NOVEL MUTILFUNCTIONAL BENZOPHENONE-BASED PHOTOINITIATORS FOR LED PHOTOPOLYMERIZATION AND 3D PRINTING

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The development of photopolymerization systems is constantly evolving due to their numerous attractive features, such as the unique spatial and temporal controllability, low energy consumption and environment friendly. It is important to develop new photoinitiating systems which could be used under mild conditions such as upon light-emitting diodes (LEDs) irradiation. A series of new photoinitiators (PIs) based on benzophenone-triphenylamine and benzophenone-carbazole hybrid structures are here specifically designed for LED photopolymerization. The formation of benzophenone-triphenylamine and benzophenone-carbazole hybrid structures not only contributes to red-shift the absorption maxima but also strongly enhances their molar extinction coefficients. Because of the benzophenone moiety, these PIs could efficiently initiate the free radical photopolymerization (FRP) of acrylates without addition of any extra hydrogen donors demonstrating a monocomponent Type II behavior. In addition, both high final conversions and polymerization rates are achieved in FRP in the presence of an amine and/or an iodonium salt. Meanwhile, the PIs can also interact with the iodonium salt to generate cationic species for the cationic photopolymerization (CP) of epoxides. They are found as a versatile PIs that can be used for both FRP and CP. Remarkably, some of them exhibit better hydrogen abstraction abilities as Type II PIs than the benchmark and commercial PI 2-isopropylthioxanthone. Furthermore, the interaction between the PIs and the different additives are investigated by the steady state photolysis and fluorescence quenching experiments. The best photoinitiating systems determined during the photopolymerization tests were selected for 3D printing experiments.

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[1] Liu, S.; Brunel, D.; Noirbent, G.; Mau, A.; Chen, H.; Morlet-Savary, F.; Graff, B.; Gigmes, D.; Xiao, P.; Dumur, F.; Lalevée, J. New multifunctional benzophenone-based photoinitiators with high migration stability and their applications in 3D printing. *Materials Chemistry Frontiers* 2021, *5*, 1982-1994.