

Abstract

Copper-catalyzed reversible-deactivation radical polymerization (Cu-RDRP) is one of the most important controlled radical polymerization (CRP) techniques. Cu-RDRP has been successfully employed for the preparation of both functional and non-functional polymers with well-defined composition and architecture. The aim of this dissertation was to identify new applications of Cu-RDRP, primarily focusing on the synthesis of complex polymeric architectures (CPAs) and optimizing polymerization conditions for important functional monomers.

CPAs with well-defined topology play a central role in today's polymer science. However, the synthesis of CPAs via Cu-RDRP suffers from the lack of a robust and efficient strategy for the attachment of initiation sites to CPA precursors, particularly macromolecular ones, and the attached initiation sites are mostly monofunctional, which significantly limits the design of new polymeric materials. In the first part of this work, trichloroacetyl isocyanate (TAI), an established NMR derivatization reagent, was readily repurposed for rapid and clean installation of trichloroacetyl groups (TAGs) as Cu-RDRP initiation sites into both small molecules and polymers. Conditions were developed under which TAGs initiate well-controlled Cu-RDRP of styrene and various (meth)acrylates. Through comprehensive NMR and triple-detection SEC studies on model compounds, it was shown that TAGs act as trifunctional initiation sites for Cu-RDRP. The TAG multifunctionality combined with the instant character of TAI reactions enables the application of unconventional synthetic procedures and preparation of novel CPA topologies. This was exemplified by the *de novo* one-pot synthesis of a peculiar "star-on-star" architecture, the preparation of β -cyclodextrin-based multi-arm star polymers, and facile grafting from otherwise problematic cellulose substrates both in solution, obtaining ultra-dense bottle-brush copolymers, and from surfaces, affording thick polymer layers with the possibility of spatial control.

As a side-product of this research, the most universal contemporary Cu-RDRP method for the (co)polymerization of an important functional monomer, 2-hydroxyethyl methacrylate (HEMA), was developed, utilizing a Cu(0) catalyst, a chlorinated initiator, and a non-polar reaction medium (1,4-dioxane). The developed method enables the preparation of well-defined poly(HEMA) of different molecular weights (MWs). The polymerization reaction rates obtained were significantly higher compared to the literature protocols. The use of a non-polar solvent enables, for the first time, a direct access to low-dispersity HEMA-rich copolymers with non-polar comonomers, including highly lipophilic ones. This is demonstrated on the successful copolymerization of HEMA with an equimolar amount of 2-ethylhexyl methacrylate and of lauryl methacrylate, yielding well-

defined amphiphilic copolymers at quantitative conversion. This work significantly expands the application scope of the HEMA monomer and demonstrates for the first time that Cu(0)-RDRP in a non-polar solvent is applicable also to comparatively polar monomers.