

Synthesis of innovative type I photoinitiators for free radical photopolymerization induced by visible light and studies of their application to 3D printing

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Photopolymerization processes are one of the most efficient methods for obtaining polymeric materials and, in addition, it is still a rapidly developing field. The most commonly used method of polymerization using light is radical photopolymerization¹. Initially, the photopolymerization process was carried out using UV light. Today this process is gaining importance in other industries, e.g. in photolithography, medicine, and microelectronics, and the fastest development of this technology is in 3D printing. Unfortunately, these industries severely limit the possibilities of using photoinitiators operating in the UV range. This is due to the harmfulness of this radiation to humans, or in the case of 3D printing, the inability to achieve adequate depth of cure². In opposition to UV process, a better light penetration can be achieved with visible light. On an example of polystyrene latex, observed was that at irradiation with light at 320 nm, penetration of light is limited to 600 µm. In comparison, by using light sources with an emission maximum at 450 nm, 4 mm layers was obtained³.

Based on the above, we have developed a new approach to obtaining radical photoinitiators. The novel photoinitiators were obtained by “modification of benzil ketals” due to the extension of their conjugation structure. Modification of the mentioned initiator allows to shift spectrum toward longer wavelengths making the new systems active under the LED with emissions maximum at 405 nm, 415 nm, or maybe even at 430 nm and higher which is rarely seen today. The efficiency of the developed systems has been tested through extensive spectroscopic studies. The photodecay capability of the novel photoinitiators was investigated in photolysis tests using light sources with emissions corresponding to 405 nm or higher. The ability to initiate the radical photopolymerization process was then investigated using real-time FT-IR and compared to a commercially available analog, 2,2-dimethoxy-2-phenylacetophenone (Irgacure 651/DMPA). Acrylate systems were tested using trimethylolpropane triacrylate (TMPTA) monomer as an example. Thiol-ene systems were tested based on 1,3,5-triallyl-1,3,5-triazinane-2,4,6-trione (TATATO) with trimethylolpropane tris(3-mercaptopropionate) (MERCAPTO) formulations. Additionally, urethane-dimethacrylate (UDMA) with the addition of triethylene glycol dimethacrylate (TEGDMA) formulation was tested. The ability to initiate the photopolymerization process was tested using light sources with emission maxima of 365, 405, 415, 455, and 470 nm on both thin (25 µm) and thick films (1,5 mm). Compared to DMPA, which showed no activity at 455 nm and very low activity already at 415 nm, some of our photoinitiators worked efficiently even at 470 nm. The above studies were confirmed during application tests using VAT 3D printing.

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References

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