Mixed-Ligand Approach to Palladium-Catalyzed Direct Arylation Polymerization: Effective Prevention of Structural **Defects Using Diamines**

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Doubling Down on Diamines for Direct Arylation Polymerization

Direct arylation polymerization of DTS-I₂ and TPD-H₂

88% yield $M_{\rm n} = 20,000 \text{ g/mol}$ $M_{\rm W}/M_{\rm D} = 3.27$

$$\mathbf{L1} = \begin{array}{c} \mathsf{MeO} \\ \mathsf{L1} = \end{array} \begin{array}{c} \mathsf{NMe2} \\ \mathsf{NMe2} \end{array}$$

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 coligand 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.

Synthesis of **Materials** and **Unnatural Products**

Key words

direct arylation palladium catalysis cross-coupling co-ligands

