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Poly(alkyl malonates) are degradable plastic candidates and promising electrolyte materials in lithium-ion batteries. However, poly(alkyl malonates) are usually made via polycondensation, as it is synthetically challenging to directly incorporate malonate moieties into the polymer backbone. We have developed the alternating and controlled anionic copolymerization of epoxides and Meldrum's acid (MA) derivatives to access poly(alkyl malonates) using (*N,N*'-bis(salicylidene)phenylenediamine)AlCl and a triaminocyclopropenium chloride cocatalyst. Ring-opening of the MA derivative proceeds exclusively with loss of a small molecule, which allows direct incorporation of the malonate moiety while prohibiting ether linkage formation. Guided by kinetic, mechanistic, and computational studies, we demonstrate controlled polymerization behavior, propose a mechanism of polymerization, and uncover a decarboxylation side reaction. Ultimately, polymerization behavior is further enhanced by tuning the nature of the small molecule released. Controlled copolymerization of MA derivatives with a range of epoxides allows access to a series of new copolymers with diverse and tunable thermal properties.