

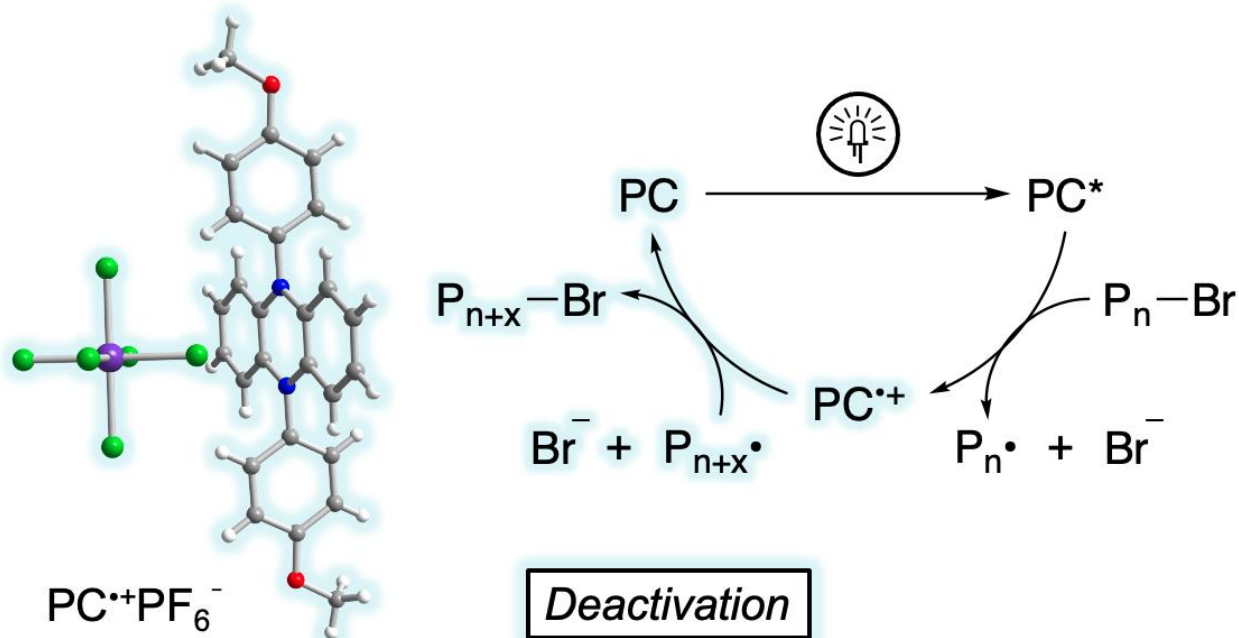
## Influences on deactivation in organocatalyzed atom transfer radical polymerization

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Organocatalyzed atom transfer radical polymerization (O-ATRP) is a controlled radical polymerization method employing organic photoredox catalysts (PCs) for the synthesis of precision polymers under mild, metal-free conditions. To control polymer growth, O-ATRP relies on reversible deactivation of the polymer, wherein reactive propagating radicals are placed in a “dormant” state. As a result, this deactivation step minimizes the concentration of radicals in solution and limits irreversible, radical-based termination reactions that would otherwise hinder polymerization control.

Despite the importance of deactivation in O-ATRP, few reports have investigated its mechanism and factors influencing it during a polymerization. Further, the species responsible for deactivation – the PC radical cations – remain poorly understood, limiting development of this polymerization method. To address these issues, this work probes the reactivity of these radical cations to understand their role in deactivation as well as their possible side reactions during O-ATRP. In addition, a number of other factors are investigated, including how the identity of the halide in O-ATRP impacts deactivation. Finally, the information gathered in these fundamental studies is applied to O-ATRP when radical cations are employed as reagents to improve a challenging polymerization. Ultimately, this work highlights the benefit of understanding the mechanism of O-ATRP, as well as the utility of radical cations as reagents in O-ATRP.



This work investigates deactivation in O-ATRP and the role of radical cations during this process.