With Polymer Photoclicks to Fluorescent Microspheres

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**Introduction** Polymer microspheres are an important and ubiquitous class of materials based on characteristics such as a small size and volume, high diffusivity and mobility, and a large specific surface area. We introduce a new class of functional, fluorescent polymer microspheres using a highly efficient, additive-free photochemical ligation technique.

**Aims** The utilisation of pre-functionalised polymers for cross-linking under conditions analogous to precipitation polymerisation – a powerful technique for the preparation of stabiliser-free microspheres – is demonstrated.1



**Methods** We demonstrate that fluorescent, narrow-disperse microspheres are rapidly and readily prepared by photo-clicking pre-functionalised polymers using the highly efficient nitrile-imine mediated tetrazole-ene cycloaddition (NITEC) reaction. Our approach requires no stabilisers, bases or initiators, and proceeds under mild UV irradiation at ambient temperature. First, precursor polymers were synthesised by nitroxide-mediated polymerisation (NMP) of styrene with chloromethylstyrene as a functional comonomer and subsequently were separately functionalised with either cross-linkable tetrazole (Tet) (***P2***) or acrylate (Acr) (***P3***) groups**.** The particle syntheses were performed by exposing the solubilized copolymers under UV-B light (λ = 300 nm) and gentle agitation. Within seconds, the clear solution turned bright yellow and the reaction was carried out for 30 or 120 min. Scanning electron microscopy (SEM) images of isolated particles showed that they are spherical and have a narrow size dispersity. The diameter of the microspheres can be tuned in the 0.25 – 0.75 μm range depending on the reaction conditions, including polymer concentration, polymer ratio and the solvent composition. Critically, we explore the application of the microspheres, including fluorescence, degradation and swellability for encapsulation.



**Conclusion** The power of this microsphere synthesis method is wide-ranging with broad application potential, especially in bioanalysis and imaging applications. Critically, the power of adding functionality to precursor polymers prior to particle synthesis adds an entirely new paradigm for the synthesis of cross-linked polymer microspheres. We envision a variety of avenues for future development, including polymer backbone/solvent combinations, alternative cross-linking chemistries, or the incorporation of additional functionality with orthogonal reactivity for increasingly advanced material design.

**References**

1. Hooker, J.P.; Delafresnaye, L.; Barner, L.; Barner-Kowollik, C. (2019). Mater. Horiz. 6, 356-363.