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Morphology of Conjugated Block Copolymer Films: Self-Assembly, Crystallization, and Phase Separation¹

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All-Conjugated Block Copolymers comprised of donor and acceptor polymer blocks are currently under development for use in organic photovoltaic devices. An attractive feature of these materials is their potential to self-assemble into well-defined donor and acceptor domains. However, achieving self-assembled film structures requires additional processing and annealing due to the high crystallization temperature of conjugated polymers and low Flory-Huggins χ interaction parameter between polymer blocks. This talk will present experimental studies into the processing-dependent morphology of all-conjugated block copolymer films relevant for organic photovoltaic devices. Conjugated block copolymer films that contain poly(3-hexyl thiophene) (P3HT) as the donor block exhibit crystallization as the predominant feature. Even at relatively low mass contents, the P3HT block crystallizes in solvent cast films. The orientation of P3HT crystallites is face-on for as-cast or low-temperature annealed films, but under annealing at elevated temperature, the crystallite orientation flips to an edge-on orientation. This behavior is observed for a wide-range of acceptor polymer blocks. Analysis of films by grazing-incidence X-ray scattering shows that conjugated block copolymers exhibit poor mesoscale ordering in solvent cast or thermally annealed films. Under solvent annealing, periodic lamellae with characteristic domain size of 4 nm are observed. The domain size is independent of block copolymer molecular weight and composition, and we hypothesize is driven by a combination of crystallization and micro-phase segregation. Finally, we investigate the morphology of PTB7 block copolymers as compatibilizers for PTB7-fullerene blends. Addition of PTB7 block copolymers can increase or decrease domain sizes, and morphology is stable to long-term thermal annealing.

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