

Uncovering the Effects of Backbone Chemistry on the Properties of Polymer-Supported N-Aryl Phenoxazine Photocatalysts

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Abstract: The incorporation of photocatalysts (PCs) into polymer supports has gained interest as a method to enhance catalytic activity, tune photophysical properties, and increase catalyst recyclability. However, it is not well understood how changing the pendent polymer group affects the environment and resulting properties of the PC. Herein, we establish a method for polymerizing an N-naphthyl phenoxazine with three methacrylate comonomers of varying polarity: methyl methacrylate (MMA), stearyl methacrylate (SMA), and tri-ethylene glycol methyl ether methacrylate (TEGMA). Analysis of these three copolymers reveals the effect of comonomer identity on PC photophysical properties. RAFT polymerization is employed to afford control over the resulting poly-PC, allowing for a direct comparison between polymers of similar molecular weights, dispersities, and incorporation of PC. It was found that each of the poly-PCs exhibit properties similar to that of the parent phenoxazine catalyst, however with a red shift of up to 60 nm in the fluorescence emission spectra, indicative of increased stabilization of the excited state, similar to the parent PC in a polar solvent. Additionally, there is a blue shift from the methacrylate monomer PC-M to PSMA-PC (≈ 8 nm), which further supports this, as the nonpolar comonomer mimics nonpolar solvent effects on the PC. These poly-PCs can also be employed in organic transformations, such as the difluoroalkylation of an alkene, with uninhibited catalytic efficiency. This method is advantageous as the poly-PC can be isolated from the reaction mixture via precipitation, suggesting reusability and avoiding the extensive purification that is typically required with homogeneous catalysis. Together, this work demonstrates the ability to incorporate organic PCs into polymer backbones via controlled polymerization to afford poly-PCs with tunable properties based on comonomer identity, limiting synthetic difficulties, and can be utilized to introduce catalysts into different solvent environments without unwanted property changes. Our approach therefore expands the applicability and recyclability of organic PCs, while maintaining N-naphthyl phenoxazine's powerful properties and catalytic performance.

Abstract Image:

