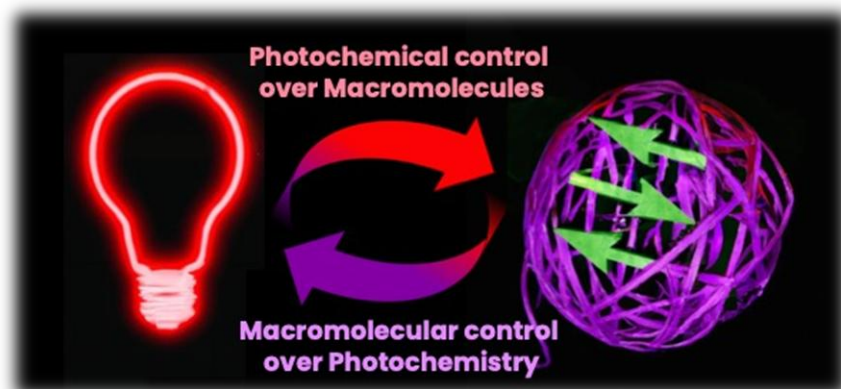


# Programming Polymer Function via Radical Ring-Opening Polymerization: From Peptides to Photochemistry

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Combining synthetic and biological building blocks unlocks vast potential for designing macromolecular architectures with emerging functionalities, including control over photoreactive processes.<sup>[1]</sup> To generate synthetic polymers, radical polymerization is arguably the most applied method across both fundamental research and industry. However, its inherent transformation of vinyl monomer feedstock into polymers with an all-carbon backbone prevents the incorporation of functional groups into the polymer main chain, thus restricting the design freedom of polyvinyl-based polymers.

This lecture discusses how radical ring-opening polymerization can be used to endow the backbone of polyvinyl polymers with function. We report a synthetic strategy that enables the incorporation of peptides spanning all 20 standard amino acids into the backbone of polymers.<sup>[2]</sup> This diversification enhances the structural and functional capabilities of synthetic polymers, enabling the engineering of polymers to mimic complex biological structures and functions, such as on-demand folding into  $\beta$ -sheet architectures.<sup>[3]</sup>

To exert control over the lifespan of polymer architectures, we have developed monomers that allow the incorporation of photochemical targets into the polymer backbone.<sup>[4]</sup> As a result, the traditionally unresponsive all-carbon backbone resulting from radical polymerization can be broken down in a flash of light. By tuning the photolysis wavelength of the embedded monomers and their distribution across the polymer chains, it becomes possible to cleave polymers selectively by choosing specific irradiation wavelengths.<sup>[5]</sup> Importantly, the self-assembly of these polymers into higher-order architectures also affects their photochemistry, enabling the switching between different photochemical outcomes depending on the self-assembly state.

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