University of Fribourg / Faculty of Science and Medicine / Adolphe Merkle Institute

Chlorophylls as Catalysts of Reversible Deactivation Radical Polymerization

Bernadetta Gajewska

Copper chlorophyllin and chlorophylls have been used as environmentally friendly and non-toxic catalysts for ATRP. Copper trisodium chlorophyllin is obtained from natural chlorophyll, from renewable feedstock, and is widely used as a major green food colorant in cosmetics and in medical devices.

Aqueous ATRP of poly(ethylene glycol) acrylate (PEGA) resulted in PEGA-chlorophyllin copolymers with narrow molecular weight distribution and controlled content of chlorophyllin. The reactions proceeded with first order kinetics, and the polymer's molecular weight increased with conversion. The resulting copolymers could find application in drug delivery and biomedical applications, or as solar energy harvesting materials. In order to suppress the incorporation of the catalyst into the growing polymer chain, the vinyl bond of chlorin e6, one of the major porphyrin components of chlorophyllin, was deactivated by hydrobromination and hydration. Complexation of copper by the porphyrin lead to a bio-derived catalyst which mediated the polymerization of PEGA and yielded homopolymers with molecular weights of around 4000 - 5000 g mol^{-1} and dispersity ≤ 1.11. UV-vis spectroscopy indicated that chlorophyllin was stable during the polymerization.

Naturally occurring chlorophyll a (Chl a) and bacteriochlorophyll a (BChl a) acted as catalysts of ATRP, initiators for continuous activator regeneration (ICAR) ATRP and activator regenerated by electron transfer (ARGET) ATRP of styrene. Polystyrenes of 4570 g mol^{-1} with dispersity values as low 1.51 were successfully obtained in catalysis by BChla extracted from *Rhodospirillum rubrum*.

Chlorophylls (Chls) and their derivatives allowed polymerizations in aqueous and organic medium which opens doors to green catalysis of all kinds of monomers.

Jury:
Prof. Nico Bruns (thesis supervisor)
Prof. Christoph Weder (internal co-examiner)
Prof. Cornelia Palivan (external co-examiner)
Prof. Fabio Zobi (president of the jury)