

# Novel Solid-state Photo-reversible Polymerization

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Reversible polymers represent a relatively new class of materials that possess bonds capable of reversibly connecting and disconnecting monomers in response to stimuli such as heat or light. These reversible bonds can be used to construct a recyclable polymer via material polymerization and depolymerization, on demand (**Fig. 1**)<sup>1</sup>. Several reversible polymerizations have been reported in the literature, however these are each based on thermally-reversible reactions, like the Diels-Alder reaction, which require high energies for depolymerization. Photo-chemical reactions, on the other hand, are considered to be greener synthetic pathways because photons do not leave residues, they can be conducted at ambient temperature, and often in the solid-state. Using these green chemical principles, our reversible-polymer designs centre on a biologically-inspired mechanism.

Thymine, like several other olefinic compounds, is known to undergo reversible photochemical [2+2]-cycloaddition in the crystalline-state to yield cyclobutane derivatives (**Fig. 2**). These versatile photoreactions have been used to prepare simple cyclobutane-dimers, complicated organic molecules with constrained geometries such as ladderanes and cyclophane, and also regiospecific oligomeric and polymeric species.

Photo-polymerization by the [2+2]-cycloaddition is of particular interest to us, since it represents a solvent-free, synthetic approach to produce new and potentially useful materials for plastics and packaging applications. A unique property of these polymers is their potential to undergo photo-reversible polymerization through cleavage of the cyclobutane ring with short-wavelength UV. In this way, polymer properties such as molecular weight can be tuned, and the polymer materials could be selectively degraded-on-demand to yield reusable starting materials. The design and synthesis of various di-thymine monomers, determination of monomer crystal structures, and characterization of the photoproducts using Nuclear Magnetic Resonance, UV-Visible Spectroscopy, Gel-Permeation Chromatography, and other polymer characterization techniques will be discussed in the presentation.

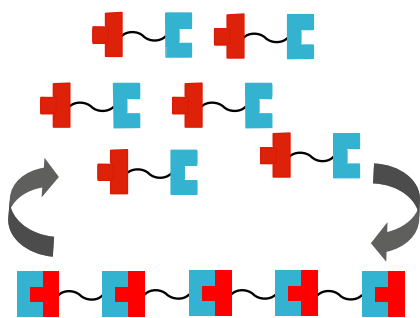


Figure 1. Schematic of a Reversible Polymer

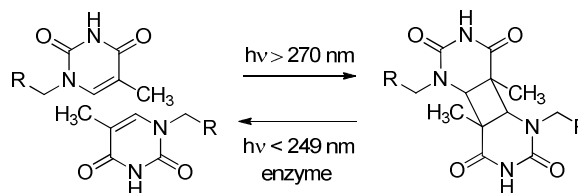


Figure 2. Crosslinking and decrosslinking of thymine derivatives

<sup>1</sup> P. Johnston, M. T. W. Hearn and K. Saito, *Aust. J. Chem.*, **2010**, 63, 631-639.

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