

Abstract

Photoinduced polymerization reactions have long attracted the attention of chemists due to their status as effective processes using naturally available resources. More recently, photopolymerization and UV curing have become increasingly popular as sustainable and eco-friendly alternatives to conventional thermal processes. Sulfur-containing functional groups have a long history in polymer chemistry, owing to their significant versatility and wide range of applications. Sulfur has been extensively utilized in the field of vulcanization of rubber, while thiols have found broad use in polymer synthesis, with the thiol-ene click reaction being one of the most renowned click chemistries. Moreover, disulfides have recently garnered attention due to their versatility and responsiveness to multiple external stimuli.

In this scenario, the present doctoral research mainly focused on the use of sulfur-containing functional groups, in particular disulfides and thiols, in photoinduced polymerization reactions and the development of stimuli-responsive coatings. Disulfides were introduced into photocurable formulations, and their responsiveness to a wide range of different triggers was exploited. Customized acrylated monomers containing disulfide bonds were used in radical photocurable systems for the production of stimuli-responsive coatings through photoinitiator-free reactions. The self-healing ability of the photocured coatings was demonstrated by heating the samples above their glass transition temperature to trigger disulfide bond exchange and enhance chain mobility. In cationically driven photoinduced reactions, disulfide-containing molecules were instead used for controlling the extent of polymerization. Their inhibitory effect on epoxy ring-opening reaction was investigated, showing their potential as a novel strategy for patterning materials. Besides disulfides, thiols functional groups were explored in the thiol-ene photocrosslinking of a non-edible vegetable oil. Different thiols crosslinkers were employed to highlight the critical influence of thiol structure on polymerization kinetics and the final networks morphology. Moreover, the reversible addition of photogenerated thiyl radicals to oil unsaturations and the consequent isomerization of double bonds were investigated.

Overall, the findings highlight the significant potential of disulfide and thiol functional groups in photopolymer science, independently of the specific chemistry or reaction mechanism involved, paving the way for the design of

smart, responsive materials and advancing the development of next-generation functional coatings with self-healing, tunable, and patternable properties.