Doubling Down on Diamines for 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 tetramethyl-ethylene diamine (TMEDA) as a co-ligand, these side reactions have been prevented and higher polymer molecular weights can be achieved.

**Comment:** The presence of TMEDA as basic co-ligand interferes with a catalytic cycle that leads to aryl halide (DTS-I$_2$) 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.

**Equations and Diagrams:**

- **Direct arylation polymerization of DTS-I$_2$ and TPD-H$_2$:**
  - **DTS-I$_2$ (Ar)**
  - **TPD-H$_2$ (ArI)**
  - **Pd$_2$(dba)$_3$ (0.5 mol%)**
  - **L1 (2 mol%)**
  - **L5 (10 mol %)**
  - **Cs$_2$CO$_3$ (3 equiv)**
  - **PivOH, PhMe, 100 °C**
  - **poly(DTS-alt-TPD)**
  - **88% yield**
  - **M$_n$ = 20,000 g/mol**
  - **M$_w$/M$_n$ = 3.27**

- **Role of TMEDA in direct arylation polymerization**

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