Discovery of a Reversible, Cationic Macrocyclization Mechanism and Control of Cyclic Copolymer Microstructure by Homopolymer Scrambling

Joshua A. Kaitz and Jeffrey S. Moore

End-capped poly(phthalaldehyde) (PPA) synthesized by anionic polymerization has garnered significant interest due to its ease of synthesis and rapid depolymerization. Yet, alternative ionic polymerizations to produce PPA have been largely unexplored. In this report, we demonstrate that a cationic polymerization of *o*-phthalaldehyde initiated by boron trifluoride results in cyclic PPA in high yield, high molecular weight, and with extremely high cyclic purity. The cyclic structure is confirmed by NMR spectroscopy, MALDI-TOF mass spectrometry, and triple detection GPC. The cyclic polymers are reversibly opened and closed under the polymerization conditions. Owing to PPA's low ceiling temperature, cyclic PPA is capable of chain-extension to larger molecular weights, controlled depolymerization to smaller molecular weights, or dynamic intermixing with other polymer chains, both cyclics and end-capped linears. These unusual properties endow the system with great flexibility in the synthesis and isolation of pure cyclic polymers of high molecular weight. We further discuss the synthesis of cyclic PPA derivatives and demonstrate the scrambling of distinct homopolymer mixtures to copolymers under the cationic polymerization conditions. Homopolymer mixtures are found to rapidly redistribute, first to multi-block cyclic copolymers, and then to random macrocyclic copolymers with extended reaction time. The reported scrambling method leads to the rapid preparation of macrocyclic copolymers of high molecular weight with variable microstructure depending on reaction times and catalyst loadings.