

Despite its long history and industrial relevance as a soft block of polyurethane elastic fibers (eg. Spandex) and thermosets, to date there are no instances of a synthesis of poly(tetrahydrofuran), p(THF), with well-defined molecular weight (MW) control extending beyond the oligomeric to low MW (<20 kDa) regimes. Herein we disclose a MW-controlled synthesis of p(THF) using a cationic hydrogen bond donor catalyst paired with an α -phosphonooxymethyl ether initiator. Precise control of M_n up to 175 kDa is demonstrated. Mechanistic studies suggest the catalyst mediates a living, reversible-deactivation cationic polymerization of THF, catalyzing the reversible anchimeric ionization of the primary alkyl phosphate chain-end to form a reactive oxonium intermediate. The catalyst possesses specificity towards phosphates over traditionally reactive leaving groups and has higher activity compared to other hydrogen bond donors, which was attributed to an intramolecular hydrogen bonding motif which is conserved on binding to the chain-end. The greater stability of the phosphate chain-end allows for isolation with complete chain-end fidelity. This is, to our knowledge, the first instance of an organocatalyzed controlled cationic ring-opening polymerization, and of a MW controlled polymerization of THF over a broad molecular weight range. We expect this system to translate to other classes of heterocyclic monomers amenable to cationic ring opening polymerization.