, Dependence of aspect ratio of the platelets on the $m_{\text{unimer}}/m_{\text{seed}}$.

a. Seeded growth of PFS₂₀[PPh₂Me]I

From PFS₂₅-*b*-P2VP₃₃₀ seed ($L_n = 298$ nm)

From PFS₂₅-*b*-P2VP₃₃₀ seed ($L_n = 58$ nm)

From PFS₅₁-*b*-P2VP₇₃₁ seed ($L_n = 142$ nm)

b. Seeded growth of PFS₆₁[PPh₂Me]I

From PFS₂₅-*b*-P2VP₂₅₀ seed ($L_n = 840$ nm)

From PFS₂₅-*b*-P2VP₃₃₀ seed ($L_n = 58$ nm)

From PFS₂₅-*b*-P2VP₃₃₀ seed ($L_n = 298$ nm)

From PFS₂₅-*b*-P2VP₃₃₀ seed ($L_n = 298$ nm)

From PFS₅₁-*b*-P2VP₇₃₁ seed ($L_n = 142$ nm)

From PFS₅₁-*b*-P2VP₇₃₁ seed ($L_n = 142$ nm)

Supplementary Figure 7 | Influence of the degree of polymerization (DP) of the PFS block for the core of the seeds and that of the homopolymers on the seeded growth. a. Seeded growth of unimer PFS₂₀[PPh₂Me]I in THF was performed from PFS-*b*-P2VP seeds (in *i*PrOH) of different length and a different DP of PFS block. 2D rectangular platelets can be formed from all of the PFS-*b*-P2VP seeds in *i*PrOH. The data shown are TEM images. **b.** Seeded growth of PFS₆₁[PPh₂Me]I from PFS-*b*-P2VP seed with different length and different DP of PFS block. Because PFS₆₁[PPh₂Me]I has a longer hydrophobic PFS chain and therefore poorer solubility than PFS₂₀[PPh₂Me]I in a polar solvent, a considerable number of spherical micelles formed in *i*PrOH, irrespective of the DP of PFS block of the seed. To improve the 2D rectangular platelet formation, a good solvent THF was added to *i*PrOH solvent to increase the solubility of unimer in such a mixing solvent. The optimized condition was *i*PrOH (30%) / THF (70%) where quantitative formation of 2D platelets was observed with the disappearance of the spherical micelles.

Seeded growth of PFS₂₀[PPh₂Me]OTs
from PFS₂₅-*b*-P2VP₃₃₀ seed ($L_n = 298$ nm)

Seeded growth of PFS₂₀[PPh₂Me]I
from PFS₂₅-*b*-P2VP₃₃₀ seed ($L_n = 298$ nm)

Seeded growth of PFS₂₀[PPh₂Me]BPh₄
from PFS₂₅-*b*-P2VP₂₅₀ seed ($L_n = 840$ nm)

Seeded growth of PFS₂₀[PPh₂Me]I
from PFS₂₅-*b*-P2VP₂₅₀ seed ($L_n = 840$ nm)

Supplementary Figure 8 | Effect of the counter-anion of PFS₂₀[PPh₂Me]X (X = I⁻, OTs⁻, BPh₄⁻) on the seeded growth. The hydrophilicity of these anions is in the order I⁻ > OTs⁻ > BPh₄⁻. In the case of I⁻ and OTs⁻, uniform rectangular platelets can also be formed from PFS-*b*-P2VP seeds. However, due to the very hydrophobic nature of BPh₄⁻, spherical micelles were also formed in that case.

Supplementary Figure 9 | Formation of rectangular platelet micelles of controlled area prepared by seeded growth of PI₂₅-b-PFS₂₂[PPh₂Me]I using a 1D cylindrical PFS₂₅-b-P2VP₃₃₀ seed. a-d, TEM images of uniform 2D rectangular platelet micelles prepared by the seeded growth of unimer PI₂₅-b-PFS₂₂[PPh₂Me]I in THF from PFS₂₅-b-P2VP₃₃₀ seed ($L_n = 298$ nm, $L_w/L_n = 1.02$) in *i*PrOH at 23 °C. $m_{\text{unimer}}/m_{\text{seed}}$ of 4:1 (a), 8:1 (b), 12:1 (c), 16:1 (d). e Linear dependence of micelle area on the $m_{\text{unimer}}/m_{\text{seed}}$. Error bars, standard deviation of measured areas. f, Dependence of aspect ratio of the platelets on the $m_{\text{unimer}}/m_{\text{seed}}$.

From PFS₂₅-*b*-P2VP₂₅₀ seed ($L_n = 840$ nm)

From PFS₂₅-*b*-P2VP₃₃₀ seed ($L_n = 298$ nm)

Supplementary Figure 10 | Formation of rectangular platelet micelles with a negatively charged surface by seeded growth of PFS₂₀-SO₃Li. TEM images of 2D rectangular platelet micelles formed by seeded growth of PFS₂₀-SO₃Li in THF from PFS₂₅-*b*-P2VP₂₅₀ seeds ($L_n = 840$ nm, left) or PFS₂₅-*b*-P2VP₃₃₀ seeds ($L_n = 298$ nm, right) in *i*PrOH, with a $m_{\text{unimer}}/m_{\text{seed}}$ of 10.

Supplementary Figure 11 | Formation of platelet aggregate through self-nucleation. a,b, TEM images of platelet aggregates from PFS₂₀[PPh₂Me]I in *i*PrOH (a) and MeOH (b) after self-nucleation at 23 °C.

Supplementary Figure 12 | 2D Seed_{HD} of PFS₂₀[PPh₂Me]I. TEM image and contour area statistics of 2D Seed_{HD} of PFS₂₀[PPh₂Me]I in MeOH.

Supplementary Figure 13 | Uniform quasi-hexagonal disk-like platelet micelles of controlled area prepared by seeded growth of PFS₂₀[PPh₂Me]I using a 2D seed_{HD} in MeOH. **a**, Schematic representation of the generation of 2D seed_{HD} and formation of uniform quasi-hexagonal disk-like platelet through seeded growth. **b-e**, TEM images of uniform quasi-hexagonal disk-like platelets prepared by the seeded growth of unimer PFS₂₀[PPh₂Me]I in THF from 2D seed_{HD} in MeOH with $m_{\text{unimer}}/m_{\text{seed}}$ values of 10:1 (b), 20:1 (c), 30:1 (d), 40:1 (e). **f,g**, AFM topography image (f) and corresponding height profile (g) of a quasi-hexagonal disk-like platelet micelle formed from a 40:1 $m_{\text{unimer}}/m_{\text{seed}}$ ratio. **h**, Linear dependence of micelle area on the $m_{\text{unimer}}/m_{\text{seed}}$. Error bars, standard deviation of measured areas.

Supplementary Figure 14 | TEM image of uniform quasi-hexagonal disk-like platelets prepared by seeded growth of unimer $\text{PFS}_{20}[\text{PPh}_2\text{Me}]\text{I}$ in THF from 2D seed_{HD} in *i*PrOH with $m_{\text{unimer}} / m_{\text{seed}}$ ratio of 20.

Supplementary Figure 15 | 2D Seed_{R1} and Seed_{R2} of PFS₂₀[PPh₂Me]I. TEM images and contour area statistics of 2D Seed_{R1} and Seed_{R2} of PFS₂₀[PPh₂Me]I dried from MeOH. The areas of the original platelet micelles prior to sonication were $A_n = 3,145,260 \text{ nm}^2$, PDI = 1.01 and $A_n = 1,394,920 \text{ nm}^2$, PDI = 1.02, respectively. Sonication of the 2D rectangular platelets led to small fragments in which we did not observe the presence of the original PFS-*b*-PVP seed micelles in the case of 2D Seed_{R1}. We believe that in this case the PFS-*b*-P2VP micelle seeds were also fragmented by sonication. The inability to detect and identify the seed fragmentation products is probably also a consequence of the low fractional composition of the seeds in the original rectangular platelets that were sonicated.

Supplementary Figure 16 | Uniform rectangular platelet micelles of controlled area prepared by seeded growth of unimer PFS₂₀[PPh₂Me]I in THF from 2D Seed_{R1} in MeOH. **a**, Schematic representation of the generation of 2D Seed_{R1} and formation of uniform rectangular platelet through seeded growth. **b**, AFM topography image of rectangular platelet micelles ($m_{\text{unimer}}/m_{\text{seed}} = 40$). **c**, AFM height profile of the rectangular platelet. **d-g**, TEM images of uniform rectangular platelets formed through seeded growth from 2D seed_{R1} with $m_{\text{unimer}}/m_{\text{seed}}$ of 10:1 (d), 20:1 (e), 30:1 (f), 40:1 (g). **h**, Linear dependence of micelle area on the $m_{\text{unimer}}/m_{\text{seed}}$. Error bars, standard deviation of measured areas. **i**, Dependence of aspect ratio of the platelets on the $m_{\text{unimer}}/m_{\text{seed}}$.

Supplementary Figure 17 | Uniform rectangular platelet micelles of controlled area prepared by seeded growth of unimer PFS₂₀[PPh₂Me]I in THF from 2D Seed_{R2} in MeOH. a, Schematic representation of formation of uniform rectangular platelet through seeded growth from 2D Seed_{R2}. **b-e**, TEM images of uniform rectangular platelets formed through seeded growth from 2D seed_{R2} with $m_{\text{unimer}}/m_{\text{seed}}$ of 10:1 (b), 20:1 (c), 30:1 (d), 40:1 (e). **f**, Linear dependence of micelle area on the $m_{\text{unimer}}/m_{\text{seed}}$. Error bars, standard deviation of measured areas. **g**, Dependence of aspect ratio of the platelets on the $m_{\text{unimer}}/m_{\text{seed}}$ ratio.

Supplementary Figure 18 | TEM image of uniform rectangular platelets prepared by seeded growth of unimer PFS₂₀[PPh₂Me]I in THF from 2D seed_{R1} in *i*PrOH with $m_{\text{unimer}}/m_{\text{seed}}$ ratio of 30.

Supplementary Figure 19 | Concentric rectangular platelet tetrablock comicelles. Concentric rectangular platelet tetrablock comicelles were prepared through the sequential, alternate addition of (i) PFS₂₀[PPh₂Me]I and (ii) PFS₂₅-*b*-P2VP₂₅₀/PFS₂₅ blend unimer (1:1 mass ratio) in THF from PFS₂₅-*b*-P2VP₂₅₀ cylindrical seed micelles in *i*PrOH/hexane (3:1, v/v) at 23 °C.

Supplementary Figure 20 | Selected area electron diffraction (SAED) pattern of platelet micelles and block comicelles. **a**, TEM image of quasi-hexagonal disk-like platelets and electron diffraction pattern of the whole platelet. The platelets were formed through seeded growth of unimer PFS₂₀[PPh₂Me]I in THF from 2D seed_{HD} in MeOH at 23 °C. **b**, TEM image of rectangular platelets and electron diffraction pattern of the whole platelet. The platelets were formed through seeded growth of unimer PFS₂₀[PPh₂Me]I from 2D seed_{R1} in MeOH at 23 °C. **c**, TEM image of rectangular platelets block comicelles with central 1D seed micelle, and electron diffraction pattern of the whole platelet and one selected area (red circle). The platelets were formed by sequential addition of unimer PFS₂₀[PPh₂Me]I and PFS₂₅-*b*-P2VP₂₅₀/PFS₂₅ (1:1, mass ratio) blend in THF to 1D PFS₂₅-*b*-P2VP₂₅₀ seed micelles in *i*PrOH/hexane (3:1, v/v) at 23 °C. Based on our previous work,⁷ PFS-*b*-P2VP cylindrical micelles possess a crystalline PFS core with the same electron diffraction pattern as the platelets in this study. We believe that the axes of the PFS chains in the seed micelles and the platelets are parallel. Comments on the additional spots observed in ED image for the platelet image at bottom right: Generally, electron diffraction is extremely sensitive to tilting of the sample.¹⁹ Probably only part (the red circled region) of the platelet located on this area of the carbon film used for ED is flat. If most of this platelet consisted of the small red region a normal ED would be collected. As ED arises from the whole platelet comicelle, the normal direction for the part of the comicelle outside the red region is not parallel to the electron beam and this causes the ED pattern to contains two weak (200) spots as extra (hkl) spots.

micelle

comicelle

Supplementary Figure 21 | Energy-dispersive X-ray (EDX) mapping analysis of 2D quasi-hexagonal disk-like platelets and block comicelles. The quasi-hexagonal disk-like platelets were prepared by the seeded growth of unimer $\text{PFS}_{20}[\text{PPH}_2\text{Me}]\text{I}$ in THF from 2D seed_{HD} of $\text{PFS}_{20}[\text{PPH}_2\text{Me}]\text{I}$ in MeOH at 23 °C. The quasi-hexagonal disk-like platelet block comicelles were prepared by addition of $\text{PFS}_{25}\text{-}b\text{-P2VP}_{250}/\text{PFS}_{25}$ (1:1, mass ratio) blend unimer to 2D quasi-hexagonal disk-like platelets in MeOH/hexane (3:1, v/v) at 23 °C. For the micelle (top) that is derived from $\text{PFS}_{20}[\text{PPH}_2\text{Me}]\text{I}$, P atoms appear to be evenly distributed over the whole platelet (figure top, center). For the block comicelle (bottom), where the central region is derived from $\text{PFS}_{20}[\text{PPH}_2\text{Me}]\text{I}$ and the peripheral block is derived from $\text{PFS}_{25}\text{-}b\text{-P2VP}_{250}/\text{PFS}_{25}$ (1:1, mass ratio), the N signal arising from P2VP corona-forming blocks is localized in peripheral block (figure bottom, center). Because both micelle and comicelle have a PFS core, a Fe signal can be detected in both regions and is also evenly distributed (figures top, right, and bottom, right). The detection of P was very difficult as a result of the very low concentration of terminal groups (note that N, which arises from the P2VP corona in the outer region of the block coplatelet, and Fe, which is present in every core repeat unit, are much easier to detect).

Supplementary Figure 22 | Schematic representations and LSCM images of green quasi-hexagonal disk-like (a) and rectangular (b) platelet block comicelles. The platelet block comicelles were synthesized by addition of blend of dye functionalized PFS homopolymers (PFS₂₂-G) and PFS₂₀[PPh₂Me]I (1:10, mass ratio) in THF to the non-fluorescent 2D quasi-hexagonal disk-like or rectangular platelet micelles, which were prepared from the seeded growth of PFS₂₀[PPh₂Me]I unimer in THF from 2D seed_{HD} or 2D seed_{R1} in MeOH at 23 °C.

Supplementary Figure 23 | Formation of hierarchical scarf-like structures. These block comicelles were prepared by adding $\text{PFS}_{20}\text{-}b\text{-P2VP}_{140}$ (a) or $\text{PFS}_{25}\text{-}b\text{-PMVS}_{170}$ (b,c) in THF to the 2D rectangular platelets in *i*PrOH (a,b) or *i*PrOH/hexane (3:1; c). In the case of $\text{PFS}_{20}\text{-}b\text{-P2VP}_{140}$, uniform scarf-like micelles can be prepared in *i*PrOH (a). However, severe aggregation of the platelets by end-to-end linking occurred when adding $\text{PFS}_{20}\text{-}b\text{-PMVS}_{170}$ to rectangular platelets in *i*PrOH (b). Dispersed amphiphilic block comicelles can be successfully prepared in *i*PrOH/hexane (3:1) solvent mixture, and further 1D alignment through hydrophobic interaction by increasing solvent polarity (c).

Supplementary Figure 24 | Formation of hierarchical structures. **a.** This sample was prepared by the seeded growth of PFS₂₀-*b*-P2VP₁₈₀ unimer in THF from 2D rectangular platelet grown from 2D seed_{R1} in MeOH at 23 °C. **b.** This sample was prepared by the seeded growth of PFS₂₀-*b*-P2VP₁₈₀ unimer in THF from 2D quasi-hexagonal disk-like platelet grown from 2D seed_{HD} in MeOH at 23 °C.

Supplementary Figure 25 | Formation of cross-shape platelets. The micelles were prepared by adding PFS₂₀[PPh₂Me]I to the cross-shape micelles (to be published) self-assembled from amphiphilic triblock comicelles M(PFS-*b*-PtBA)-*b*-M(PFS-*b*-PDMS)-*b*-M(PFS-*b*-PtBA)²⁰ (M = micelle segment, PFS = polyferrocenyldimethylsilane, PtBA = poly(*tert*-butyl acrylate), and PDMS = polydimethylsiloxane) in *i*PrOH.

Supplementary Figure 26 | Influence of solvent composition and temperature on the self-nucleation of PLLA₂₄[PPh₂Me]I and PLLA₃₄[PPh₂Me]I. a,b, TEM images of diamond shaped micelles formed by self-nucleation of PLLA₂₄[PPh₂Me]I (a) and PLLA₃₄[PPh₂Me]I (b) in *i*PrOH/CHCl₃ (10:1, v/v) or *i*PrOH/CHCl₃ (100:2, v/v) or MeOH/CHCl₃ (10:1, v/v), at 23 °C or 65 °C.

Supplementary Figure 27 | Quasi-1D seeds of PLLA₂₄[PPh₂Me]I. **a,b**, TEM micrograph (a) and AFM topography image (b) of quasi-1D seeds of PLLA₂₄[PPh₂Me]I ($c = 0.1 \text{ mg/mL}$) in *i*PrOH/CHCl₃ (10:1). **c**, Histograms showing the contour length of the seeds. **d**, AFM height profile of the seeds.

Supplementary Figure 28 | 2D seeds of PLLA₃₄[PPh₂Me]I. **a,b**, TEM micrographs of 2D seeds of PLLA₃₄[PPh₂Me]I ($c = 0.1$ mg/mL) in (a) *i*PrOH/CHCl₃ (10:1) and (b) MeOH/CHCl₃ (10:1). **c**, DLS volume distribution for 2D seeds of PLLA₃₄[PPh₂Me]I (0.005 mg/mL) in MeOH (red) and *i*PrOH (black). Due to the high dilution, the amount of CHCl₃ is negligible. **d**, Histograms showing the contour length of the seeds in MeOH/CHCl₃ (10:1). **e,f**, AFM topography image (e) and the height profile (f) of 2D seeds of PLLA₃₄[PPh₂Me]I in MeOH/CHCl₃ (10:1).

Supplementary Figure 29 | Uniform diamond platelet micelles of controlled area prepared by seeded growth of unimer PLLA₃₄[PPh₂Me]I in CHCl₃ from 2D seeds of PLLA₃₄[PPh₂Me]I in *i*PrOH at 23 °C. **a, Schematic representation of the formation of diamond platelets through seeded growth. **b-e**, TEM images of uniform diamond platelets formed by seeded growth from 2D seeds with $m_{\text{unimer}}/m_{\text{seed}}$ of 5:1 (b), 10:1 (c), 20:1 (d), 40:1 (e). **f**, Linear dependence of micelle area on the $m_{\text{unimer}}/m_{\text{seed}}$. Error bars, standard deviation of measured areas.**

Supplementary Figure 30 | MALDI-TOF mass spectra of $\text{PFS}_{20}\text{PPh}_2$ (top) and $\text{PFS}_{20}[\text{PPh}_2\text{Me}]\text{I}$ (bottom)

Supplementary Figure 31 | MALDI-TOF mass spectra of PLLA₂₄PPh₂ (top) and PLLA₂₄[PPh₂Me]I (bottom)

Supplementary Figure 33 | ^1H (top) and ^{31}P (bottom) NMR spectra of $\text{PFS}_{20}\text{PPh}_2$ and $\text{PFS}_{20}[\text{PPh}_2\text{Me}]\text{I}$ in CDCl_3

Supplementary Figure 34 | ¹H (top) and ³¹P(bottom) NMR spectra of PLLA₂₄PPh₂ and PLLA₂₄[PPh₂Me]I in CDCl₃

Supplementary Figure 35 | ¹H (top) and ³¹P(bottom) NMR spectra of PLLA₃₄PPh₂ and PLLA₃₄[PPh₂Me]I in CDCl₃

Supplementary Table 1 | Contour area data for rectangular platelet micelles prepared by the seeded growth of unimer PFS₂₀[PPh₂Me]I in THF from PFS₂₅-*b*-P2VP₂₅₀ seed micelles ($L_n = 840$ nm, $L_w / L_n = 1.03$) in *i*PrOH at 23 °C.^[a]

Area data	$m_{\text{unimer}} / m_{\text{seed}}$							
	4	8	12	16	20	24	32	40
A_n (nm ²)	148,460	280,120	414,010	569,020	681,400	789,590	1,104,050	1,398,790
A_w (nm ²)	151,420	286,220	420,850	576,660	688,920	795,820	1,112,840	1,407,700
A_w / A_n	1.02	1.02	1.02	1.01	1.01	1.01	1.01	1.01
σ / A_n	0.14	0.15	0.13	0.12	0.11	0.09	0.09	0.08

[a] As measured from TEM micrographs of a minimum of 200 platelets. σ , standard deviation of measured areas.

Supplementary Table 2 | Contour area data for 2D quasi-hexagonal disk-like platelet micelles prepared by the seeded growth of unimer PFS₂₀[PPh₂Me]I in THF from 2D seed_{HD} ($A_n = 7990$ nm², $A_w / A_n = 1.54$) in MeOH at 23 °C.^[a]

Area data	$m_{\text{unimer}} / m_{\text{seed}}$				
	0	10	20	30	40
A_n (nm ²)	7,990	111,540	212,690	341,030	461,370
A_w (nm ²)	12,250	124,530	226,210	354,520	474,790
A_w / A_n	1.54	1.12	1.06	1.04	1.03
σ / A_n	0.73	0.34	0.25	0.20	0.17

[a] As measured from TEM micrographs of a minimum of 200 platelets. σ , standard deviation of measured areas.

Supplementary Table 3 | Contour area data for rectangular platelet micelles prepared by the seeded growth of unimer PFS₂₀[PPh₂Me]I in THF from 2D seed_{R1} ($A_n = 9540$ nm², $A_w / A_n = 1.59$) in MeOH at 23 °C.^[a]

Area data	$m_{\text{unimer}} / m_{\text{seed}}$				
	0	10	20	30	40
A_n (nm ²)	9,540	334,910	624,130	937,300	1,394,920
A_w (nm ²)	15,120	356,510	651,800	974,610	1,429,010
A_w / A_n	1.59	1.06	1.04	1.04	1.02
σ / A_n	0.77	0.25	0.21	0.20	0.16

[a] As measured from TEM micrographs of a minimum of 200 platelets. σ , standard deviation of measured areas.

Supplementary Table 4 | Contour area data for 2D diamond-shaped platelet micelles prepared by the seeded growth of unimer PLLA₂₄[PPh₂Me]I in CHCl₃ from quasi-1D seed ($L_n = 200$ nm, $L_w / L_n = 1.09$) of PLLA₂₄[PPh₂Me]I in *i*PrOH at 23 °C.^[a]

Area data	$m_{\text{unimer}} / m_{\text{seed}}$			
	5	10	15	20
A_n (nm ²)	93,830	182,150	283,230	394,770
A_w (nm ²)	99,650	193,130	297,820	410,010
A_w / A_n	1.06	1.06	1.05	1.04
σ / A_n	0.25	0.25	0.23	0.20

[a] As measured from TEM micrographs of a minimum of 200 platelets. σ , standard deviation of measured areas.

Supplementary Table 5 | Contour area data for 2D diamond-shaped platelets prepared by the seeded growth of unimer PLLA₃₄[PPh₂Me]I in CHCl₃ from 2D seed ($A_n = 6540$ nm², $A_w / A_n = 1.38$) of PLLA₃₄[PPh₂Me]I in *i*PrOH at 23 °C.^[a]

Area data	$m_{\text{unimer}} / m_{\text{seed}}$				
	0	10	20	30	40
A_n (nm ²)	6,540	122,540	210,830	402,920	778,910
A_w (nm ²)	9,000	129,840	220,590	411,760	794,550
A_w / A_n	1.38	1.06	1.05	1.02	1.02
σ / A_n	0.62	0.25	0.22	0.15	0.14

[a] As measured from TEM micrographs of a minimum of 200 platelets. σ , standard deviation of measured areas.

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