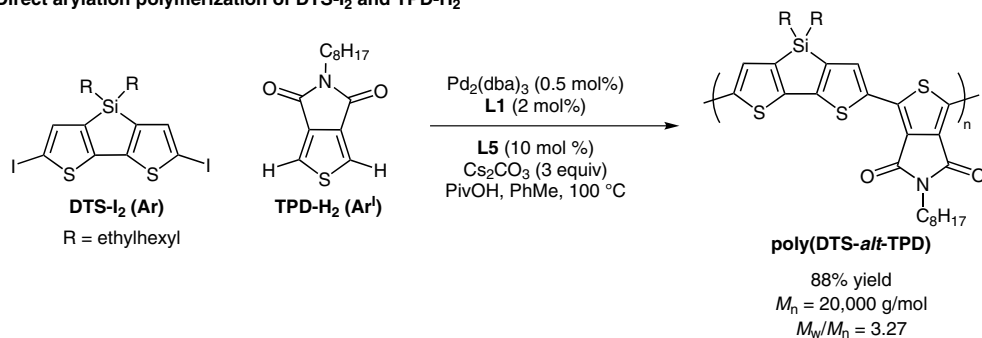
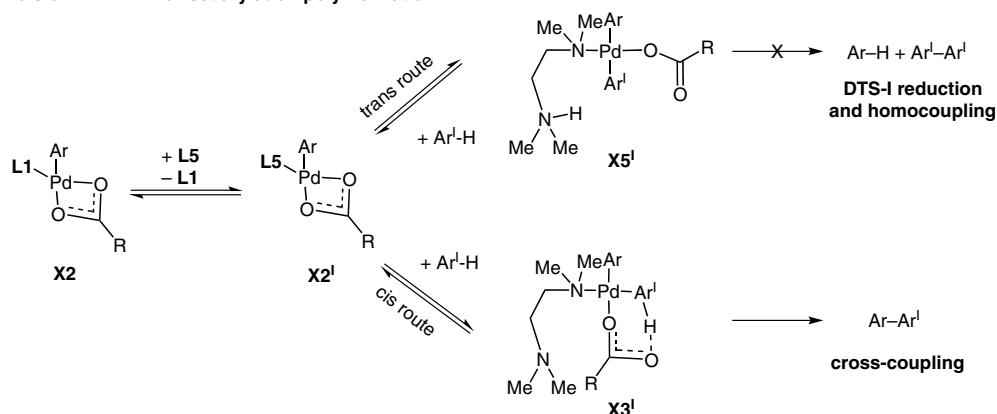


Doubling Down on Diamines for Direct Arylation Polymerization

Direct arylation polymerization of DTS-I₂ and TPD-H₂



Role of TMEDA in direct arylation polymerization



Significance: Side reactions such as homo-coupling and C–H activation at undesirable positions lead to branching, cross-linking, and the formation of insoluble materials during direct arylation polymerization (DArP). The authors developed a novel, mixed ligand catalyst system for palladium-catalyzed DArP. With the addition of tetramethylethylenediamine (TMEDA) as a co-ligand, these side reactions have been prevented and higher polymer molecular weights can be achieved.

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Comment: The presence of TMEDA as basic co-ligand interferes with a catalytic cycle that leads to aryl halide (DTS-I₂) reduction and homo-coupling of an unfunctionalized arene (DTS), the so-called trans route. This promotes the desired cross-coupling reaction to form poly(DTS-*alt*-TPD) through the cis route.