Nickel- or Palladium-Catalyzed Cross-Coupling Polycondensation

**Significance:** The authors describe a cross-coupling polycondensation of Grignard reagents and various aromatic ethers or ammonium salts to form π-conjugated polymers with high molecular weight through C–O or C–N bond cleavage. The reaction proceeds under mild conditions in the presence of commercially available Ni or Pd catalysts.

**Comment:** Interestingly, the optimized reaction conditions showed that the quality and purity of the organometallic compound critically influenced the yield and reactivity of this polycondensation. In the presence of mono-Grignard reagents, the chain-growth was terminated and the molecular weight was reduced.

**Method A:**

\[
\text{BrMg} + _{R1} \overset{\text{Catalyst A or B}}{\text{MeO}} + \text{ArOMe} \\
\text{0.3 M in PhMe, 12 h}
\]

**Catalyst A:** NiCl2(PCy3)2 (5.0 mol%) 
PCy3 (10.0 mol%)

**Catalyst B:** Ni(cod)2 (5.0 mol%) 
ICY (10.0 mol%)

**Selected examples:**

**Method A:**

- Catalyst A, r.t., 96% yield 
  \( M_n = 23.2 \text{ kDa}, \ PDI = 3.02 \)

- Catalyst B, 70 °C, 86% yield 
  \( M_n = 13.6 \text{ kDa}, \ PDI = 2.56 \)

- Catalyst A, r.t., 92% yield 
  \( M_n = 17.9 \text{ kDa}, \ PDI = 2.58 \)

**Method B:**

\[
\text{BrMg} + _{R1} \overset{\text{Catalyst A, r.t., 96% yield}}{\text{MeO}} + \text{ArOMe} \\
\text{0.3 M in PhMe, 12 h}
\]

- Catalyst A, r.t., 96% yield 
  \( M_n = 19.7 \text{ kDa}, \ PDI = 2.58 \)

- Catalyst B, 70 °C, 82% yield 
  \( M_n = 12.7 \text{ kDa}, \ PDI = 2.11 \)

- Catalyst A, r.t., 96% yield 
  \( M_n = 23.2 \text{ kDa}, \ PDI = 3.02 \)

**Selected examples:**

**Method B:**

- Catalyst A, r.t., 96% yield 
  \( M_n = 17.9 \text{ kDa}, \ PDI = 2.58 \)

**Category:** Metal-Mediated Synthesis

**Key words:** magnesium, nickel catalysis, cross-coupling