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.

**Selected examples:**

**Method A:**
- Catalyst A or B, 0.3 M in PhMe, 12 h
- 11 examples up to 96% yield
- Catalyst A: NiCl₂(PCy₃)₂ (5.0 mol%), PCy₃ (10.0 mol%)
- Catalyst B: Ni(cod)₂ (5.0 mol%), ICy (10.0 mol%)

**Method B:**
- Catalyst A: MgBr, BrMg, 0.3 M in PhMe, r.t., 12 h
- 3 examples up to 95% yield
- Catalyst: Pd(PPh₃)₂Cl₂ (1.0 mol%)

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