

Electronic Supplementary Information

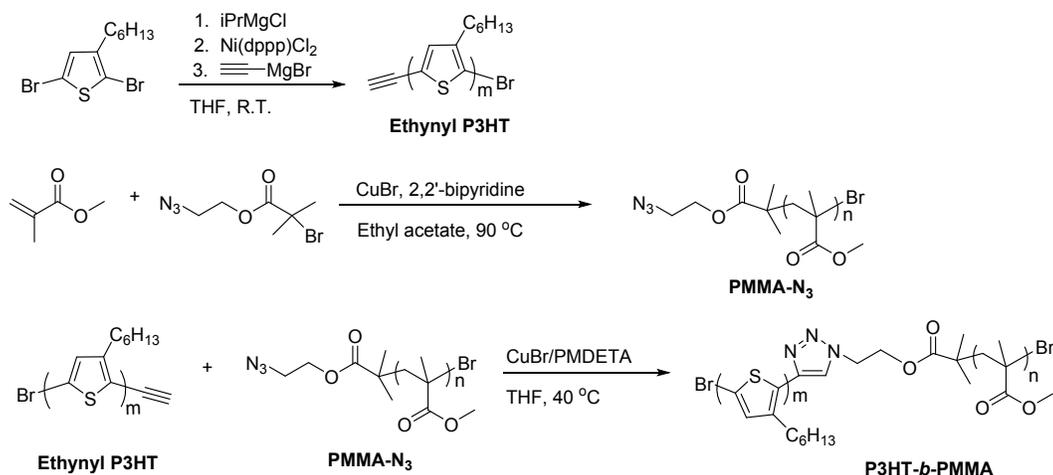
Hierarchically honeycomb-structured films by directed self-assembly in “Breath Figure” templating of ionizable “clicked” PH3T-*b*-PMMA diblock copolymers: Ionic bonding group/counter-ion effect on porous polymer film morphology.

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Experimental Details

Synthesis of ethynyl terminated PH3T (Ethynyl P3HT). Ethynyl functionalized P3HT was synthesized according to the procedure described in the previous work. To a flame-dried 100 mL Schlenk flask 2,5-dibromo-3-hexyl thiophene (2 g, 6.13 mmol) and THF (8 mL) were added. Isopropyl magnesium chloride (3.1 mL, 6.13 mmol) was added and then the mixture solution was stirred at room temperature for 2 hours under N₂ atmosphere. Additional 40 mL of THF and Ni(dppp)Cl₂ (0.184 g, 0.34 mmol) were added and stirred for 10 min. 3.7 mL (1.84 mmol, 30 mol % of monomer) of magnesium chloride (2.0 M in THF) was added and then the mixture was stirred for an additional 2 min. The mixture was poured about 500 mL of methanol to precipitate the polymer. The collected polymer was dissolved in chloroform and precipitated in acetone again.

Synthesis of azido terminated PMMA (PMMA-N₃). Azido-terminated PMMA was prepared by ATRP initiated by 2-azidoethyl 2-bromoisobutyrate. Polymerization of methyl methacrylate was conducted in ethyl acetate solution at 90 °C using [Cu(I)Br] : [2-azidoethyl 2-bromoisobutyrate] : [2,2'-bipyridine] = 1:1:3 and [MMA] : [2-azidoethyl 2-bromoisobutyrate] = 50:1. 10 mL of ethyl acetate and 4.68 g (46.8 mmol) of methyl methacrylate (MMA) was added to a flame-dried 100 mL Schlenk flask. The solution was degassed by three freeze-pump-thaw cycles. 0.44 g (2.82 mmol) of 2,2'-bipyridine was added with nitrogen purging and the mixture was degassed by two freeze-pump-thaw cycles. Then 0.13 g (0.94 mmol) of CuBr was added with nitrogen purging and degassed by twice freeze-pump-thaw cycles before addition of 0.22 g (0.94 mmol) of 2-azidoethyl 2-bromoisobutyrate at room temperature. After one more freeze-pump-thaw cycle, the mixture solution was stirred at 90 °C for 15 min. The resulting polymer solution was diluted with THF and passed through a basic alumina column to eliminate catalyst and then the polymer was isolated by precipitation into the mixture of methanol and water (1/1= v/v).



Scheme S1. Synthesis of ethynyl-terminated P3HT, azido-terminated PMMA, and P3HT-*b*-PMMA block copolymer. ¹

Synthesis of P3HT-*b*-PMMA. Ethynyl- P3HT (0.36 g, 0.11 mmol, 1.2 equiv), PMMA-N₃ (0.2 g, 0.09 mmol, 1.0 equiv) and CuBr (0.12 mg, 0.9 mmol, 10 equiv) were added to a Schlenk flask. The flask was evacuated and backfilled three times with nitrogen before 40 mL of THF was added. After all reagents were dissolved in THF and PMDETA (0.15 g, 0.9 mmol, 10 equiv) was added to the flask. The mixture solution was stirred at 50 °C and the completion of the reaction was monitored by GPC. The resulting solution was passed through a basic alumina column to remove catalyst and then the resulting polymer was precipitated in methanol. The obtained polymer was filtered through an extraction thimble and then washed by Soxhlet extraction with methanol, acetone, hexane, and chloroform. Acetone and hexane washing were used to get rid of homo PMMA and P3HT, respectively. The last chloroform solution was concentrated and then poured into methanol to get the desired block copolymer. The polymer was dried in a vacuum oven.

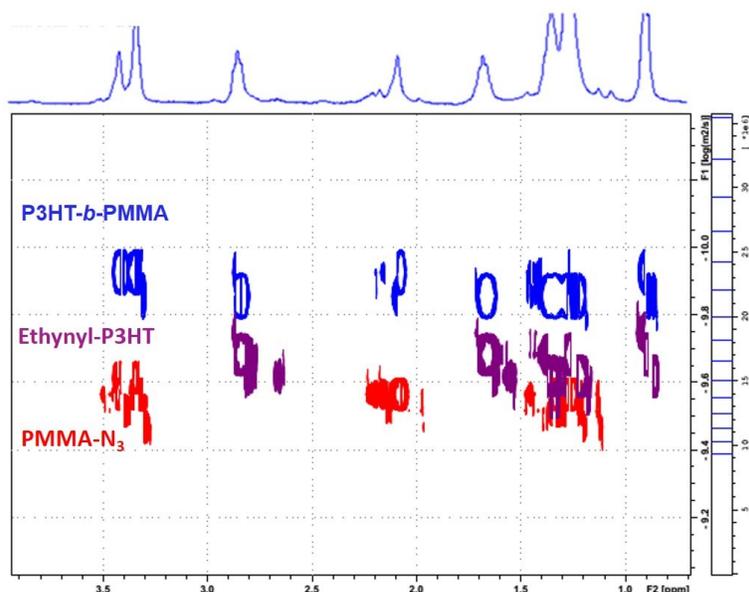
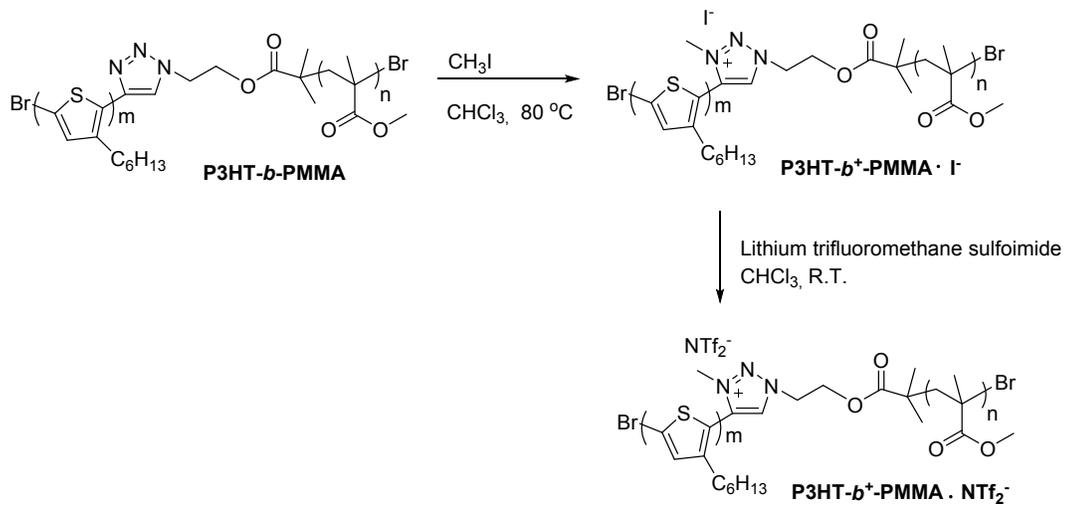


Figure S1. Superimposed DOSY ^1H spectra of P3HT-*b*-PMMA and two homopolymers in benzene- d_6 . The ^1H spectrum of block copolymer is shown at the top.

As shown in Figure S1, ^1H signals corresponding to ethynyl-P3HT, azido-PMMA, and P3HT-*b*-PMMA had different diffusion coefficients and only one diffusion coefficient was observed from P3HT-*b*-PMMA, which allowed us to conclude that one single diblock copolymer was present in the sample and free of any homopolymers.

Synthesis of P3HT-*b*⁺-PMMA/I⁻. A solution of P3HT-*b*-PMMA (160 mg, 2.8×10^{-2} mmol) and methyl iodide (16 mL, 240 mmol) in chloroform (8 mL) was stirred at for 3 days at 80 °C. The resulting polymer was precipitated in diethyl ether and dried in a vacuum oven.

Synthesis of P3HT-*b*⁺-PMMA/NTf₂⁻. A solution of P3HT-*b*⁺-PMMA/I⁻ (80 mg, 1.4×10^{-2} mmol) and LiNTf₂ (12 mg, 4.2×10^{-2} mmol) in THF (8 mL) was stirred for 3 days at room temperature. THF was removed and the solid was dissolved in chloroform. The polymer solution was washed with water and precipitated in diethyl ether. The obtained solid polymer was dried in a vacuum oven.



Scheme S2. Synthesis of 1, 2, 3-triazolium-linked P3HT-*b*⁺-PMMA diblock copolymers.

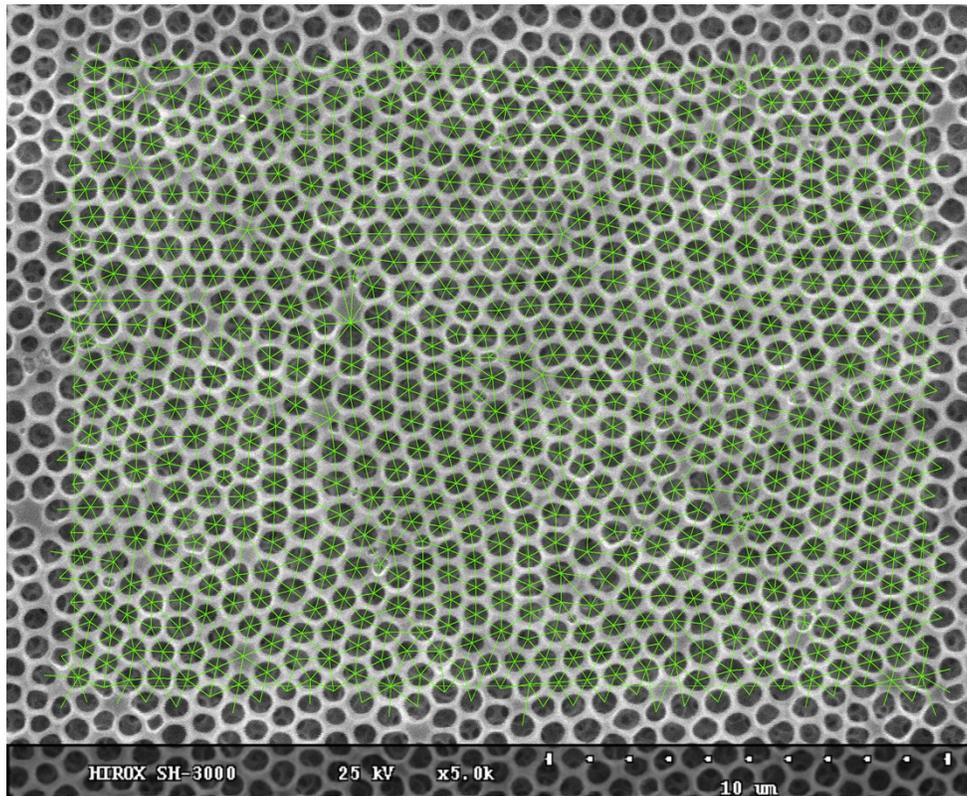
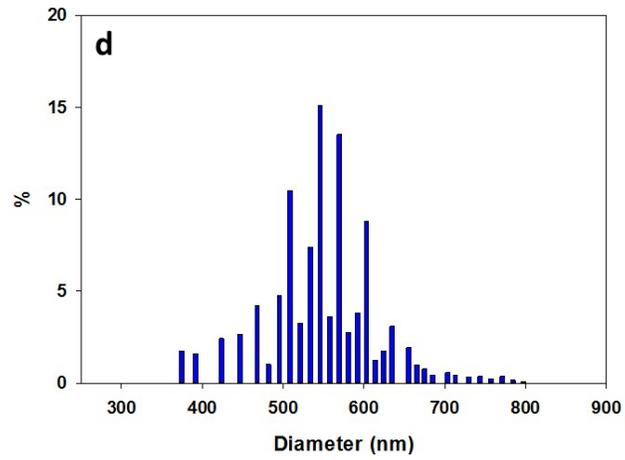
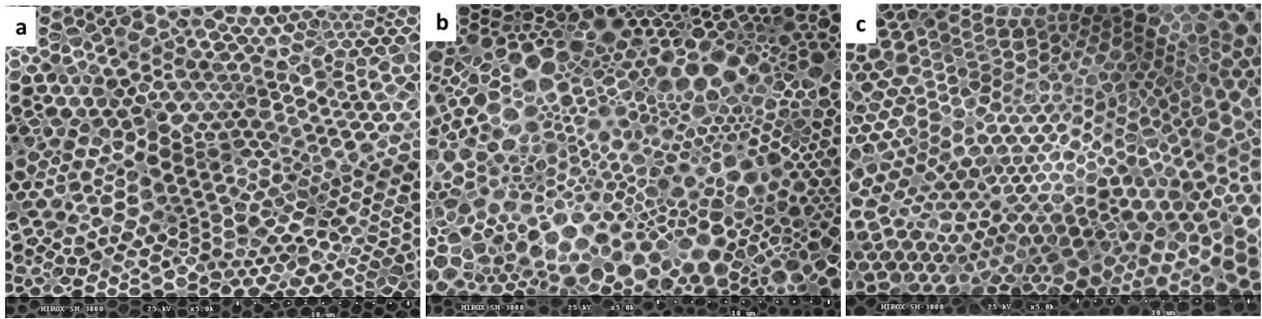


Figure S2. SEM photos & P1 honeycomb film pore size distribution (average diameter = 550 nm).

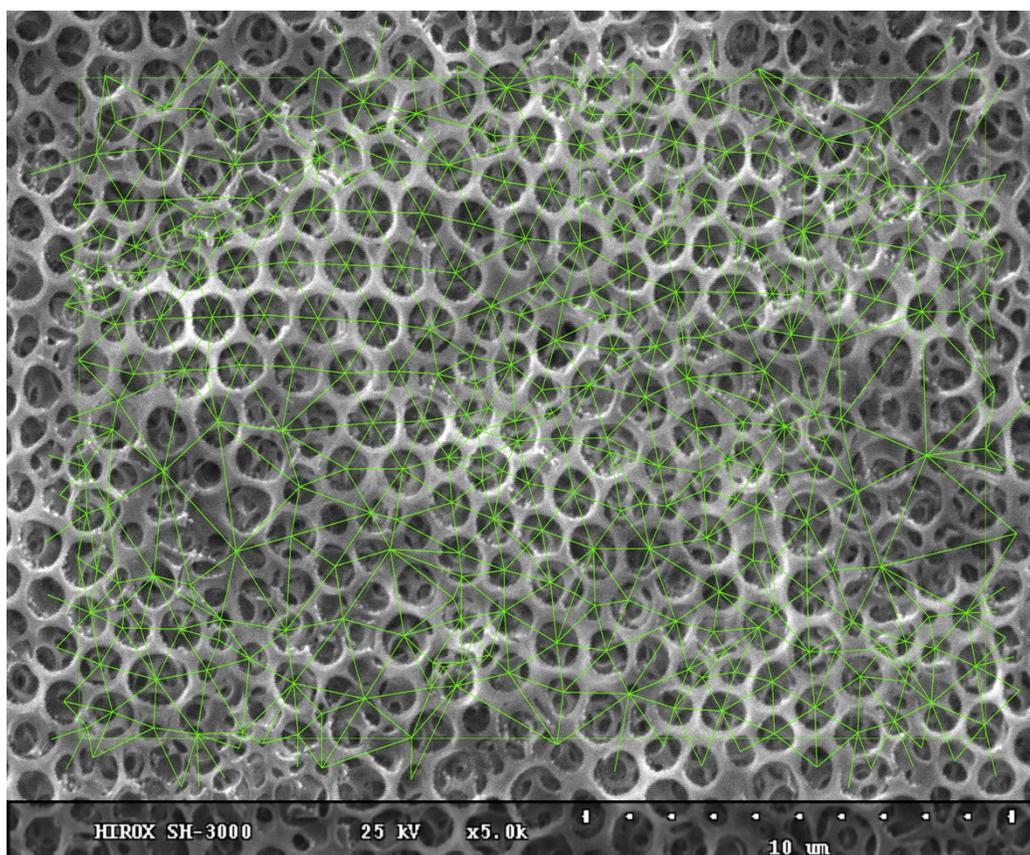
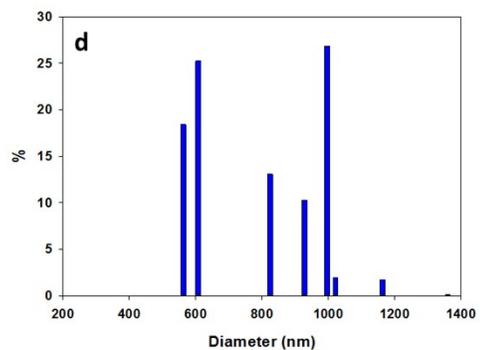
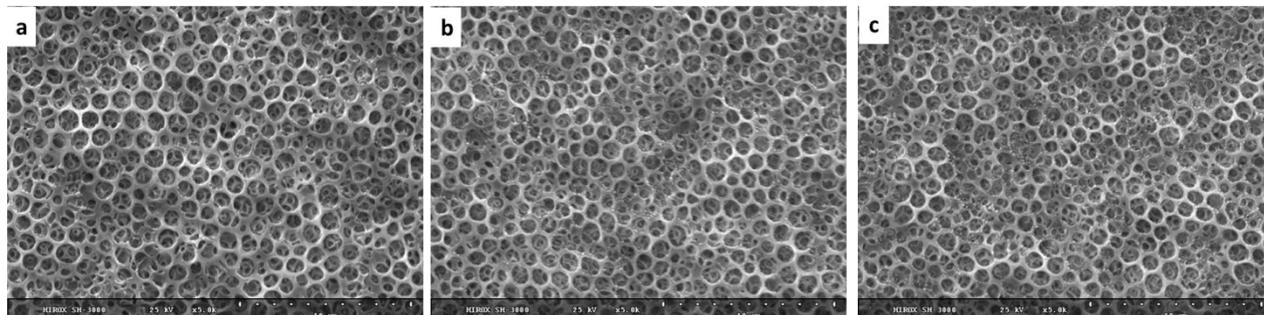


Figure S3. SEM photos & P2 honeycomb film pore size distribution (average diameter = 770 nm).

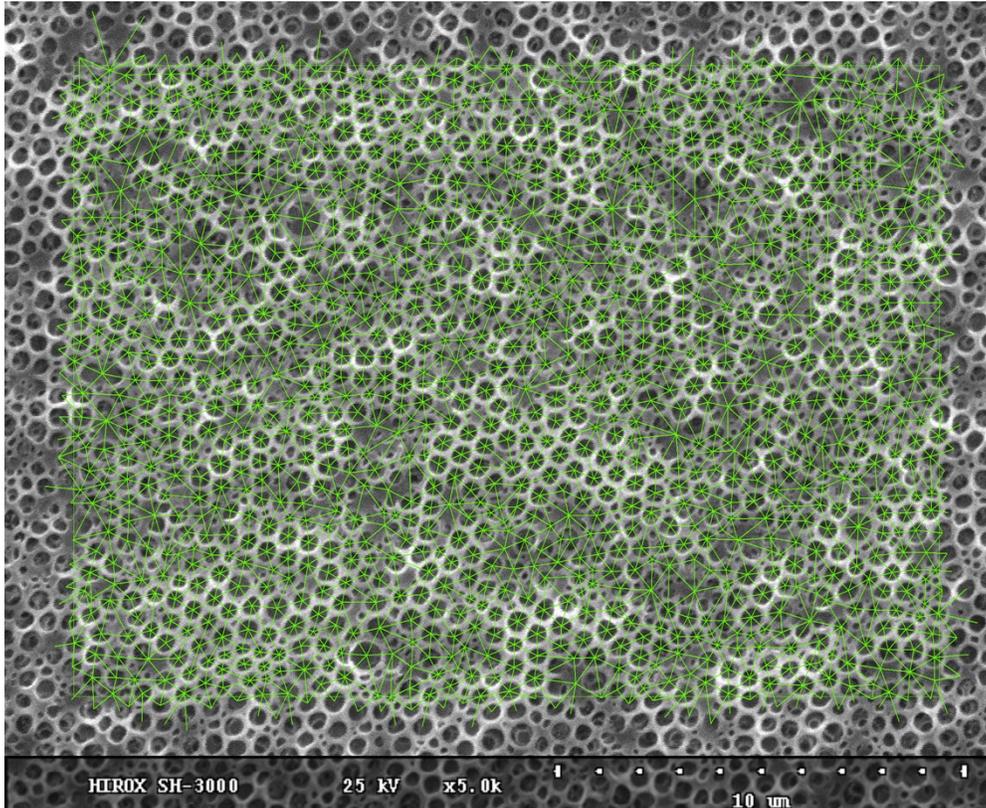
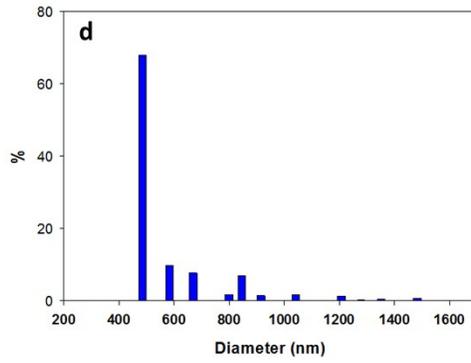
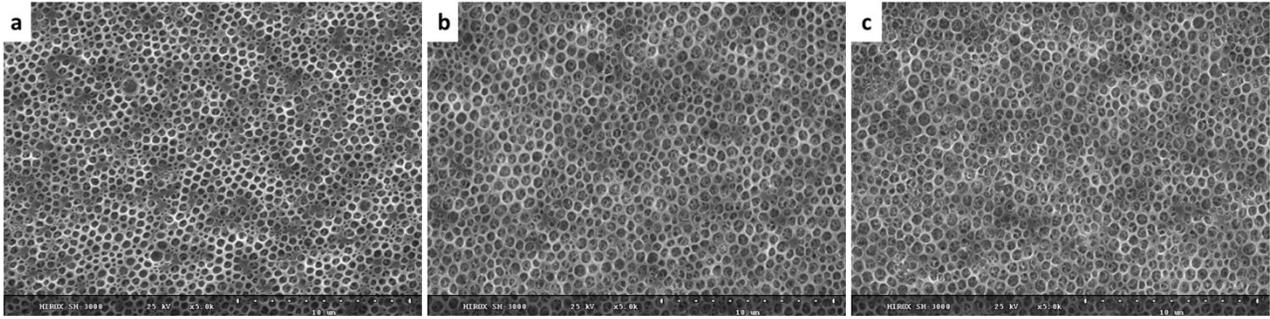


Figure S4. SEM photos & P3 honeycomb film pore size distribution (average diameter = 520 nm).

Voronoi Number

Voronoi Number						Average number			
P1 zone a1		5,996	P1 zone a2		5,997	P1I zone a3		5,998	5,997
Nb	Events		Nb	Events		Nb	Events		
	4	4		4	12		4	7	
	5	86		5	140		5	90	
	6	491		6	365		6	448	
	7	86		7	133		7	93	
	8	1		8	13		8	5	
	9	1		9	1				

P2 zone a1		5,984	P2 zone a2		5,974	P2 zone a3		5,974	5,977
Nb	Events		Nb	Events		Nb	Events		
	4	28		4	26		3	2	
	5	87		5	96		4	28	
	6	98		6	125		5	136	
	7	60		7	68		6	194	
	8	31		8	26		7	103	
	9	2		9	5		8	35	
	10	1		10	1		9	4	

P3 zone a1		6,001	P3 zone a2		6,002	P3 zone a3		5,996	6,000
Nb	Events		Nb	Events		Nb	Events		
	4	23		4	26		4	28	
	5	303		5	200		5	240	
	6	564		6	374		6	360	
	7	270		7	176		7	167	
	8	34		8	25		8	42	
	9	4		9	8		9	14	
				10	1				

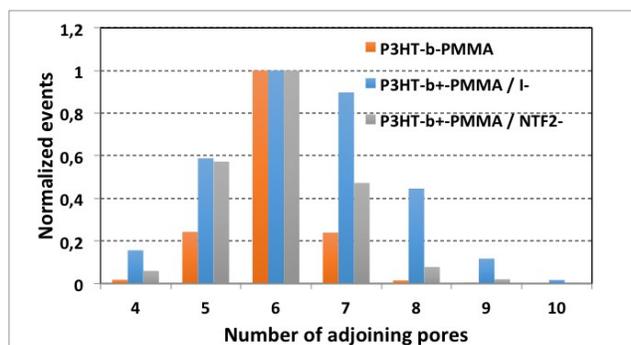
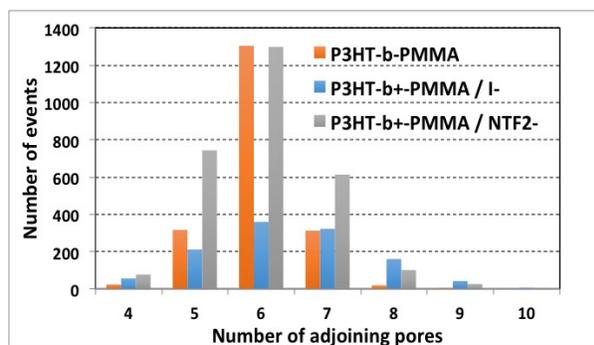


Figure S5. Distribution (left) and normalized distribution (right) of adjoining pores number to a central pore.

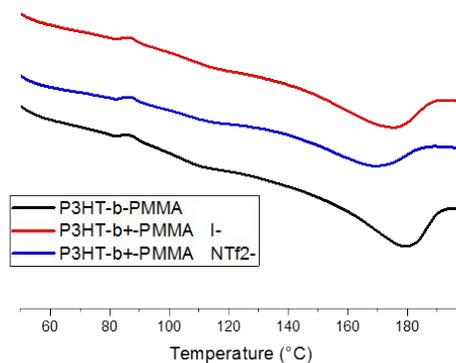


Figure S6. DSC curves (a) the second heating cycle and (b) the second cooling cycle of BCPs (endotherm down).

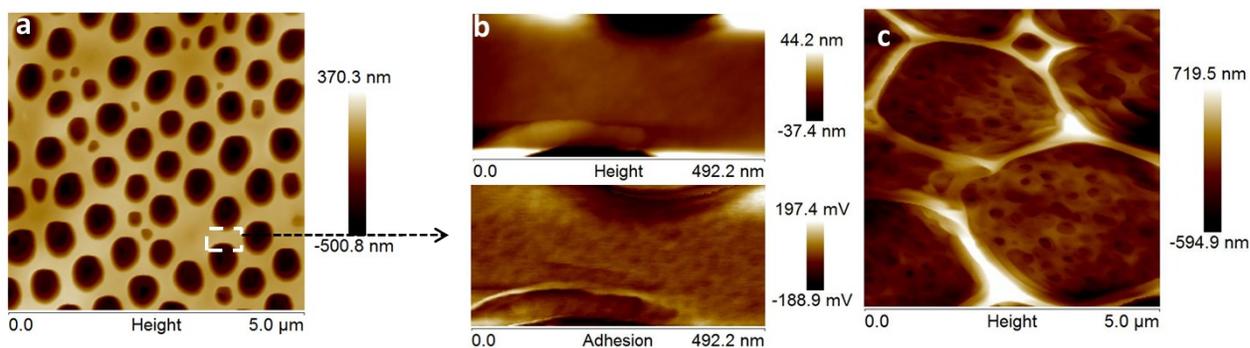


Figure S7. AFM images of the **P1** honeycomb film **before (a, b)** and **after (c)** thermal annealing at 80 °C for 1h.

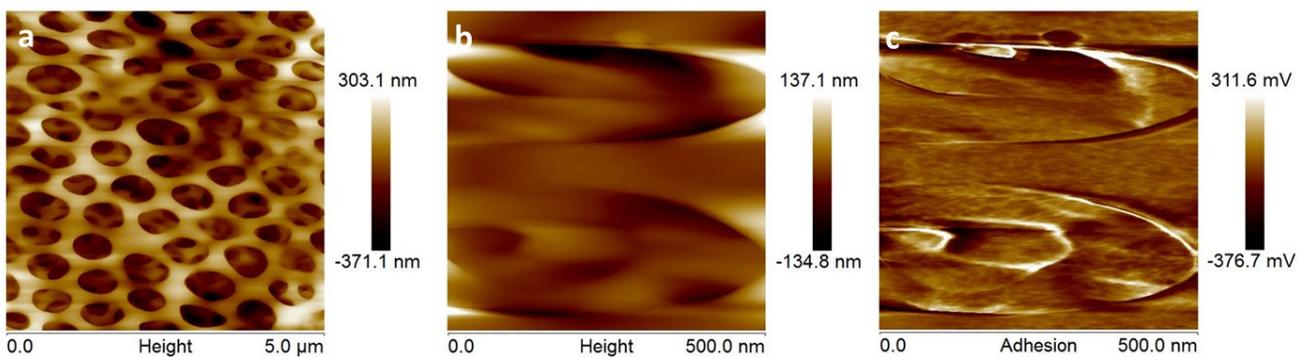


Figure S8. AFM images of the **P2** honeycomb film **after thermal annealing at 100 °C for 1h.**