Sustainable Photoinitiating Systems Derived from Biomass. Type I + II Photoinitiators for Free Radical Polymerization, and Light-Mediated ATRP

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Different biomass served as raw material for synthesizing Carbon Nanodots (**CD**s). Their different origin resulted in different efficiencies for free radical polymerization and a photo-ATRP setup using as co-catalyst either $CuBr_2$ or $FeBr_3$ at a scale <100 ppm. Alternatively, a metal-free approach also successfully worked with **CD**s available from hemicellulose linked in an organic network and confined **CD**s obtained from cellulose in a silica-confined network. The latter exhibited a room temperature phosphorescence (**RTP**) greater than 100 ms, indicating triplet state formation as a new concept. The triplet state connects the system to a metal-free photo-ATRP reaction protocol, while systems with no efficient triplet formation failed. Lignin itself was also found to work in a photo-ATRP setup using $CuBr_2$ as a metal co-catalyst. Photocatalysts derived from *Kerria lacca* resulted in the lowest value; that is ≈1.1, using Cu(TPMA)Br2 in a range of <100 ppm and Ethyl-α-bromo phenylacetate as initiator. Confined CDs derived from cellulose worked in the photo-ATRP at a level of only 9 ppm, resulting in a small dispersity of the polymers obtained. The polymers obtained exhibited a different dispersity of molecular weight depending on the biomass origin of the **CD**.

Alternatively, hydrothermal treatment of furfural available from hemicellulose provided **CD**s with aldehyde groups on the surface. These structural patterns also enabled covalent binding of photoactive groups resulting in homolytic cleavage of the attached group upon UV exposure. This connects to Type I photoinitiators whose photoinitiating properties will be shown at this conference for the first time. The low cytotoxicity of the **CD**s was also remarkable.

Furthermore, results obtained demonstrated the use of a sustainable photocatalyst with multiple purposes comprising demethylated lignin (**Fe_3O_4@D-wood**). This was made by the treatment of wood and iron oxide. The same material became the subject of photocatalytic explorations for water treatment and material synthesis by radical photopolymerization opening the door to materials facilitating multiple uses for different purposes. Exposure of **Fe_3O_4@D-wood** with artificial sunlight showed an improved activity considering the photochemical oxidation of organic pollutants in the presence of H2O2. The efficient generation of reactive radicals brought this system also to photopolymerization. Here, radicals based on reactive oxygen species (**ROS**) generated in the catalytic cycle can be seen as the dominating species to initiate radical polymerization. A mixture of UDMA and TPGDA showed good reactivity with cumene hydroperoxide (**CHP**). Photocatalyst used for water treatment facilitates reuse for photopolymerization.