TWO-IN-ONE: λ-ORTHOGONAL PHOTOCHEMISTRY ON A RADICAL PHOTOINITIATING SYSTEM

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ABSTRACT

We introduce an alkyne functional radical photoinitiator, 2-(4-(2-hydroxy-2-methylpropanoyl)phenoxy)ethyl hex-5-ynoate, and evidence that both reactive moieties – the alkyne and the photoinitiator terminus – can be independently addressed with light of disparate wavelength (λ-orthogonality). The alkyne functionality is subjected to a visible light (420 nm) induced copper-catalyzed Huisgen reaction, which is employed for the selective functionalization of the initiator with a poly(ethylene glycol) (PEG) chain. This reaction proceeds completely λ-orthogonal in the presence of the UV-reactive photoinitiating moiety. Conversely, we demonstrate that the alkyne functionality of the photoinitiator is quantitatively orthogonal to UV irradiation emitted by the pulsing action of an excimer laser (351 nm, pulsed laser polymerization, PLP) and the generated radical species. In turn, the PEGylated initiator can readily be employed as a macrophotoinitiator during PLP. The stability of the functional moieties was confirmed by size exclusion chromatography – electronspray ionization mass spectrometry (SEC-ESI-MS). The introduced λ-orthogonally addressable dual functional initiator can be used in a wide range of applications, including surface lithography and post-synthetic modification of photo-cured materials.

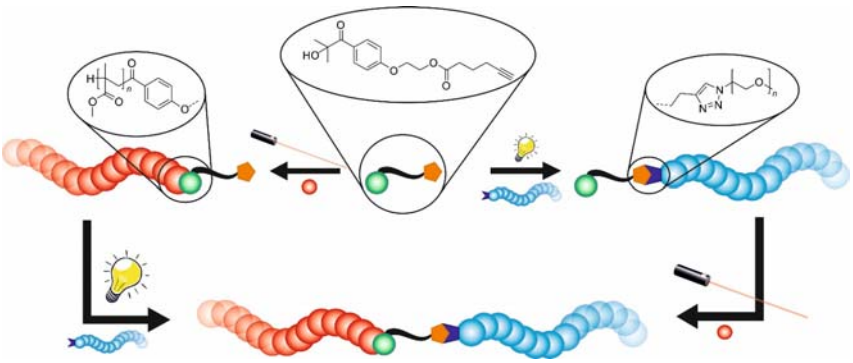

Fig. 1: A bifunctional photoinitiator is presented that can undergo CuAAC and free radical polymerization λ-orthogonally.

References: Hurrle, S.; Lauer, A.; Gliemann, H.; Mutlu, H.; Woell, C.; Goldmann, A. S.; Barner-Kowollik, C. *Macromol. Rapid Commun.* **2017**, in press.