Supplementary Information

Interfacial self-assembly of amphiphilic conjugated block copolymer into 2D nanotapes

Xiao-Shuai Guo^a, Ze-Kun Zhang ^a, Tian-Yu Zhang^a, Zai-Zai Tong^b, Jun-Ting Xu*,^a,

Zhi-Qiang Fan^a

^aMOE Key Laboratory of Macromolecular Synthesis and Functionalization, Department of Polymer Science & Engineering, Zhejiang University, Hangzhou 310027, China

^bKey Laboratory of Advanced Textile Materials and Manufacturing Technology (ATMT), Ministry of Education, Department of Materials Science and Engineering, Zhejiang Sci-Tech University, Hangzhou 310018, China



Figure S1. TEM images of evaporation-induced interfacial self-assembly morphologies of $P3HT_{25}$ -*b*-PAA₇₃ under low evaporation rate (a) and high evaporation rate (b, c, d) of oil solvents (*p*-xylene/anisole mixed solvent is chosen as oil solvent).

The interfacial self-assembly morphologies of P3HT₂₅-*b*-PAA₇₃ under different evaporation rates of oil solvent are shown in Figure S1. When the evaporation rate is relatively low, P3HT₂₅-*b*-PAA₇₃ can form nanotapes (see Fig. S1a). By contrast, various geometries expect for nanotapes of P3HT₂₅-*b*-PAA₇₃ are formed under relatively high evaporation rate (Figs. S1b, S1c and S1d). The morphologies of these assemblies look like irregular nanotapes densely surrounded by nanowires. Although it is difficult to explain the mechanism for the formation of each nanostructure, the unstable environment for the ordered packing of P3HT segments caused by quick evaporation of oil solvent may account for this phenomenon. The interfacial self-assembly at the oil-water interface would not be much affected by the quick evaporation rate of oil solvent in the early stage because there is enough oil solvent

stock at the oil-water interface. Hence, despite the existence of some structural defects caused by quick evaporation of oil solvent, the nucleation and packing of P3HT segments can proceed in two dimensions, leading to the formation of irregular nanotapes. Nevertheless, it is time-consuming for the P3HT segments to arrange themselves into the growth front of crystals apparently while increasing the evaporation rate would reduce the time scale of this procedure. So the number of defects may increase in the later stage as the oil solvent further evaporates, which would mainly interrupt the packing of alkyl side chains, thereby forming 1D nanowires which epitaxially grow on the lateral surface of nanotapes.



Figure S2. TEM images of self-assembly morphologies of P3HT₂₅-*b*-PAA₇₃ at the oil- water interface under different temperatures of water subphase. (a) T = 0 °C, (b) T = 30 °C and (c) T = 50 °C.

The interfacial self-assembly morphologies of P3HT₂₅-*b*-PAA₇₃ at different temperatures are shown in Fig. S2. It can be seen that regular nanotapes are formed only at 30 °C, while clustered nanowires and irregular nanotapes are formed at 0 °C and 50 °C respectively. It suggests that 30 °C is the most suitable temperature for the formation of nanotapes among these temperatures. For the interfacial self-assembly of P3HT₂₅-*b*-PAA₇₃ at 0 °C, although the lowest evaporation rate of oil solvent prolongs the time scale of the self-assembly process at the oil-water interface, the abilities of chain segments to diffuse and adjust their conformation at the oil-water interface are poor. So it's difficult for P3HT segments to find a favorable conformation for the packing of side chains at low temperature. Meanwhile, P3HT segments become less soluble in oil solvent at 0 °C and the interchain π - π interaction is strengthened between P3HT backbones. For these reasons, semi-crystalline nanowires are formed

driven by interchain π - π interaction. Increasing the temperature of water subphase improves the kinetic energy of polymer chains, endowing them with more flexibility to adjust their location and conformation at the oil-water interface. So when the temperature of water subphase is increased to 30 °C, a part of polymer chains with specific conformation, which facilitates the packing of alkyl side chains and π - π interaction, would arise at the oil-water interface. This allows the P3HT segments to assemble in two dimensions. However, the increased temperature of water subphase also accelerates the evaporation rate of oil solvent, thus reducing the time scale in which P3HT segments adjust their conformation and arrange themselves into the front crystal surface. Hence, when the temperature of water subphase is further increased to 50 °C, the number of structural defects increases leading to the formation of irregular nanotapes.



Figure S3. TEM images of self-assembly morphologies of homopolymer P3HT at the oil-water interface using different oil phase solvents ((a) *p*-xylene, (b) anisole). For interfacial self-assembly, 0.1 mg/ml P3HT was first dissolved in *p*-xylene (a) or anisole (b) and the solutions were firstly heated to 90 °C for 3 h, then 200 μ L of the solution was quickly transferred to water surface with preset temperature (30 °C) and left for 48 h.



Figure S4. TEM images of self-assembly morphologies of P3HT-*b*-PAA at the wateroil interface with various subphase pH values (*p*-xylene/anisole mixed solvent is chosen as oil solvent). (a) pH = 6.5, (b) pH = 13.



Figure S5. FT-IR spectra of IS film (a) and SC film (b) in the region 1355 - 1500 cm⁻¹. The black hollow circle symbols represent the experiment data, and curves represent the fitting data.



Figure S6. Raman spectrum of P3HT-*b*-PAA ultrathin films fabricated by self-assembly at the oil-water (pH = 6.5) interface in the region of 500-1700 cm⁻¹.

Wavenumber (cm ⁻¹)	Assignment ¹
~727	C-S-C deformation mode
~1000	C-C (carbon and carbon of the hexyl substituent) stretching deformation
~1091	C-H bending
~1181	C-H bending mode with C–C inter-ring stretch mode
~1211	Inter-ring C–C stretch mode
~1381	C-C intraring stretch mode
~1451	Symmetric C=C stretch mode

Table S1 Assignments of Raman peaks for P3HT-b-PAA in Figure S6.



Scheme S1. Schematic descriptions of the orientations of thiophene rings on water surface. (a) "Ring edge-on" orientation; (b) "Ring face-on" orientation.



Figure S7. IR spectra of P3HT-*b*-PAA ultrathin film fabricating by interfacial self-assembly at the oil-water (pH = 6.5) interface in the region 600-3150 cm⁻¹.

Wavenumber(cm ⁻¹)	Assignment
819	Thiophene ring, C-H out-of-plane
1374	CH ₃ methyl deformation
1452	Thiophene ring, sym. C=C
1506	Thiophene ring, antisym. C=C
1554	antisymmetric stretching frequencies of the carboxylate ion (COO ⁻)
1710	C=O vibration of the carboxylic group
2854	CH ₂ sym. Stretching
2929	CH ₂ antisym. Stretching
2960	CH ₃ antisym. Stretching

Table S2 The assignments of the IR absorption peaks for P3HT-*b*-PAA in Figure S7.



Figure S8. FTIR-RAS spectra of $P3HT_{25}$ -*b*-PAA₇₃ IS film at different incidence angles. The black hollow circle symbols represent the experiment data, and curves represent the fitting data.



Figure S9. XRD pattern of pristine P3HT-b-PAA powder.

The XRD result of pristine P3HT-*b*-PAA powder is shown in Figure S9. The (100) peak with high intensity is located at 5.2°, corresponding to lattice parameter *a*. The (010) peak is located at 23.4°, corresponding to lattice parameter *b*. After calculation, the lattice constants *a* and *b* are 1.67 nm (alkyl interchain distance) and 0.38 nm (π -stacking distance) respectively. The values of the lattice constants *a* and *b* are similar to those of orthorhombic crystal unit cell of P3HT.² So the crystal system of pristine P3HT-*b*-PAA powder should be orthorhombic.

Calculations of the reduced tethering density ($\tilde{\sigma}$) of PAA chains on the surfaces of P3HT-*b*-PAA nanosheets

The reduced tethering density $(\tilde{\sigma})$ of PAA segments can be defined as:

$$\tilde{\sigma} = \sigma_{\rm t} \, \pi R_{\rm g}^2 \qquad (1)$$

where σ_{t} is the tethering density of PAA segment, which is designated as the number of tethered PAA segment in per square nanometer. R_{g} is the radius of gyration of a free PAA chain with the same molecular weight in the P3HT₂₅-*b*-PAA₇₃ BCP. For PAA₇₃, the value of R_{g} is about 2.5 nm.³

The value of $\tilde{\sigma}$ reflects the crowdedness of the PAA segments tethered on the P3HT crystal surface. As described above, the P3HT segments are perpendicular to P3HT/PAA interface, thus σ_t^4 can be calculated as:

$$\sigma_{\rm t} = \frac{N}{(n_{\rm f} + 1)a_0 b_0} \qquad (2)$$

Where *N* is the number of P3HT stem in a unit cell of P3HT crystal (N = 1), n_f is the folding number of P3HT block ($n_f = 0$ for extended P3HT chain and $n_f = 1$ for once-folded P3HT chain.). a_0 and b_0 are the lattice constants for the orthorhombic unit cell of P3HT crystal along *a*- and *b* -axes, which are 16.7 Å and 3.8 Å, respectively. It is inferred that the arrangement mode of P3HT segments in P3HT₂₅-*b*-PAA₇₃ nanotapes follows the crystal model of pristine P3HT₂₅-*b*-PAA₇₃ powder (Fig. S9). The calculated value of σ_f is 1.58 nm⁻² for $n_f = 0$ and 0.79 nm⁻² for $n_f = 1$, respectively.

References

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