

Electrophile-dependent Kinetic Aryl Ether Formation: Selective Synthesis of Poly(*m*-phenylene oxides) over Oxacalixarenes



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Poly(*m*POs) are potentially useful thermostable materials with properties similar to PEEK plastics, but have previously proven difficult to synthesize by S_NAr or other means due to competing cyclooligomer (oxacalixarene) formation. The Katz laboratories have recently discovered that poly(*m*POs) are indeed accessible in high yield by S_NAr reactions through AA-BB type step-growth polymerization (Eq 1). Mechanistic investigations have revealed that the linear (polymeric) vs. cyclic (oligomeric) product distributions are strongly dependent on the substitution pattern of the electrophilic monomer, biasing the growing chains with either extended (anti-biased) or coiled (syn-biased) conformations. The synthesized poly(*m*POs) have high thermal and aqueous stability but are readily depolymerized in polar aprotic media. Thus, the materials have potential engineering and biomedical uses, as well as the benefit of facile post-use recycling or processing.

