Photobase generators : Polyvalent tools for polymerization under irradiation

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Photochemical generation of free radicals and acids is a widely used process in photopolymerization reactions. Recently, photobase generators (PBG) systems have emerged as new source of initiating species allowing the catalysis of different reactions (thiol-Michael, thiol-isocyanate, thiol-epoxy…). The versatility of PBGs will be highlighted through different examples. The process of light-triggered polymerization of dopamine will be first described. Irradiation of quaternary ammonium salts of phenylglyoxylic acid used as photobase generators activates the release of a strong base in water followed by an important pH jump. This initiates the polymerization of dopamine, leading to an on-demand formation of highly adhesive coating on steel. Then, photopolymerization of a thiol/epoxy/isocyanate ternary network was thoroughly investigated. Polymerization kinetics demonstrated that the thiol-isocyanate reaction is completed in a matter of seconds while the thiol-epoxy reaction exhibits a catalytic character over a few days leading to a post-consolidation of the coating. Moreover, the presence of the thiourethane network enhances the thiol-epoxy properties by increasing the physical cross-linking due to higher content of hydrogen bonding. Compositional variations between thiol/epoxy and thiol/isocyanate and the resulting final thermomechanical properties and hardness offer many advantages in the development of materials with tunable properties.