

Enzymatic radical polymerizations: Understanding a new-to-nature reactivity to engineer living cells and create synthetic cells

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Enzymatic polymerizations allow the implementation of controlled radical polymerizations into life-like and living systems. Here, we demonstrate biocatalytic atom transfer radical polymerizations (bioATRP) to drive polymerization-induced self-assembly (PISA) to create giant polymersomes with the ability to encapsulate the protein expression system of bacteria, thereby creating self-synthesizing artificial cells that can act as microreactors for enzymes and produce their own proteins within their lumen. Moreover, we demonstrate how enzymes displayed on the surface of yeast cells can graft polymers on the surface of the cells, thereby engineering their surface with synthetic polymers. These examples showcase how enzymatic polymerizations can be used to create synthetic biology systems and engineered living materials in which the polymers serve as *in situ* synthesized biorthogonal building blocks, opening up application opportunities at the interface of biology and polymer chemistry.

