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PHOTO-CONTROLLED RAFT POLYMERIZATION BY DIRECT LASER WRITING FOR LIVING ADDITIVE MANUFACTURING

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Résumé

Additive manufacturing (AM) based on photopolymerization provides simple, fast and controlled ways to produce complex objects. However, the photopolymerization process of most photocurable resins results in “dead” polymer chains that cannot be reconfigured after fabrication. Controlled/living radical polymerization (CRP) provides a solution to enable reconfiguration. It is well known that several strategies, such as NMP, RAFT or ATRP, allow the facile synthesis of well-defined polymers with living features. Recently, researchers have sought to regulate the activation and deactivation in CRP by using external stimuli. Among those regulators, light is the most attractive due to its low cost, ubiquity and controllability. Photo-CRP combined with AM technologies will be a strong tool for living AM.[1,2] In our work, first, we developed a photoiniferter, Macro-dithiocabamate (Macro-DTC, Figure a), by photo-controlled RAFT polymerization of butyl acrylate (BA) under blue LED light. Compared with the commercial thiocarbonate (TTC), DTC has higher absorbance at 500 nm - 600 nm,[3] which allows the use of a commercial Direct Laser Writing (DLW, 532 nm) system. Then, from a mixture of Macro-DTC with pentaerythritol tetraacrylate (PETA, 50 wt%) and without other additives, high resolution 3D objects (Figure b) were obtained by DLW at 532 nm. Furthermore, Trimethylolpropane triacrylate (TMPTA) was successfully repolymerized multiple times on the surface of a square made from PETA and Macro-DTC (50 wt%/50 wt%). Finally, well defined structures, made from a temperature-responsive polymer, poly(*N*-isopropylacrylamide) (PNIPAM), were fabricated on the surface of the same square as mentioned. By AFM measurements under water, the swollen and shrunken state of PNIPAM was shown clearly. This photo-controlled RAFT polymerization process, mediated by a Macro-photoiniferter without any other additives, combined with DLW, provides a method for integrating new functional and stimuli-responsive materials.

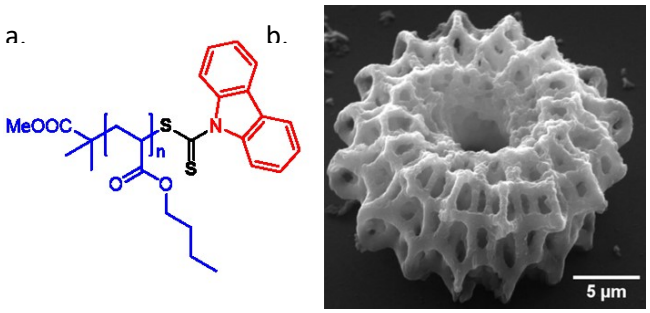

Figure. *a. The chemical structure of Macro-DTC. b. 3D structure made from Macro-DTC and PETA by DLW at 532 nm.*

Références

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2) Zhiheng Zhang, Nathaniel Corrigan, Ali Bagheri, Jianyong Jin, Cyrille Boyer, *Angew. Chem. Int. Ed*. **2019**, *58* (50), 17954-17963.
3) Benjamin Cabannes-Boué, Qizhi Yang, Jacques Lalevée, Fabrice Morlet-Savary, Julien Poly, *Polym. Chem*. **2017**, *8* (11), 1760-1770.