IRON CATALYST AT PPM SCALE: NOVEL NIR SENSITIZED SYSTEM FOR PHOTOINDUCED ATRP

N. Meckbach, C. Kütahya, B. Strehmel

Niederrhein University of Applied Sciences, Faculty of Chemistry and Institute for Coatings and Surface Chemistry, Adlerstr. 1, 47798 Krefeld, Germany

In controlled living polymerization techniques, atom transfer radical polymerization (ATRP) is the most used strategy for the targeted synthesis of tailor-made polymers. A major disadvantage, however, is the requirement for transition metal complexes which must have two stable oxidation states but do not form metal oxides.[1]

A successfully developed and applied strategy is the in-situ formation of transition metal complexes by photochemical reduction using photoinitiators or photosensitizers. A system successfully developed in the past, which reported on the NIR-sensitized photo-induced atom transfer radical polymerization[2], was transferred to a new transition metal/catalyst system in this work. A zwitterionic polymethine with a barbital group in the *meso*-position, which has a sensitizing activity at room temperature under NIR light, was used as a photosensitizer while other cyanines with the same methine pattern with no barbiturate group showed no polymerization; that is 5-(6-(2-(3-Ethyl-1,1-dimethyl-1H-benzo[e]indol-2(3H)-ylidene)ethylidene)-2-(2-(3-ethyl-1,1-dimethyl-1H-benzo[e]indol-3-ium-2yl)vinyl)cyclo-hex-1-en-1-yl)-1,3-dimethyl-2,6-dioxo-1,2,3,6-tetrahydropyrimidin-4-olate. Spectroscopic investigation evidenced formation of a species absorbing at 870 nm that also enabled initiation of polymerization at this wavelength. Fe(III) was used as a catalyst in combination with tetrabutylammonium bromide (TBABr), tris (2-pyridylmethyl) amine (TPMA) and tris (4-methoxyphenyl) phosphine (TMPP). TBABr showed the best results. As an alkyl halide initiator, α-bromophenyl acetate (EBPA) was used. The polymers exhibited controlled molecular weight characteristics (dispersities between 1.1-1.3). There are also well-functioning chain end functionalities. The chain end functionality of the polymers obtained was confirmed by chain extension and block copolymerization experiments. Various light ON/OFF experiments illustrate the function of Fe(III), TBABr, and EBPA in the system used. It also worked under aerobic conditions.

---

[1] K. Matyjaszewski, *Macromolecules* **2012**, *45*, 4015-4039.

[2] C. Kütahya, C. Schmitz, V. Strehmel, Y. Yagci, B. Strehmel, *Angew. Chem., Int. Ed.* **2018**, *57*, 7898-7902.