Thin film solar cell that can be processed from solution, covering polymer-based bulk heterojunction (BHJ) organic photovoltaics (OPVs), small molecule-based BHJ OPVs and hybrid perovskite type OPVs, hold tremendous promise as a potential renewable and economically viable energy sources. In OPV devices, the quality of the active layer, consisting of polymer/molecule:PCBM blends, which establishes the absorption characteristics of the device, plays a critical role. The morphology of the active layer, including the molecular orientation, ordering, interfacial behavior and phase separation characteristics, is essential. The processing conditions used to generate these active layer, i.e. nature of the solvents and/or additives, rate of solvent evaporation, and rates of ordering and phase separation, give rise to a delicate balance of multiple kinetic processes that ultimately define the structure and morphology of the active layer and device performance. Achieving the highest power conversion efficiencies (PCEs) requires a fundamental understanding of and control over these processes so as to control the material crystallization and optimize the morphology. This is exemplified by several recent studies in our laboratories on mixtures of polymer PTB7-Th with PC71BM where, with the use of di-iodooctane (DIO) as a processing agent and by varying the concentration of the PC71BM, PCEs in excess of 10.61% have been achieved by optimization of the processing conditions; and on mixture of small molecule DRCN7T, with PC71BM where, slightly changing chemical structure and thermal treatment can optimize the PCEs to 9%. Processing OPV devices in industrial setting using slot die coating has also been investigated, with the best performance up to 9.2% achieved and detailed mechanism of phase separation elucidated.