Analysis of diverse direct arylation polymerization (DArP) conditions toward the efficient synthesis of polymers converging with stille polymers in organic solar cells

Despite the emergence of direct arylation polymerization (DArP) as an alternative method to traditional cross-coupling routes like Stille polymerization, the exploration of DArP polymers in practical applications like polymer solar cells (PSCs) is limited. DArP polymers tend to have a reputation for being marginally inferior to Stille counterparts due to the increased presence of defects that result from unwanted side reactions in direct arylation, such as unselective C-H bond activation and homocoupling. We report ten DArP protocols across the three major classes of DArP to generate poly[(2,5-bis(2-hexyldecyloxy)phenylene)-alt-(4,7-di(thiophen-2-yl)benzo[c][1,2,5]thiadiazole)] (PPDTBT). Through evaluation of the method and resulting photophysical and electronic properties, we show not all DArP methods are suitable for generating device-quality alternating copolymers. When DArP PPDTBT was synthesized in superheated THF with Cs$_2$CO$_3$, neodecanoic acid, and P(o-anisyl)$_3$, it generated polymers of exceptional quality that performed comparably to Stille counterparts in both roll coated ITO-free and spin-coated ITO devices.