# Coumarin-3-oxoacetic Acids as Amphiphilic Photoinitiators for Free Radical and Cationic Photopolymerizations with UV–Vis LED Irradiation

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High-performance photoinitiators (PIs) play a crucial role in photopolymerization. Compared with traditional photo resource mercury lamp used in photocuring, ultraviolet–visible (UV-Vis) light-emitting diodes (LEDs) have attracted growing attention due to their environmental friendliness, low heat emission and long lifetimes. Recently, PIs that match the UV-Vis light sources have been extensively exploited, including coumarins, benzophenones, camphorquinones, thioanthrones, phenothiazines, and several metal organic compounds. Coumarins, derived from fungi, bacteria, and plants, are considered green renewable resources and find applications in food processing, biomedicine, and optoelectronics. The high electron-transfer quantum yields of coumarins make them attractive candidates for designing efficient PIs.[1, 2] Herein, three coumarin-3-oxoacetic acids (COXAs) as amphiphilic PIs used in photocured technology were synthesized and studied. As one kind of amphiphilic PIs, COXAs can be used both in traditional organic photocured technology and water-based photocured technology which is more in line with the tenets of green chemistry as it eliminates volatile organic gas (VOCs) emissions. These PIs exhibit good UV absorption in the range of 300-500 nm. The real-time fourier transform infrared (RT-FTIR) and photo DSC experiments were operated. The results showed that not only can they be used as Norrish I PIs or Norrish II PIs to initiate free radical polymerization (FRP) of acrylate monomers but also sensitize iodonium salt and sulfonium salt to initiate cationic polymerization (CP) of epoxy and oxetane monomers. Moreover, they can initiate the deep curing of Tri-(propylene glycol) diacrylate (TPGDA) in in the very low concentration which is 0.01%. The curing depth can exceed 9 cm within 5 min irradiated by 415nm LED (100 mW • $cm^{-2}$). Furthermore, they can also initiate the deep curing of the water-soluble monomer polyethylene glycol (400) diacrylate (PEG (400) DA) to approach to the same depth as TPGDA at the same irradiation condition, even in various proportions of water. Meanwhile, COXAs exhibit acceptable photobleaching phenomenon. The photochemical and photophysical properties of COXAs were studied in terms of absorption, fluorescence spectroscopy fluorescence quenching, electron spin resonance, liquid chromatograph mass spectrometer and cyclic voltammetry experiments to disclose the photoinitiation mechanism. Additionally, cytotoxic experiments were carried out, and the results showed that the three PIs, especially COXA-N, had good cytocompatibility. In total, this work highlights the potential of a series of novel visible light initiators, COXAs, exhibiting efficient photobleaching, excellent depth curing, high conversion rates, thermal stability and low cytotoxicity, which are promising prospects for different photocuring applications.

References

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