Novel strategies for constructing polyolefin-containing block copolymers

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Polyolefin, as by far the most commonly produced polymer worldwide, accounts for a huge fraction of the global plastics market. However, despite the promising future of block copolymer development, there is significant dissonance between the dominance of polyethylene and its under-representation as a component in block copolymers. Here, we established a complete set of methods for constructing polyolefin-containing di- and triblock copolymers. The first part is a universal one-pot synthesis strategy for accessing polyolefin-containing diblock copolymers. My approach consists of performing a series of post-polymerization strategies to first access a hydroxyl-terminated polymer that can then be used as an initiator for the ring-opening polymerization of cyclic esters and cyclic ethers. In the second part, I developed two independent methodologies that yield polyethylene- and polypropylene-containing triblock copolymers, with the polyolefin as the center block. The approach for polyethylene employs a series of post-polymerization functionalizations, while the approach for polypropylene consists of a selective copolymerization. In both cases, dihydroxyl polyolefins as macroinitiators were obtained in quantitative yields and subsequently converted into amphiphilic triblock polymers via the ROP of tert-butyl glycidyl ether and the subsequent hydrolysis of the tert-butyl ether group. The amphiphilic nature of the block polymer was established via dynamic light scattering.