

Supporting Information

Direct Formation of Organic Semiconducting Single Crystals by Solvent Vapor Annealing on Polymer Base Film

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1. Water contact angle on the polymer film spun on UV-ozone treated SiO₂ substrates used in Fig. 1 & Fig. S1: PMMA ~ 70°, PVP ~ 65°, PS ~ 90°, CYTOP ~ 105°.
2. Solubility in chloroform: C8-BTBT ~ 80 mg/ml, C10-BTBT ~ 24 mg/ml, C8-BTBT ~ 8.6 mg/ml, TIPS-PEN > 100 mg/ml.
3. The solubility of polymers were examined roughly in this way: 1) spin polymers to form films (30-50 nm thick); 2) immerse the substrates in the selected solvents; 3) if the film disappears after shaking the substrates for 5 sec, it is marked with “√” in the Table 1 in the manuscript; if the film still appears after shaking the substrates for 30 sec, it is marked with “X”. The tested solubilities in organic solvents are (unit: mg/ml):

	PVP	PMMA	PS
THF	120~130	> 10*	70~85
Chloroform	< 0.1	50~60	90~110
Cyclohexane	< 0.1	< 0.1	6~8

*heated at 40°C and cooled down to room temperature.

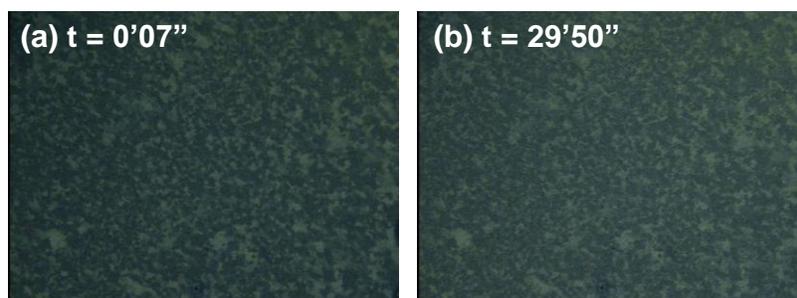


Fig. S1. Optical images of as-spun C8-BTBT film on a bare Si/SiO₂ substrate: a) when SVA starts; b) SVA for 30 min, not showing obvious dissolution. Snapshots from a video captured under the cross-polarized microscope (dimension: 688 x 516 μm). The same for Fig. S2 and Fig. S5.

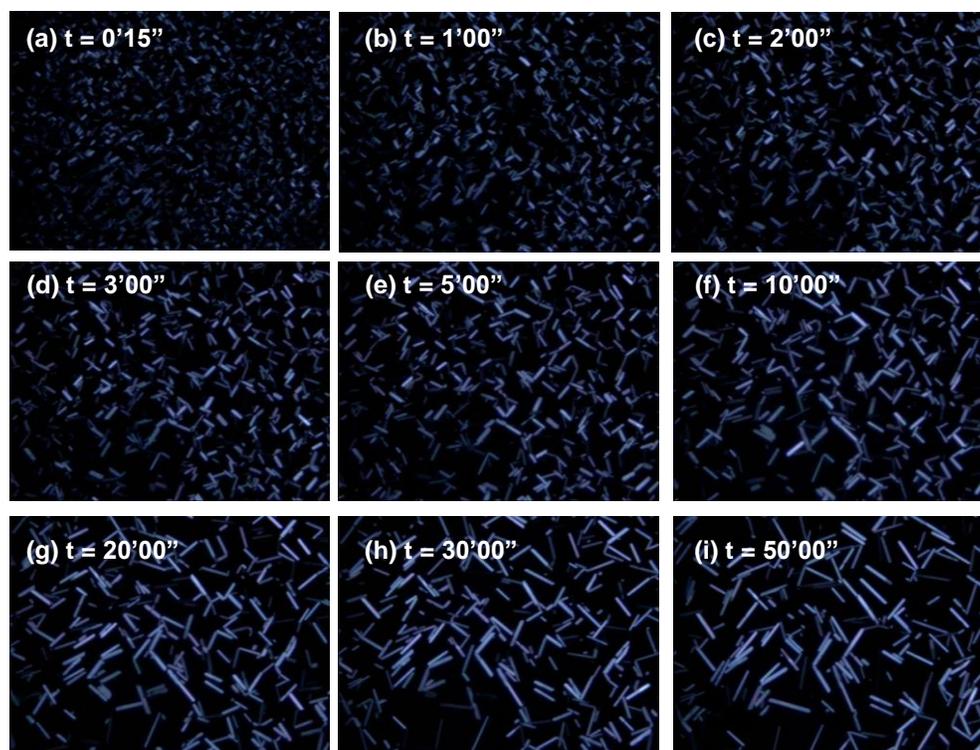


Fig. S2. Optical images of crystal growth of C8-BTBT on PMMA substrate in PASVA, indicating Ostwald ripening.

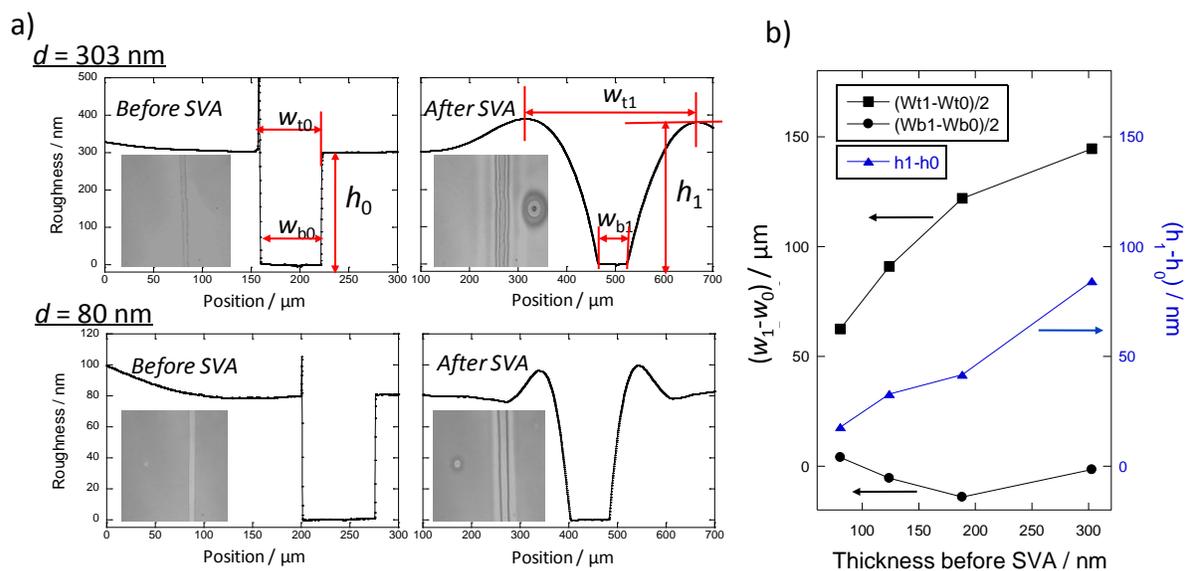


Fig. S3. a) Surface profilometry perpendicular to a scratch before and after chloroform chloroform SVA for 12 hours: thick film ($d = 303$ nm) and thin film ($d = 80$ nm). The insets are the images of the scan area taken by the microscope of the scanner (see the textures around the

defects before and after SVA). w_t , w_b , and h stand for the width of the top channel and bottom channel, and height of the channel edge, respectively. The subscript 0 and 1 stands for the values before and after SVA. b) Change of w_t , w_b , and h after chloroform SVA for 12 hours.

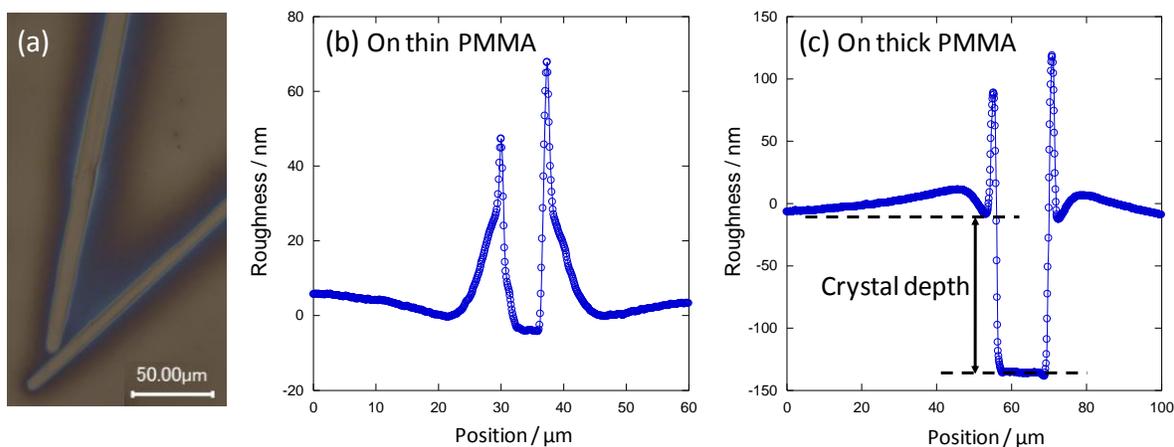


Fig. S4. (a) Optical image of a sample with single crystals rinsed by cyclohexane. Surface profile scanning across the crystal-removed regions of the samples with: (b) thin PMMA film (33 nm), and (c) thick PMMA film (155 nm), showing that PMMA climbs up the crystal sides. From (b) and (c), we found crystals are deep in thick PMMA.

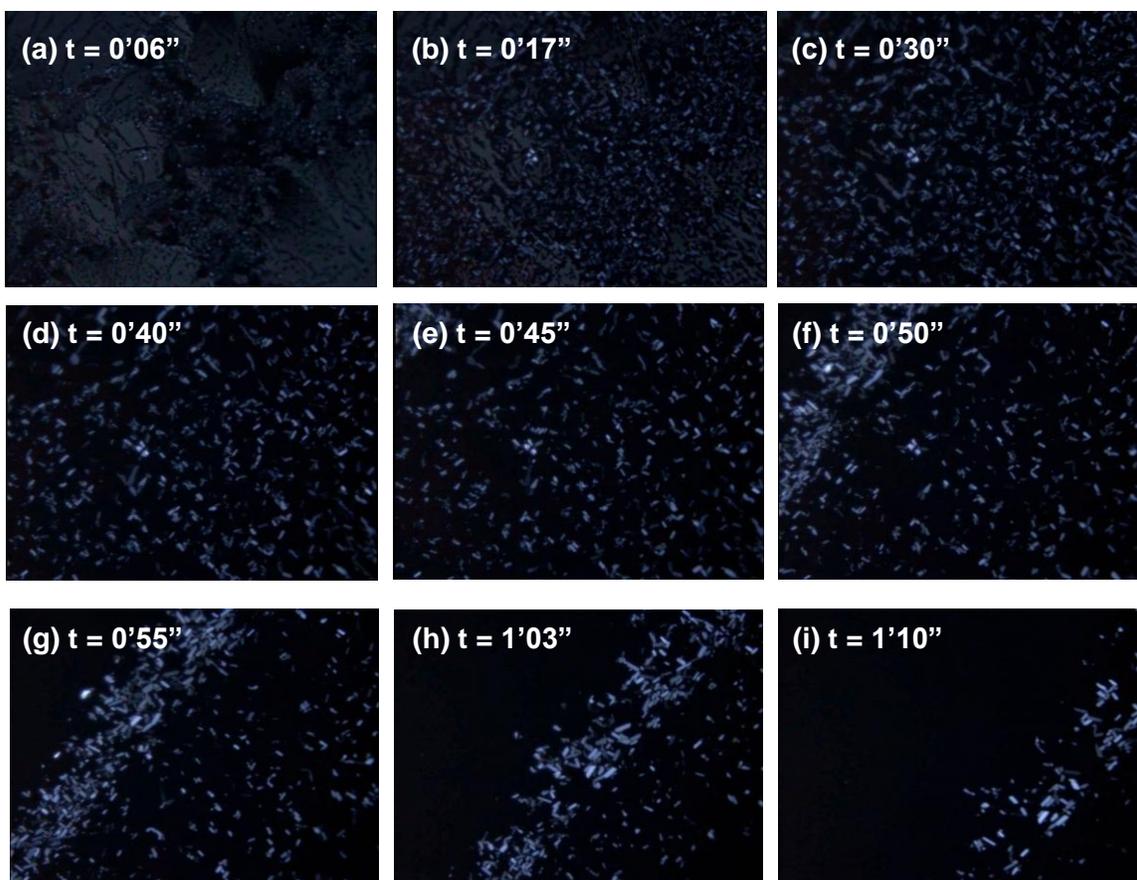


Fig. S5. A strong capillary wave generated by SVA float all the crystals to the sample edge (captured from a video).

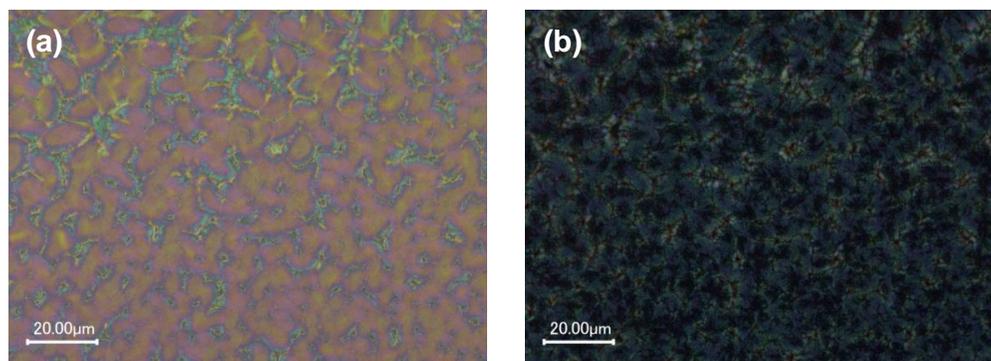


Fig. S6. Optical image of TIPS-PEN (spin-coated on Si/SiO₂) after SVA for 15 hours: (a) without a polarizer; (b) with a polarizer.