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Supporting Information

Hydrogen Bond Regulated Platelet Micelles by Crystallization-Driven Self-Assembly and Templated Growth for Poly(ε-Caprolactone) Block Copolymer

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Materials and Characterizations

Materials. Diphenyl phosphate (DPP) was recrystallized from dried $CHCl_3$/Hexane (3:1) and dried over P_2O_5 for 1 week before use. Dimethyl sulfoxide (DMSO) was purified by vacuum distillation and stored in a drying tower. 1,4-Dioxane, and N, N-dimethylacrylamide (DMA) and 2-hydroxyethyl acrylate (HEA) were purified by passing through basic alumina before use. 4-dimethylaminopyridine (DMAP), N-(3-dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride (EDCl) and dichloromethane (CH_2Cl_2) were purchased from MACKLIN and used as received. 2,2'-azobis(2-methylpropionitrile) (AIBN) was recrystallized twice from methanol and stored in the dark at 4 °C. 2,2,2-Trifluoroethanol (TFE) were purchased from MACKLIN and used as received. The BOPIPY R6G was purchased from Lumiprobe and used as received. Fluorescent group aminochloromaleimide (ACM dye, 3-(3-chloro-4-(isopropylamino)-2,5-dioxo-2,5-dihydro-1H-pyrrol-1-yl) propyl methacrylate) was prepared according to the paper published.[S1] Dual-head initiator, 2-cyano-5-hydroxypentan-2-yl ethyl carbonotrithioate (chain transfer agent, CTA), was synthesized according to a previous report.[S2] The polymers used in this study containing PCL_{60}-CTA, PCL_{60}-*b*-$P4VP_{360}$ were synthesized according to our previous work.[S3] Graphene oxide (GO) dispersion (tablet diameter 50-200 nm, concentration 1 $mg \cdot mL^{-1}$, solvent ethanol) was purchased from XFNANO.

Characterization. Size-exclusion chromatography (SEC) measurements were performed on PL-GPC 50 with RI and using $CHCl_3$ or THF at 40 °C as the eluent at a flow rate of 1.0 $mL \cdot min^{-1}$. SEC data was calibrated against polystyrene standards

and analyzed using Cirrus v3.3 software. ^{1}H NMR spectra were recorded at 400 MHz on a BRUKER AVANCE AV400MHz spectrometer in $CDCl_3$ or d_6-DMSO. Chemical shifts are reported as δ in parts per million (ppm) downfield from the internal standard trimethylsilane. Samples for transmission electron microscopy (TEM) analysis were prepared by drop casting 30 μL of sample (0.1 mg • mL^{-1}) onto a carbon-coated copper grid placed on filter paper. Samples were stained with a l % uranyl acetate solution to facilitate imaging of the thin organic structures unless specified. Imaging was performed on a JEM-1230 transmission electron microscope operating at 120 kV. ACM-dye (405 nm) and BODIPY R6G (458 nm) labelled 2D platelets were imaged using confocal laser scanning microscope (CLSM) FV1200-IX81 (Olympus, Japan). The size distribution of polymer coil in different solvents were detected by dynamic light scattering (DLS) using a Horiba Zetasizer apparatus (LB-550 V) equipped with a 5.0 mW laser diode operating at 650 nm at room temperature.

Sample Synthesis

Synthesis of PHEA Homopolymer. Typically, CTA (2.7 mg, 0.011 mmol), HEA (0.25 g, 2.155 mmol) and AIBN (0.37 mg, 0.0022 mmol) were dissolved in DMSO (2 mL) and placed in an ampoule. The solution was then freeze pump-thawed three times and heated for 18 h at 80 °C. The reaction was quenched by immersion of the ampoule in liquid nitrogen and the polymer was precipitated in ice-cold ethyl acetate three times and then in ice-cold ether three times before being dried under vacuum.

The polymerization degree of PHEA homopolymer was calculated to be 182, yielding PHA_{182}. This polymer was prepared for the investigation of the presence of H-bond in ethanol as a control experiment.

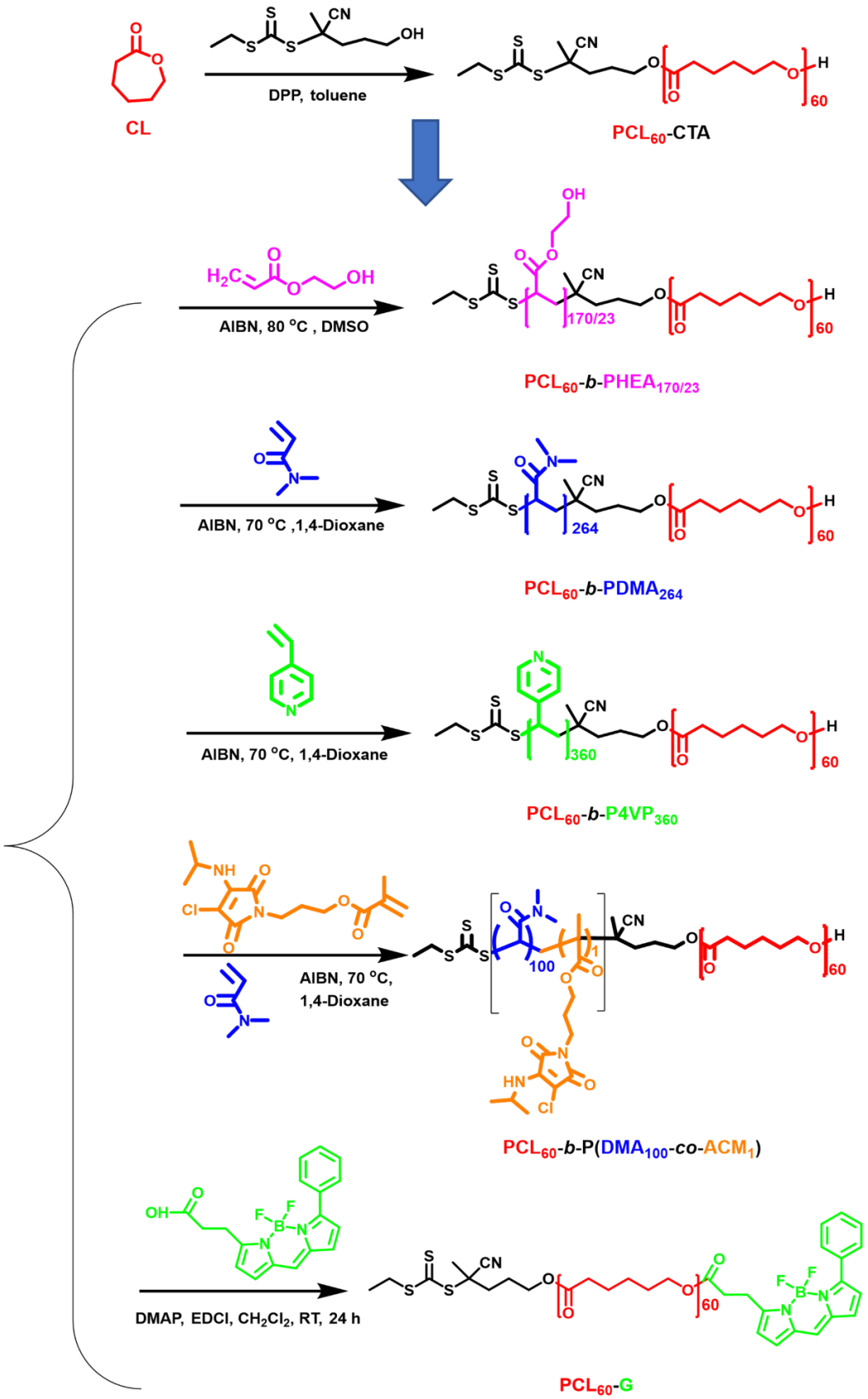
Synthesis of PCL_{60}-*b*-$PHEA_{170}$. The synthesis of BCPs with different corona chemistries was described in **Scheme S1**. PCL_{60}-CTA (100 mg, 0.014 mmol), HEA (0.328 g, 2.829 mmol) and AIBN (0.505 mg, 0.003 mmol) were dissolved in DMSO (2 mL) and placed in an ampoule. The solution was then freeze pump-thawed three times and heated for 30 h at 80 °C. The reaction was quenched by immersion of the ampoule in liquid nitrogen and the polymer was precipitated in ice-cold ethyl acetate three times and then in ice-cold ether three times before being dried under vacuum. The composition was calculated from ^{1}H NMR by analysis of the specific peaks belonging to PCL and PHEA (**Figure S1**). The synthesis of PCL_{60}-*b*-$PHEA_{23}$ BCP was used in a same method with [PCL-CTA]/[HEA]/[AIBN]=1:30:0.2 and the polymerization degree was estimated from ^{1}H NMR (**Figure S2**).

Synthesis of PCL_{60}-*b*-$PDMA_{264}$. PCL_{60}-CTA (100 mg, 0.014 mmol), DMA (0.420 g, 4.243 mmol) and AIBN (0.842 mg, 0.005 mmol) were dissolved in 1,4-dioxane (2 mL) and placed in an ampoule. The solution was then freeze pump-thawed three times and heated for 2 h at 70 °C. The reaction was quenched by immersion of the ampoule in liquid nitrogen and the polymer was precipitated in ice-cold n-hexane three times before being dried under vacuum. The composition was calculated from ^{1}H NMR by analysis of the specific peaks belonging to PCL and PDMA (**Figure S3**).

Synthesis of PCL_{60}-*b*-$P(DMA_{100}$-*co*-$ACM_1)$. PCL_{60}-CTA (100 mg, 0.014 mmol),

DMA (200 mg, 2.02 mmol), ACM (13.8 mg, 0.044 mmol), and AIBN (0.44 mg, 0.0274 mmol) were dissolved in 1,4-dioxane (2 mL) and placed in an ampoule. After three freeze-pump-thaw cycles, the solution was heated for 24 h at 70 °C. The reaction was quenched by immersion of the ampoule in liquid nitrogen and the polymer was precipitated in ice-cold diethyl ether before drying under vacuum. The composition was calculated from ^{1}H NMR by analysis of the specific peaks belonging to PCL, PDMA and ACM (**Figure S4**).

Synthesis of PCL$_{60}$-G. The BOPIPY R6G was selected to modify the core domains of PCL. PCL$_{60}$-CTA (100 mg, 0.014 mmol), BODIPY R6G (4.9 mg, 0.014 mmol), 4-dimethylaminopyridine (DMAP 0.85 mg, 0.007 mmol) and N-(3-dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride (EDCl 26.9 mg, 0.14 mmol) were dissolved in 2 mL CH_2Cl_2 and stirred for 24 h. The reaction mixture was precipitated in cold ethanol three times to yield pure the end-functionalized fluorescently labelled polymer, PCL$_{60}$-G.



Scheme S1. Synthetic route of PCL based polymers with different corona segment via ring opening polymerization (ROP) and then reversible addition−fragmentation chain transfer (RAFT) polymerization.

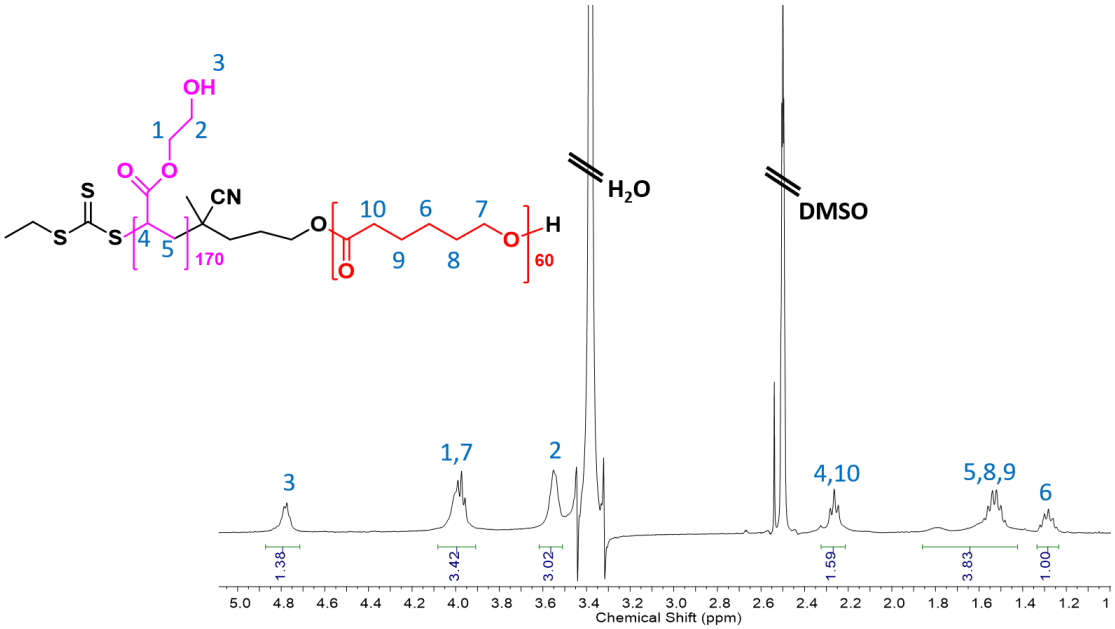


Figure S1. ^{1}H NMR spectrum of PCL_{60}-*b*-$PHEA_{170}$ in d_6-DMSO.

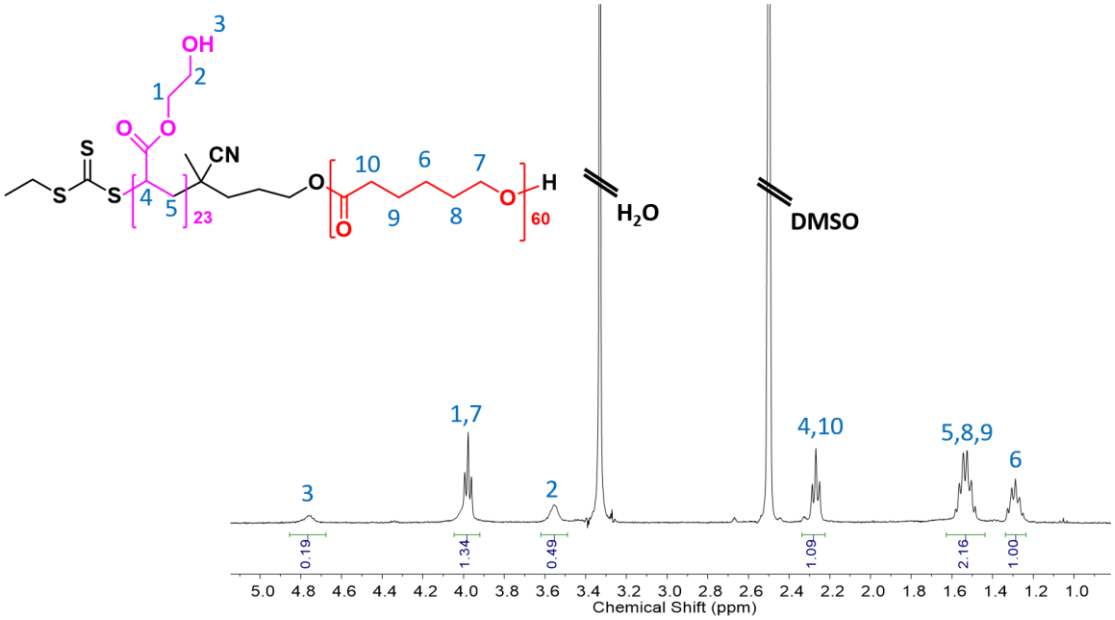


Figure S2. ^{1}H NMR spectrum of PCL_{60}-*b*-$PHEA_{23}$ in d_6-DMSO.

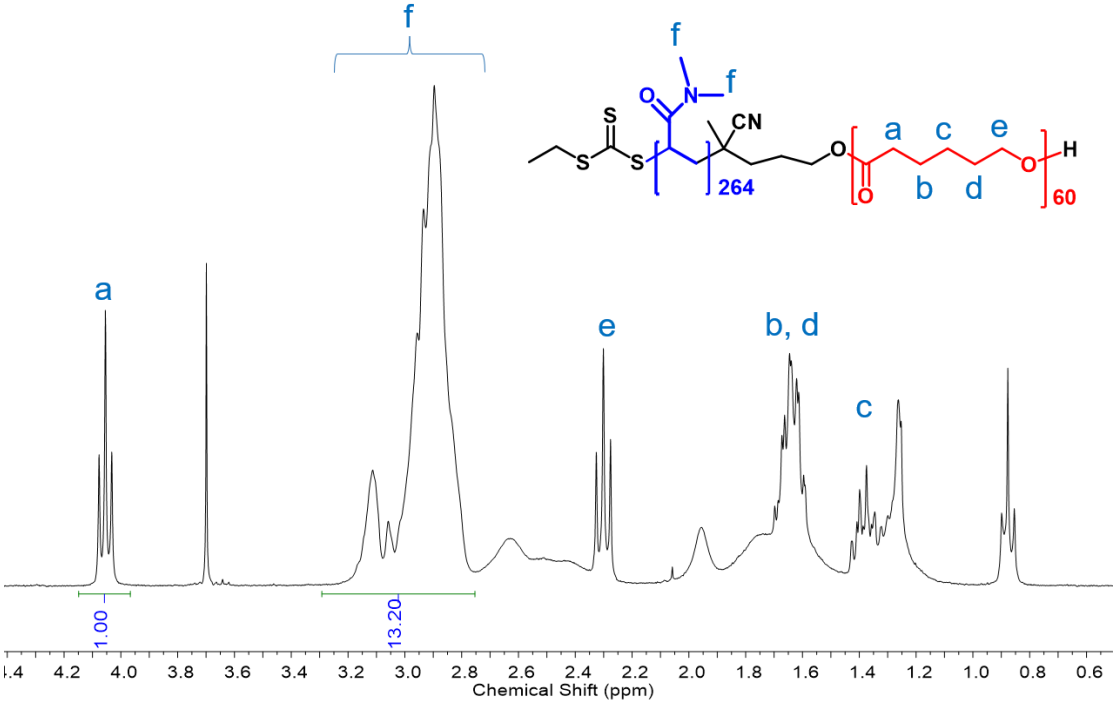


Figure S3. ^{1}H NMR spectrum of PCL_{60}-*b*-$PDMA_{264}$ in $CDCl_3$.

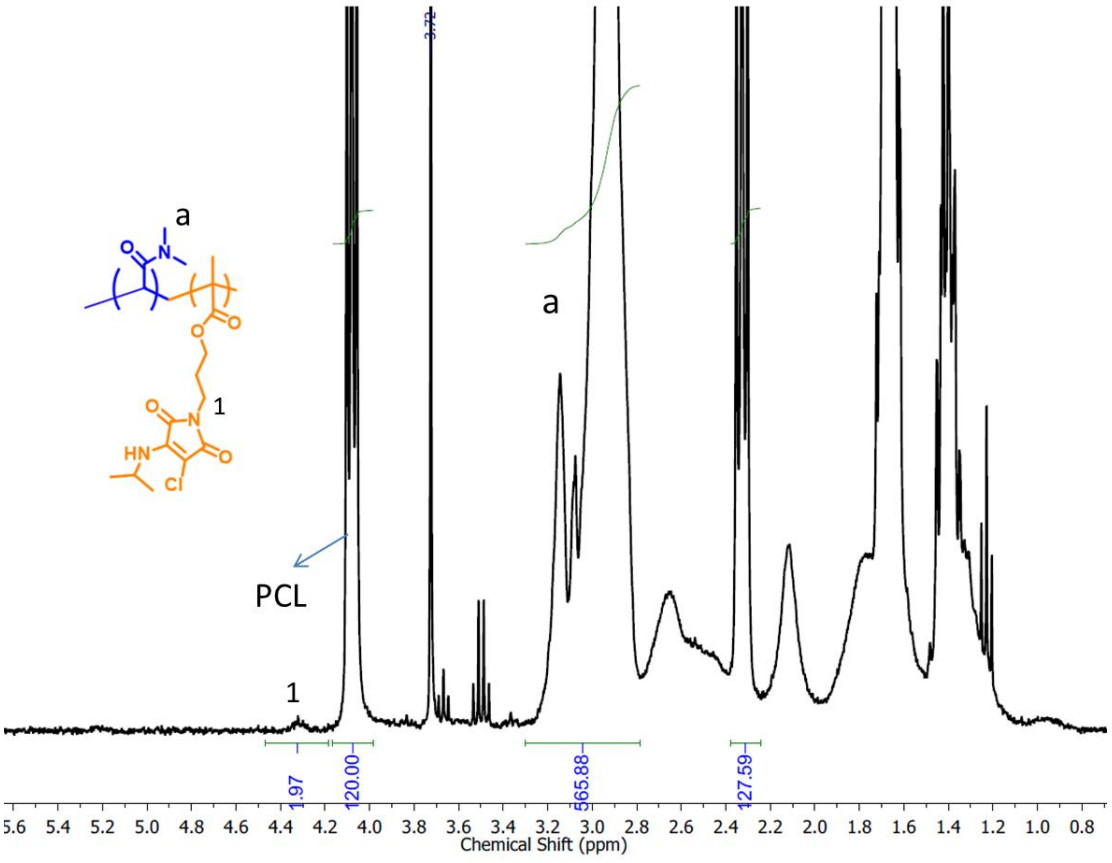


Figure S4. ^{1}H NMR spectrum of PCL_{60}-*b*-P(DMA_{100}-*co*-ACM_1) in $CDCl_3$.

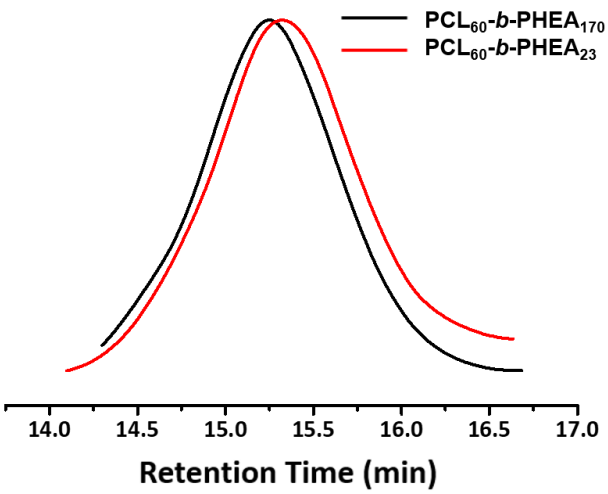


Figure S5. SEC traces of PCL_{60}-*b*-$PHEA_{170}$ and PCL_{60}-*b*-$PHEA_{23}$ using THF as eluent with 1 mL·min^{-1} at 40 °C.

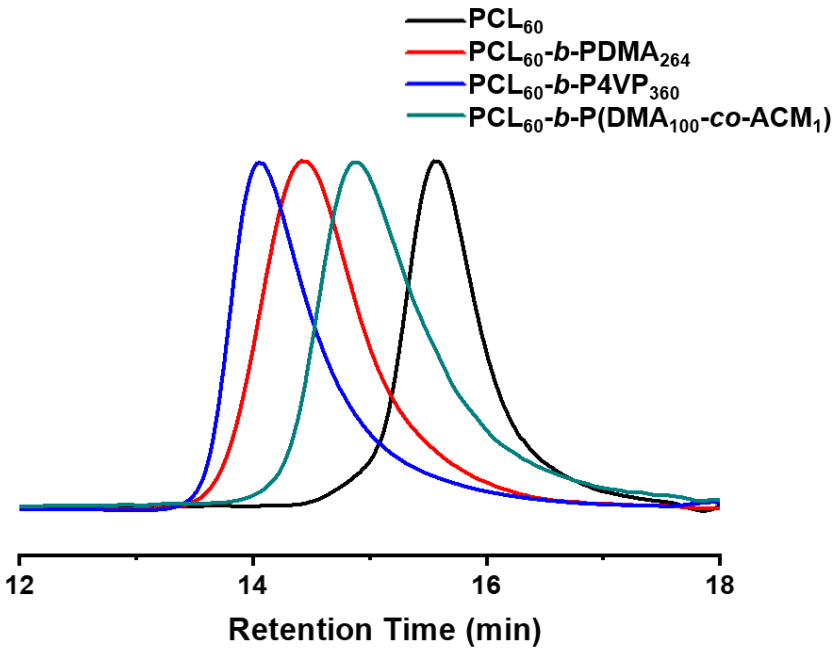


Figure S6. SEC traces of PCL_{60}, PCL_{60}-*b*-$PDMA_{264}$, PCL_{60}-*b*-$PDMA_{360}$ and PCL_{60}-*b*-P(DMA_{100}-*co*-ACM_1) using $CHCl_3$ as eluent with 1 mL·min^{-1} at 40 °C.

Table S1. Molecular Characterizations of Synthesized Polymers.

Polymer (NMR) [a]	$M_{n,\,NMR}$ [a] (kDa)	$M_{n,\,GPC}$ (kDa)	$Đ_M$
PCL_{60}	7.07	11.8 [b]	1.12 [b]
PCL_{60}-*b*-$PDMA_{264}$	33.2	36.8 [b]	1.11 [b]
PCL_{60}-*b*-$P4VP_{360}$	44.6	38.2 [b]	1.18 [b]
PCL_{60}-*b*-P(DMA_{100}-*co*-ACM_1)	18.7	18.2 [b]	1.24 [b]
PCL_{60}-*b*-$PHEA_{170}$	26.8	7.75 [c]	1.23 [c]
PCL_{60}-*b*-$PHEA_{23}$	9.8	7.18 [c]	1.25 [c]

a) The polymer compositions were calculated from ^{1}H NMR spectra;
b) The polydispersity of PCL and BCPs were obtained from SEC analysis using $CHCl_3$ as the eluent with poly (methyl methacrylate) standards;
c) The polydispersity of PCL-*b*-PHEA BCPs were obtained from SEC analysis using THF as the eluent with polystyrene standards. Since the PCL-*b*-PHEA BCPs are unable to dissolve in $CHCl_3$ solvent due to high polarization of PHEA segment, THF was selected as the eluent to calculate the polydispersity of PCL-*b*-PHEA.

Preparation of Seed micelles. Typically, taking PCL_{60}-*b*-$P4VP_{360}$ seed micelles as an example, PCL_{60}-*b*-$P4VP_{360}$ (10 mg) was added to 2 mL ethanol in a vial with a concentration of 5.0 mg·mL^{-1}. The sample was then heated at 70 °C for 3 h without stirring and subsequently cooled to room temperature. Polydisperse PCL_{60}-*b*-$P4VP_{360}$ cylinders were obtained after aging the sample for 7 days at room temperature. Then, the well-developed polydisperse cylindrical micelles were sonicated to uniform short micelles using a sonication probe in an ice bath (0 °C) for 20 min. The obtained uniform short micelles were used as seed micelles for following epitaxial crystallization. The 1D uniform seed micelles of PCL_{60}-*b*-$PDMA_{264}$ were prepared in a same method. For PCL_{60}-*b*-$PHEA_{170}$, since polydisperse platelet micelles instead of cylinders were formed through spontaneous nucleation, the seed micelles of PCL_{60}-*b*-$PHEA_{170}$ were sonicated for 50 min to yield irregular small plate as seed micelles.

Seeded Epitaxial Growth. Homopolymer and corresponding block copolymer (1:1,

w/w) dissolved in a good solvent (PCL/PCL-*b*-PHEA in DMSO, PCL/PCL-*b*-PDMA, PCL/PCL-*b*-P(DMA-*co*-ACM) and PCL/PCL-*b*-P4VP in $CHCl_3$, 10 mg • mL^{-1}) was added to an ethanol dispersion of 1D seed micelles (0.01 mg • mL^{-1}) or 2D platelet micelles (0.01 mg • mL^{-1}) and then aged for 24 h at room temperature before observation by TEM.

Living Growth of PCL/PCL-*b*-PHEA Blend. Taking the strategy of adding 20% TFE in advance as an example, 1D PCL_{60}-*b*-$P4VP_{360}$ seed micelle solution with a concentration of 0.01 mg • mL^{-1} was dispersed in the mixed solution of TFE/EtOH (20:80 in volume). Different amounts of PCL_{60}/PCL_{60}-*b*-$PHEA_{170}$ blend unimer dissolved in $CHCl_3$ (5, 10, 15, 20, 25 μL, 10 mg·mL^{-1}) were added to the above seed micelle solution. After shaking for 5 s, the solution was aged for 24 h before observation by TEM.

Construction of Seeded Growth Template by Hydrogen Bond. After obtaining 2D block co-micelles, seed micelle suspension of PCL_{60}-*b*-$P4VP_{360}$ (0.1 mg·mL^{-1} in ethanol, H-bond acceptor, H_A) was added to the 2D block co-micelles suspension (H-bond donor, H_D) with a mass ratio of 0.2:1 (H_A: H_D). After shaking for 5 s, the solution was aged for 24 h before observation by TEM.

Epitaxial Growth of PCL_{60}-*b*-$P4VP_{360}$ from Seed Micelles Anchored on 2D Platelet Template. Different amounts of PCL_{60}-*b*-$P4VP_{360}$ unimer dissolved in $CHCl_3$ (10 mg·mL^{-1}) was added to a suspension containing seed micelles that anchored on 2D platelet template via H-bond. After a shaking for 5 s, the solution was aged for 24 h before observation by TEM.

Statistics of the Area and Length of Micelles. ImageJ (NIH, US) software was used to calculate the number average area (A_n) and weight average area (A_w) of platelets from more than 50 micelles. The values of A_n and A_w are calculated using the following formula:

$$A_n = \frac{\sum_{i=1}^{i=n} A_i n_i}{\sum_{i=1}^{i=n} n_i} \qquad (1)$$

$$A_w = \frac{\sum_{i=1}^{i=n} A_i^2 n_i}{\sum_{i=1}^{i=n} A_i n_i} \qquad (2)$$

where n_i is the number of platelets, A_i is the area of platelets, and n is the total number of platelets examined for each sample. The distribution of platelet area is characterized by A_w/A_n. The statistics for the length analysis of the 1D seed micelles was achieved using the same method.

The number average lengths (L_n) and weight average lengths (L_w) of the cylindrical micelles were calculated either. Values of L_n and L_w were calculated using the following equations:

$$L_n = \frac{\sum_{i=1}^{N} N_i L_i}{\sum_{i=1}^{N} N_i} \qquad (3)$$

$$L_w = \frac{\sum_{i=1}^{N} N_i L_i^2}{\sum_{i=1}^{N} N_i L_i} \qquad (4)$$

where N_i is the number of 1D cylinders, L_i is the cylinders length, and N is the total number of micelles examined for each sample. The distribution of cylinder lengths is characterized by L_w/L_n.

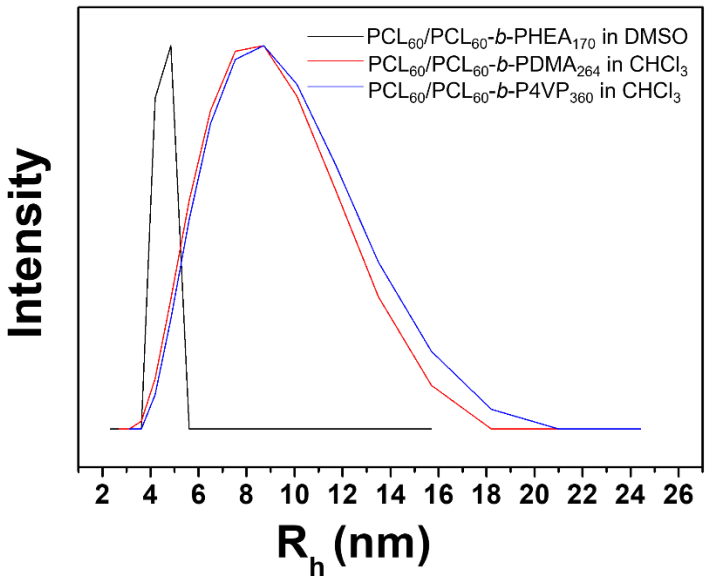


Figure S7. Hydrated radius of different polymer blends in good solvents tested by DLS.

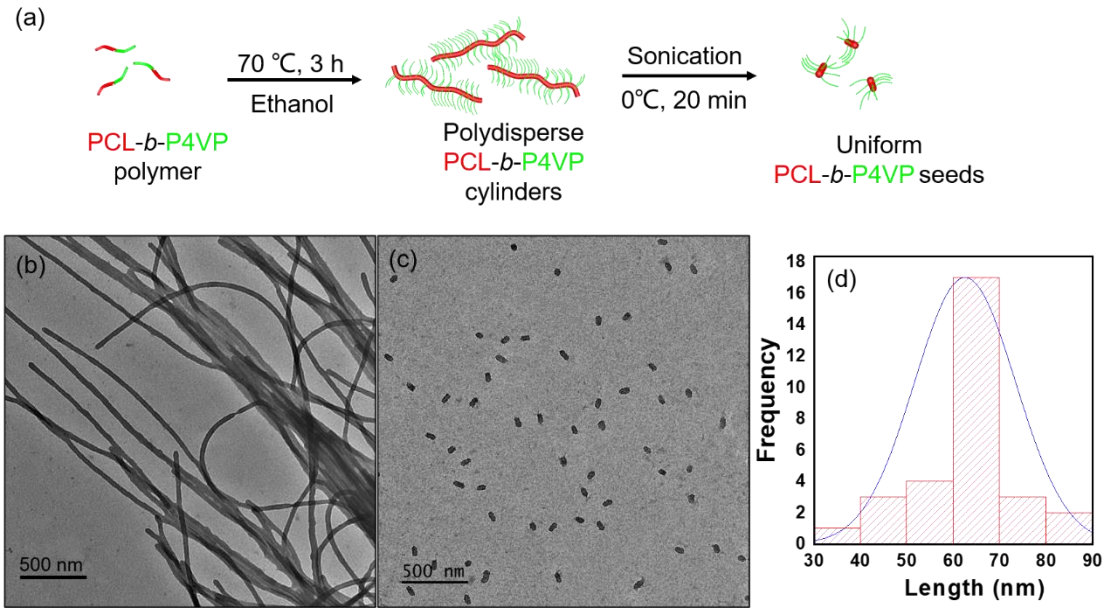


Figure S8. (a) Schematic diagram of the acquirement of monodisperse PCL_{60}-*b*-$P4VP_{360}$ seed micelles; (b) TEM image of polydisperse PCL_{60}-*b*-$P4VP_{360}$ cylindrical micelles; (c) Seed micelles by long micelles subjected to sonication for 20 min; (d) Corresponding length distribution of seed micelles of PCL_{60}-*b*-$P4VP_{360}$ with length of about 62 nm. TEM samples were stained with a 1 wt% solution of uranyl acetate in EtOH.

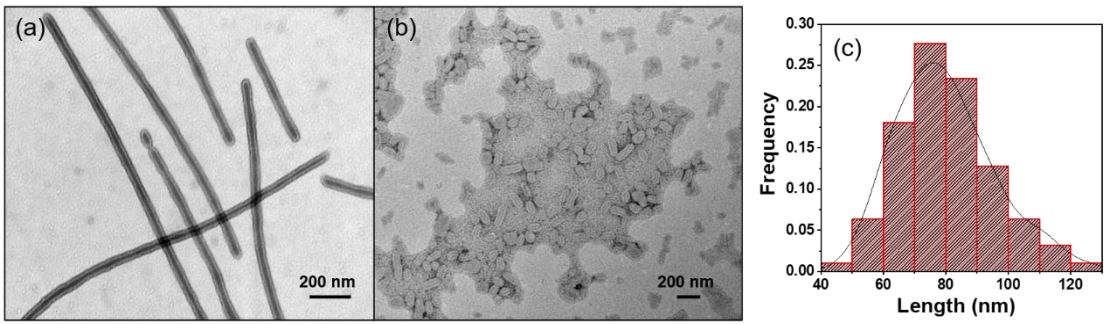


Figure S9. (a) TEM image of polydisperse PCL_{60}-*b*-$PDMA_{264}$ cylindrical micelles; (b) Seed micelles by long micelles subjected to sonication for 20 min; (c) Corresponding length distribution of seed micelles of PCL_{60}-*b*-$PDMA_{264}$ with length of about 78 nm. TEM samples were stained with a 1 wt% solution of uranyl acetate in EtOH.

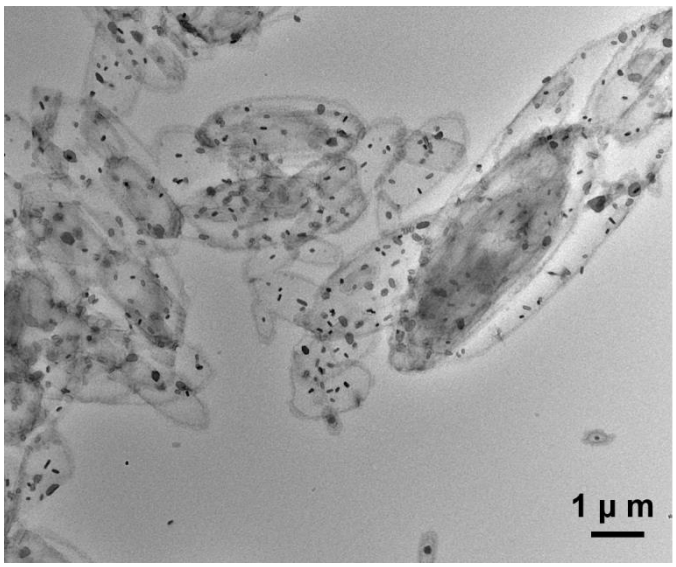


Figure S10. TEM image of 2D uneven and stacked platelets obtained by adding 10 µL of PCL_{60}/PCL_{60}-*b*-$PHEA_{170}$ (1:1, w/w) unimer solution (m_{unimer}/m_{seed}=10) to the 1D PCL_{60}-*b*-$PDMA_{264}$ seed solution and aged for 24 h. TEM samples were stained with a 1 wt% solution of uranyl acetate in EtOH.

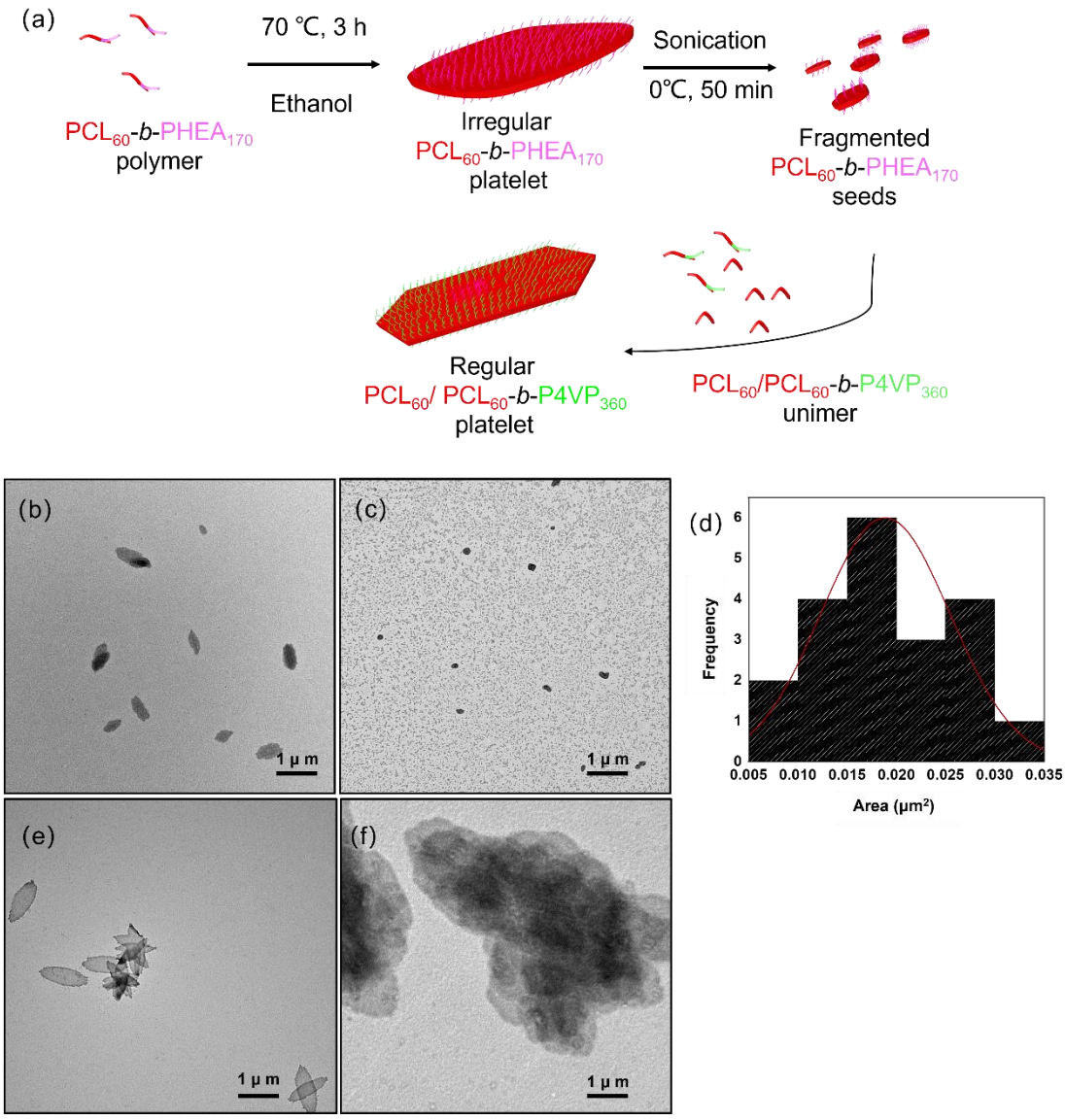


Figure S11. (a) Schematic illustration of preparation of uniform PCL_{60}/PCL_{60}-*b*-$P4VP_{360}$ using 2D fragmented PCL_{60}-*b*-$PHEA_{170}$ seeds in ethanol; (b) TEM image of polydisperse 2D platelets obtained by spontaneous nucleation of PCL_{60}-*b*-$PHEA_{170}$; (c) TEM image and (d) corresponding area distribution of monodisperse fragmented micelles obtained from sonicating the polydisperse 2D platelets for 50 min at 0 °C using a sonication probe. (e) TEM image of 2D platelets of PCL_{60}/PCL_{60}-*b*-$P4VP_{360}$ epitaxially grown from PCL_{60}-*b*-$PHEA_{170}$ seeds. (f) TEM morphologies of addition of PCL_{60}/PCL_{60}-*b*-$P4VP_{360}$ in ethanol without PCL_{60}-*b*-$PHEA_{170}$ seeds. TEM samples were stained with a 1 wt% solution of uranyl acetate in EtOH.

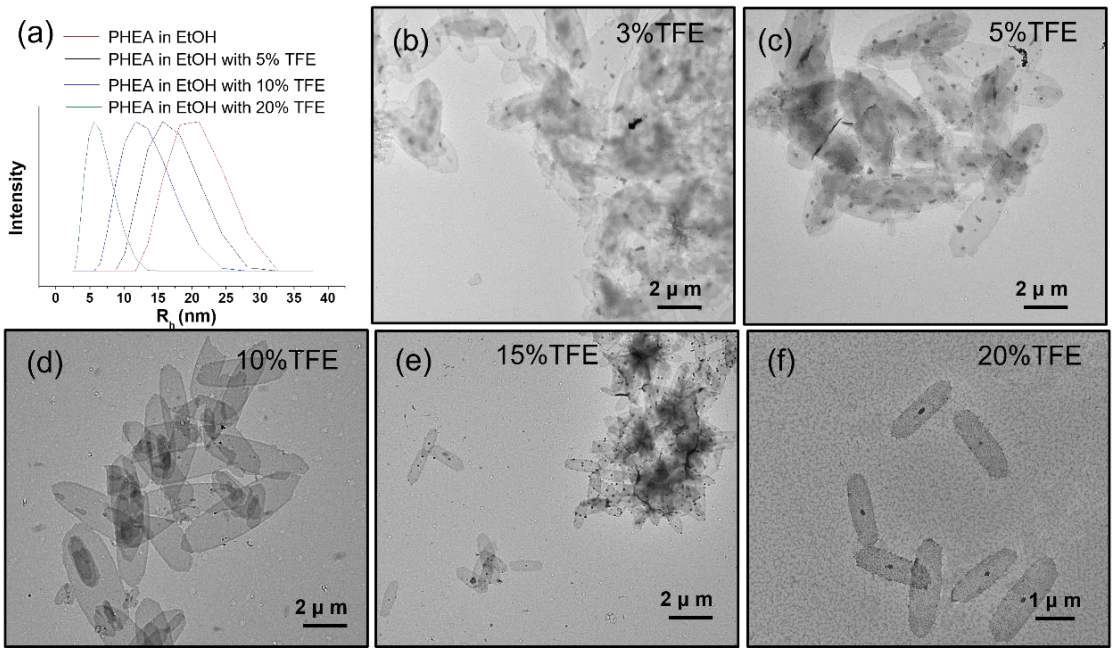


Figure S12. (a) Change of hydrated radius (R_h) of PHEA homopolymer in EtOH with different volumes of TFE tested by DLS. TEM images of 2D platelets obtained by adding (b) 3%, (c) 5%, (d) 10%, (e) 15%, (f) 20% volume of TFE to the 1D PCL_{60}-*b*-$P4VP_{360}$ seed micelle ethanol solution in advance, then subsequently adding 10 μL of PCL_{60}/PCL_{60}-*b*-$PHEA_{170}$ (1:1, w/w) unimer solution to the 1D seed micelle solutions containing different amount of TFE with m_{unimer}/m_{seed}=10. TEM samples were stained with a 1 wt% solution of uranyl acetate in EtOH.

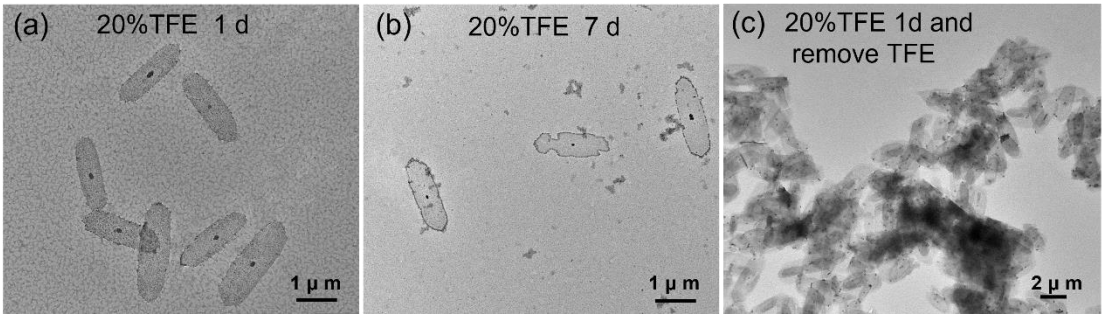


Figure S13. **Effect of TFE solvent on the morphology of 2D platelets.** TEM image of well-developed 2D platelets of PCL_{60}/PCL_{60}-*b*-$PHEA_{170}$ (1:1, w/w) epitaxially grown from 1D PCL_{60}-*b*-$P4VP_{360}$ seed solution containing 20% TFE and then aged for (a) 1 day and (b) 7 days. (c) TEM image of as-prepared well-developed 2D platelets after removing TFE by rotary steaming at room temperature. TEM samples were stained with a 1 wt% solution of uranyl acetate in EtOH.

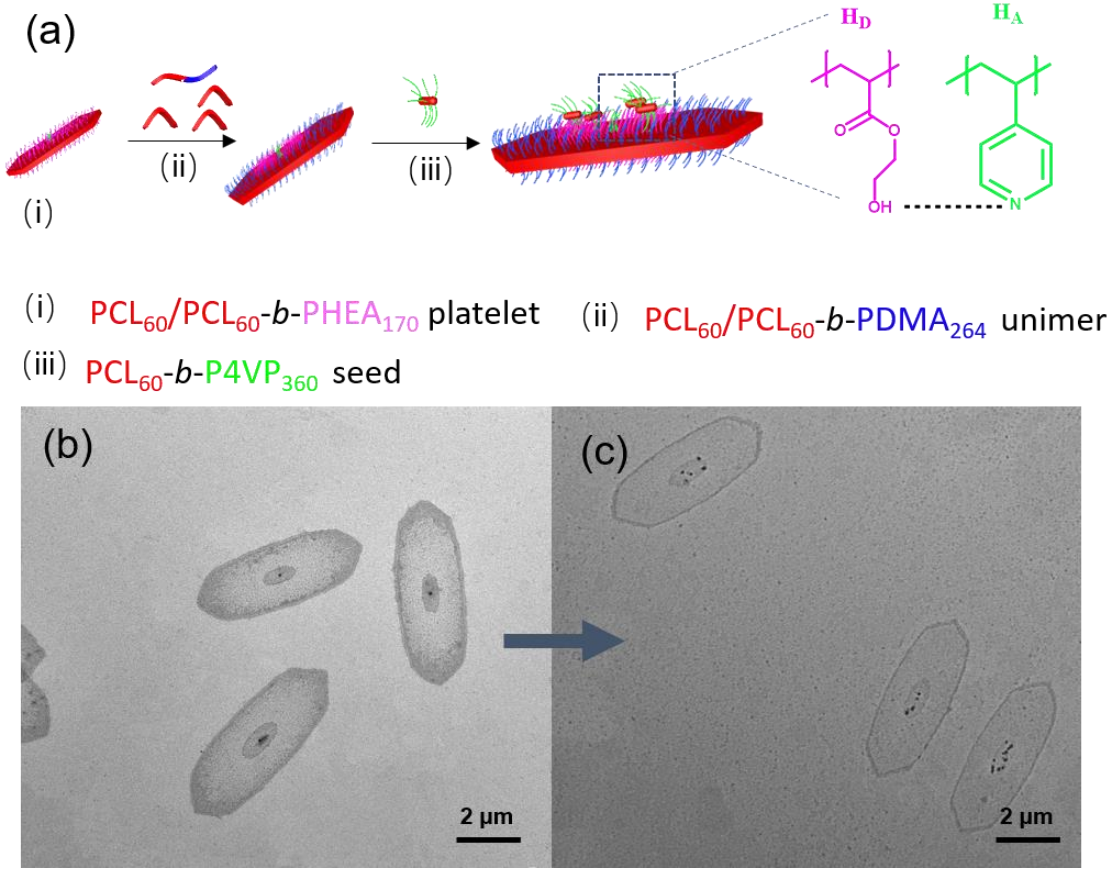


Figure S14. (a) Schematic illustration of the process of construction of 2D diblock co-micelles and selective depositing of PCL_{60}-*b*-$P4VP_{360}$ seed micelles on the platelet surface. (b) TEM image of 2D diblock co-micelles prepared by addition of 20 μL PCL_{60}/PCL_{60}-*b*-$PDMA_{264}$ blend unimers (1:1, w/w, 10 $mg \cdot mL^{-1}$) into 2D PCL_{60}/PCL_{60}-*b*-$PHEA_{170}$ platelet micelles (0.02 $mg \cdot mL^{-1}$, 1 mL). (c) Selective depositing 1D PCL-*b*-P4VP seed micelles on the PHEA region of 2D block co-micelles by H-bond.

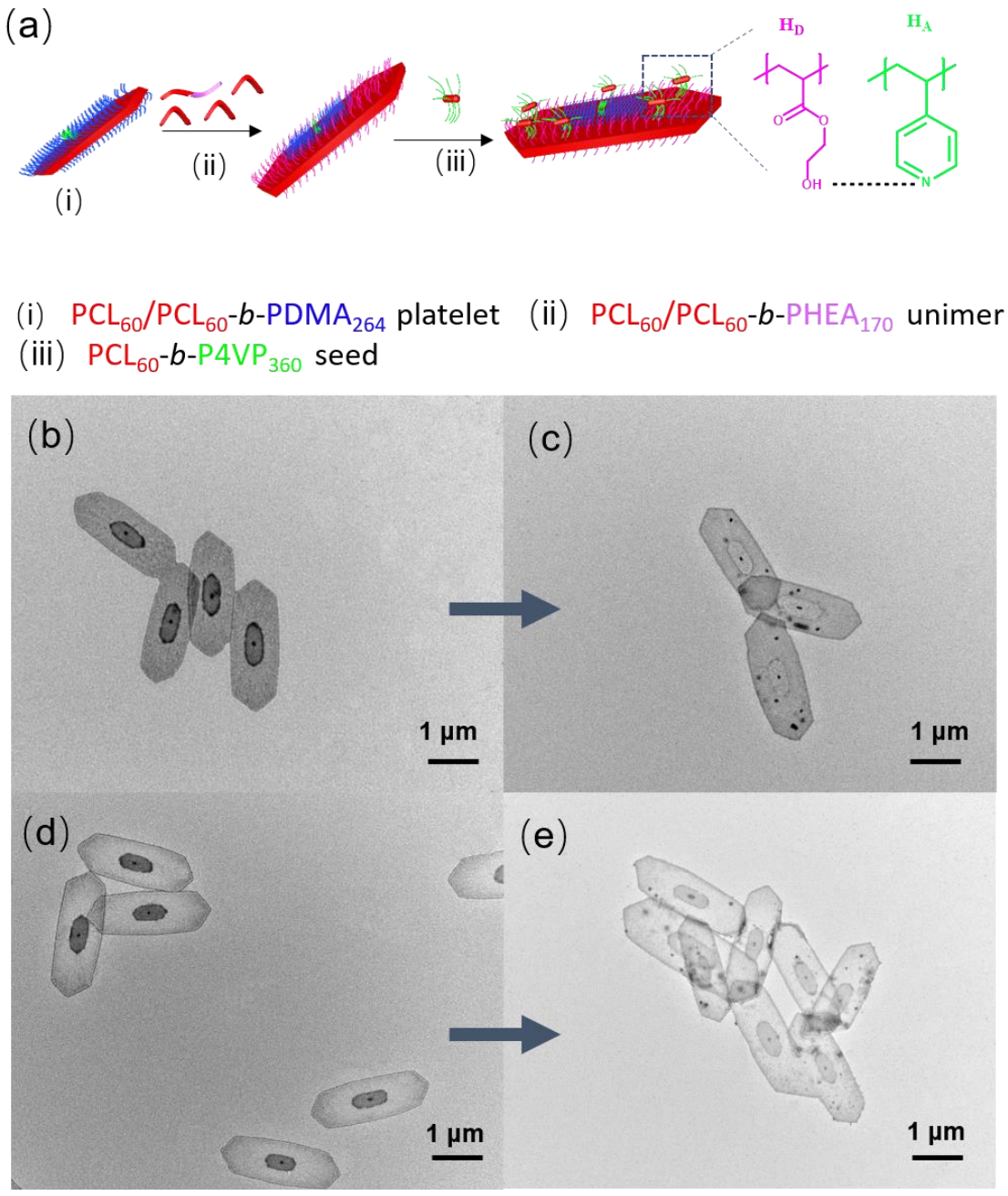


Figure S15. (a) Schematic illustration of the construction of 2D diblock co-micelles and selective depositing of PCL_{60}-*b*-$P4VP_{360}$ seed micelles on the platelet surface. TEM image of 2D diblock co-micelles prepared by addition of 3 μL of (b) PCL_{60}/PCL_{60}-*b*-$PHEA_{170}$ blend unimers (10 mg·mL^{-1}) and (d) PCL_{60}/PCL_{60}-*b*-$PHEA_{23}$ blend unimers (10 mg·mL^{-1}) into 2D PCL_{60}/PCL_{60}-*b*-$PDMA_{264}$ seed micelles (0.01 mg·mL^{-1}, 1 mL), respectively. Selective deposition of 1D PCL_{60}-*b*-$P4VP_{360}$ seeds (c) and (e) on the PHEA surface region of (b) and (d), respectively.

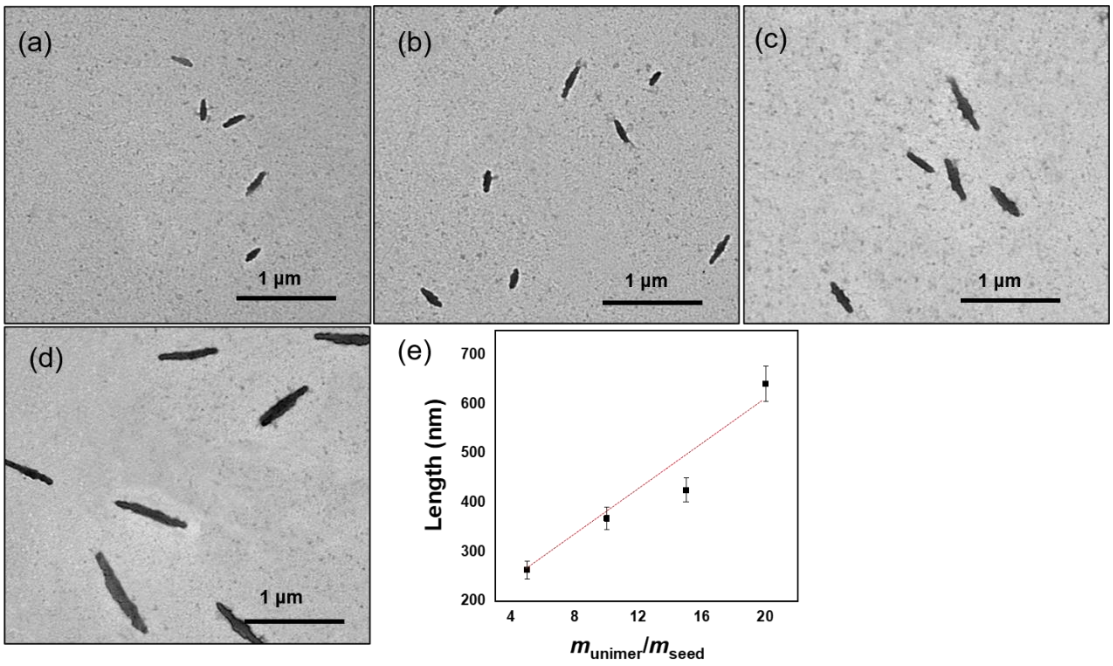


Figure S16. TEM image of 1D non-quasilinear cylindrical micelles by adding (a) 5 μL, (b) 10 μL, (c) 15 μL, (d) 20 μL of solely PCL_{60}-*b*-$P4VP_{360}$ unimer solution to the 1D PCL_{60}-*b*-$P4VP_{360}$ seed solution and aged for 24 h. (e) Plot of number-average 1D quasi-linear cylindrical micelles length *vs* m_{unimer}/m_{seed} (the error bars represent the standard deviation). TEM samples were stained with a 1wt % solution of uranyl acetate in EtOH.

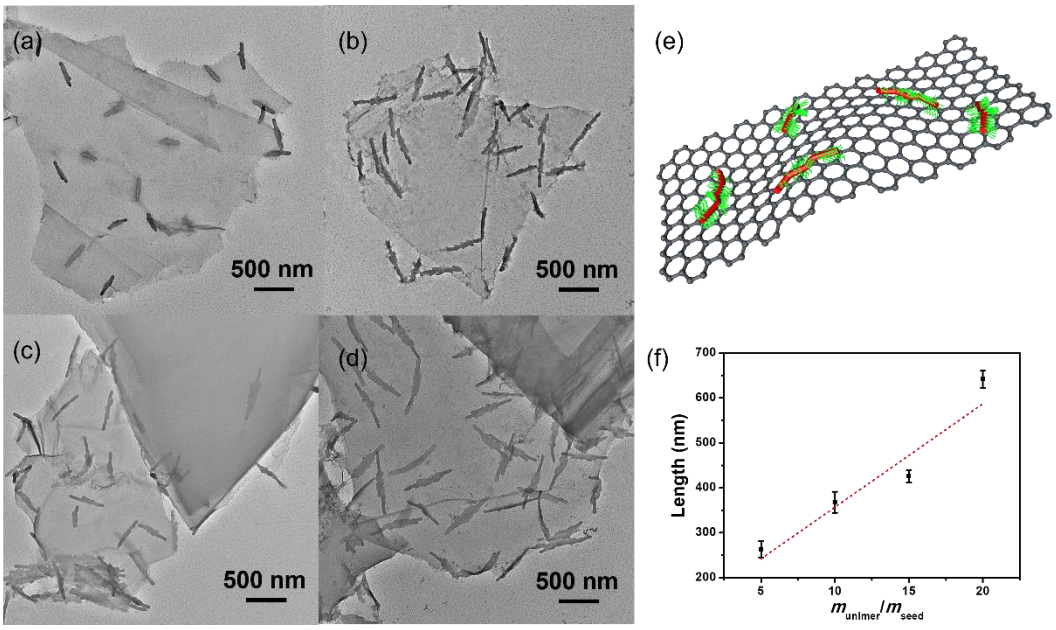


Figure S17. TEM image of 1D non-quasilinear cylindrical micelles by adding (a) 5 μL, (b) 10 μL, (c) 15 μL, (d) 20 μL of solely PCL_{60}-*b*-$P4VP_{360}$ unimer solution to the 1D PCL_{60}-*b*-$P4VP_{360}$ seed solution that fixed on GO sheets. (e) Schematic illustration of the non-quasilinear cylindrical micelles lying on the GO surface. (f) Plot of number-average 1D quasi-linear cylindrical micelles length *vs* m_{unimer}/m_{seed} (the error bars represent the standard deviation). TEM samples were stained with a 1wt % solution of uranyl acetate in EtOH.

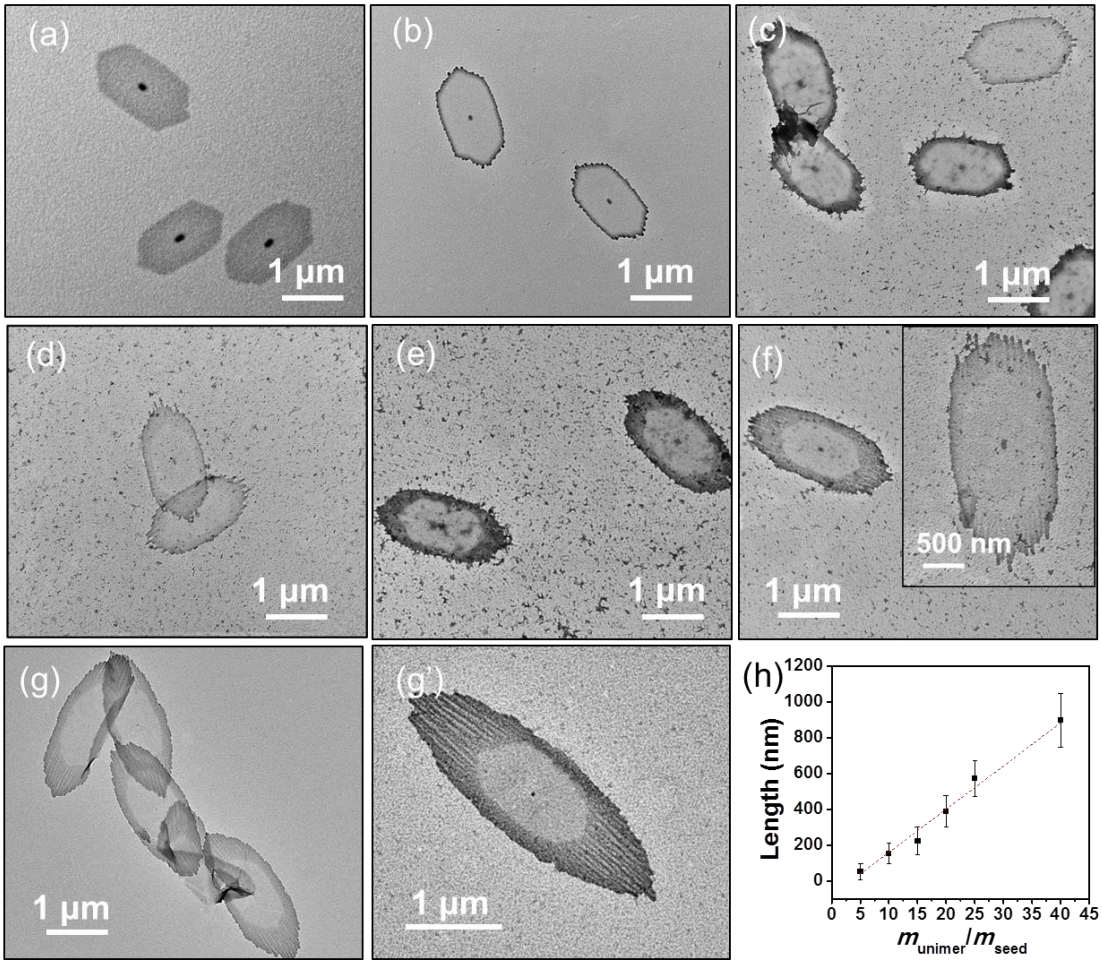


Figure S18. (a) TEM image of 2D PCL_{60}/PCL_{60}-*b*-$PDMA_{264}$ platelet prepared by seeded growth. TEM images of "platelet-fiber" structure by adding solely PCL_{60}-*b*-$P4VP_{360}$ unimer in the presence of 2D PCL_{60}/PCL_{60}-*b*-$PDMA_{264}$ platelet with a m_{unimer}/m_{seed} of (b) 5, (c) 10, (d) 15, (e) 20, (f) 25, inset is the enlarge one, (g) 40 and (g') high evolution of one micelle, respectively. (h) Plots of number-average 1D quasi-linear cylindrical micelles length against m_{unimer}/m_{seed} from 2D platelets (the error bars represent the standard deviation). TEM samples were stained by the 1 wt% solution of uranyl acetate in EtOH.

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