Supporting Information

Confined Crystallization within Cylindrical P3EHT Block Copolymer Microdomains

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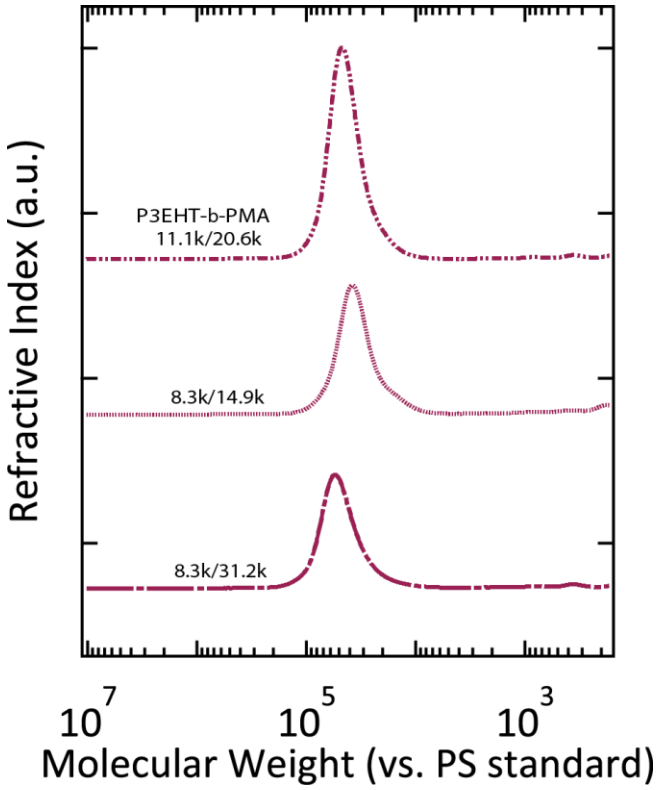
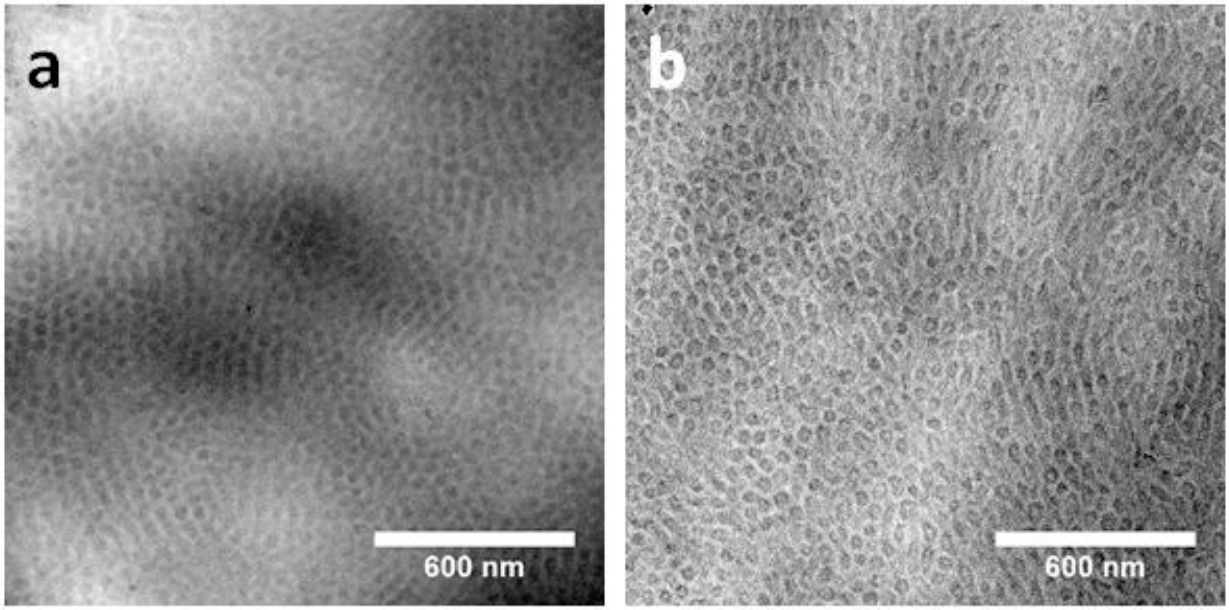
Gel Permeation Chromatography



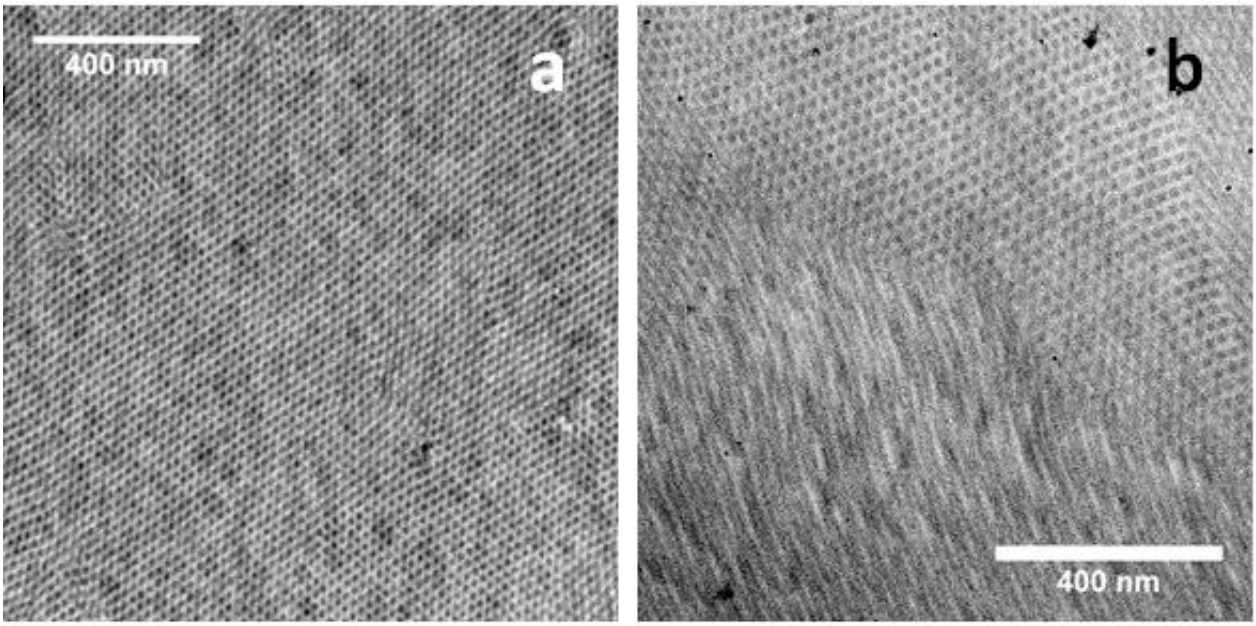
SI Figure 1. GPC of studied P3EHT-*b*-PMA cylinder-forming diblocks. Molecular weight calibrated via polystyrene standards.

Impact of Staining on TEM of P3EHT-*b*-PMA Cylinders



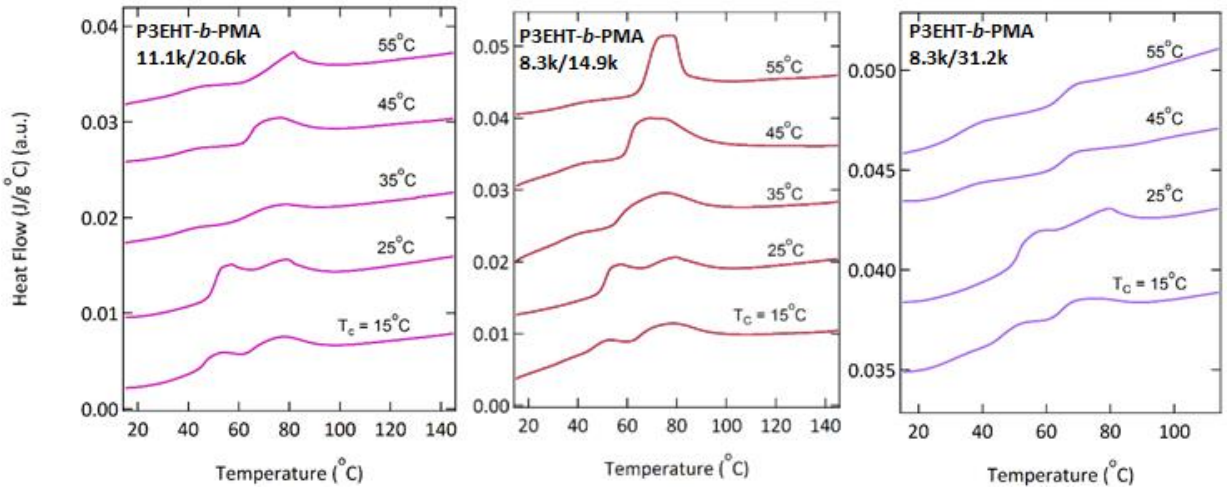
SI Figure 2. While unstained P3EHT-*b*-PMA (here, P3EHT-*b*-PMA 11.1/20.6k) provides sufficient contrast for TEM bright-field imaging of microdomains (left), staining with RuO_4 enhances contrast, particularly between amorphous and crystalline components within cylindrical microdomains (right).

Behavior of P3EHT-b-PS Cylinders

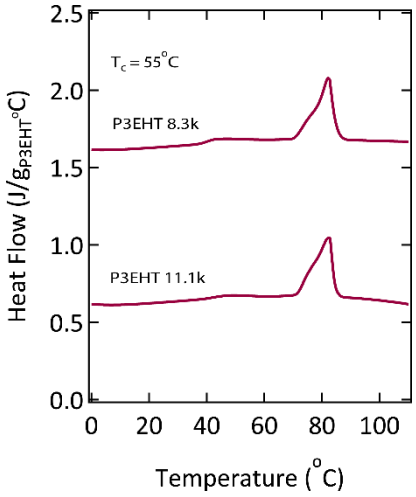


SI Figure 3. TEM of RuO_4 stained cylinder-forming P3EHT-*b*-PS cylinder forming diblocks (a) 8.3k/14.1k (b) 8.3k/12.5k

Supplementary Differential Scanning Calorimetry



SI Figure 4. Crystallization temperature-dependent crystallization from T_c = 15°C to T_c = 55°C for cylindrically confined P3EHT. Note that samples were exposed to room temperature on a DSC autosampler for ~1 day prior to running after being removed from temperature controlled ovens leading to the weak crystallinity in P3EHT-*b*-PMA 8.3k/31.2k 45°C and 55°C traces.



SI Figure 5. Constituent homopolymers isothermally crystallized at 55°C to achieve high crystalline perfection. The melting points are similar to the melting point achieved in cylindrical confinement via crystallizing at 25°C followed by annealing at 65°C.

Calculation of Inter-Chain Distances in Confined P3EHT-*b*-PMA Cylinders

Calculations to find the inter-chain distances along the interfaces of confined P3EHT-*b*-PMA cylinders are similar to calculations described in the supporting information of our previous work.[1] Calculations are based upon the P3EHT unit cell[2] containing two dimers with a = 15.16 Å, b = 10.83 Å, c = 7.72 Å and angles $\alpha = 109.86°$, $\beta = 103.03°$, $\gamma = 69.84°$. The real-space 001 vector follows along the chain direction (and the value of 7.72 Å corresponds to the contour length of two P3EHT monomers), but in the triclinic unit cell the 100 and 010 vectors do not correspond directly to molecular spacings. Thus, the values of 'a' and 'b' do not directly represent either the exact alkyl chain stacking distance or π-stacking distance respectively. To find the average chain-chain spacing down the long-axis and along the circumference of the cylinder, we take the projections of the unit cell dimension in the directions perpendicular to the chain direction both along the long axis and along the circumference, yielding the periodicity of the unit cell in the appropriate direction. This calculation yields a value of 14.77 Å per unit cell repeat along the long axis and 9.74 Å along the circumference, respectively. Minimal curvature occurs along the microdomain circumference over the unit cell repeat distance of 9.74 Å (cylinder diameters are between 118 Å and 198 Å following crystallization). Since the unit cell is composed of two dimers, it is important to realize that the circumference value of 9.74 Å corresponds to two chains. This consideration yields the values shown in Figure 5 of the manuscript. Finally, since we assume an interdigitated structure, on average every other crystalline chain spans the interface, giving an average distance between block copolymer junction chains of 0.97 nm around the circumference of the cylinders and an average of 2.96 nm along the long axis of the cylinders. The interfacial area may be found directly from these values as 1.43 nm^2 per chain that spans the interface, or indirectly by calculating the area of the unit cell intersecting the plane perpendicular to the chain. In calculating the interfacial area it is important, again, to realize that the unit cell corresponds to two chains; since the diblock structure is interdigitated, on average only one of these will span the interface.

References:

1. Davidson, E. C.; Beckingham, B. S.; Ho, V.; Segalman, R. A., Confined Crystallization in Lamellae Forming Poly(3-(2 '-ethyl)hexylthiophene) (P3EHT) Block Copolymers. *J Polym Sci Pol Phys* **2016,** *54* (2), 205-215.
2. Himmelberger, S.; Duong, D. T.; Northrup, J. E.; Rivnay, J.; Koch, F. P. V.; Beckingham, B. S.; Stingelin, N.; Segalman, R. A.; Mannsfeld, S. C. B.; Salleo, A., Role of Side-Chain Branching on Thin-Film Structure and Electronic Properties of Polythiophenes. *Adv Funct Mater* **2015,** *25* (17), 2616-2624.