In Situ GIWAXS Analysis During Spin-Coating of Solvent and Additive Effects on Organic Electronic Thin Film Microstructure Evolution

The influence of solvent and processing additive for spin-coating organic electronic polymer thin films is investigated by *in situ* grazing incident wide angle x-ray scattering (GIWAXS) techniques to assess how device optimization choices impact pathways and kinetics of crystallization, as well as the resulting morphology of organic electronic thin films. Films of **PTB7**, **P3HT** and **p-DTS(FBTTh$_2$)$_2$** are spun from solutions in chloroform (CF), chlorobenzene (CB), and 1,2-dichlorobenzene (DCB) and solutions with 1% and 3% v/v of the processing additives 1-chloronapthalene (CN), diphenyl ether (DPE), and 1,8-diiodooctane (DIO). Through this *in situ* characterization multiple crystallization pathways are identified, with i) the single-solvent systems exhibiting rapid (i.e., <3s) crystallization after a solvent boiling point dependent film thinning transition, and ii) the solvent + additive mixture systems exhibiting different crystallization pathways with distinct intermediate morphological forms correlated with additive molecular structures and demonstrating crystallization formation times ranging from minutes (CN, DPE) up to hours (**PTB7**:DIO). It is also clear that the polymer/small molecule solution properties play a key role in how the additive interacts, demonstrated by solution self-aggregating **PTB7**, solution free-chain **P3HT** and small molecule **p-DTS(FBTTh$_2$)$_2$** having divergent interactions with select additives. These results shed light on how spin casting parameters impact morphological formation and provide an important knowledge base that can be used by device engineers to better direct performance optimization studies.

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