

SUSTAINABLE PHOTOPOLYMERIZATION. MATERIALS, DEVICES AND PROCESSES FOR TAILOR-MADE POLYMERS

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Sustainable Carbon Nanodots (CDs) have received increased attention after their first introduction as photoinitiating component in combination with blue light LEDs in 2020. They originate from distinct biomass resulting in different efficiencies for free radical photopolymerization, photo-ATRP and photo-CuACC reaction. Biomass derived from lac dye, alginate, and citric acid served as raw material to make the CDs.

Free radical photopolymerization operated well in combination with iodonium salts comprising weak coordinating anions such as $[\text{CF}_3\text{SO}_2)_2\text{N}]^-$ and $[\text{Al}(\text{OC}_4\text{F}_9)_4]^-$ resulting in different polymerization efficiencies of TPGDA. Singlet states of photoexcited CDs uptake a major function in these systems as concluded by time resolved fluorescence spectroscopy studied by global analysis. More emitting species influence the dynamics of the excited state.

Photoinduced controlled radical polymerization proceeded well with CDs originating from lac dye comprising olefinic moieties in the originating biomass. Polymers obtained exhibited a dispersity of 1.1 using $\text{Cu}(\text{TPMA})\text{Br}_2$ as catalyst and Ethyl- α -bromo phenylacetate as initiator. Experiments based on a metal free photo-ATRP protocol failed while mainly free radical polymerization occurred. The CDs used can also initiate CuACC reaction resulting in formation of triazole structures.

New NIR-LED systems will also move photopolymers in a greener direction. They have been available as high-intensity emitting devices enabling both radical and cationic polymerization. Functionalized cyanines absorbing between 700-1000 nm operate as absorbers/sensitizers in combination with new NIR-LED devices available as compact prototypes emitting either at 805 nm, 860 nm or 940 nm with outstanding intensities. They also facilitate to substitute oven processes resulting in tremendous saving of energy and processing time because such absorbers easily facilitate temperatures in the coating larger than 100 °C and operate ON/OFF cycles on demand. NIR sensitized controlled radical polymerization also proceeded well with a heptamethine based cyanine comprising a barbiturate group in the *meso*-position. This substitution pattern responsibly results in controlled radical polymerization in combination with either $\text{Cu}(\text{TPMA})\text{Br}_2$ or FeBr_3 as catalyst and an alkyl halide. Polymers obtained applying a photo-ATRP protocol resulted in a dispersity of 1.2 where also monomers with UV-absorbing moieties worked well.

Monomers derived from sustainable feedstock complement the pattern.

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