

# PHOTOCAGED AMINES AS BASE CATALYSTS FOR RING-OPENING POLYMERIZATION OF *N*-CARBOXYANHYDRIDES

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Ring-opening polymerization (ROP) of *N*-carboxyanhydrides (NCAs) has attracted considerable attention as a means to prepare synthetic polypeptides with tunable molecular weight and chemical structure, and the ability to incorporate different functional groups into the polymer. The use of light to spatially and temporally control the ROP of NCAs could expand the applicability of synthetic polypeptides, including in the field of additive manufacturing.

In this work, we investigate the photoinduced ROP of  $\gamma$ -benzyl-L-glutamate (BLG) NCA using various photocaged amines (photobases) as catalysts (Figure 1), using members from two distinct groups, i.e., i) ammonium salts and ii) carbamate photobases. When irradiated with light at 365 nm, the photobases are photolyzed and the amines are released, acting as a base. We have shown that the photoreleased amines can trigger the polymerization of BLG NCA and that the polymerization process is influenced by the choice of photobase. Furthermore, the ROP of BLG NCA catalysed by an uncaged amine differs from that of the corresponding free amine in the polymerization rate and molecular weight characteristics of the obtained polypeptide, as confirmed by  $^1\text{H}$  NMR and FTIR spectroscopies and SEC.

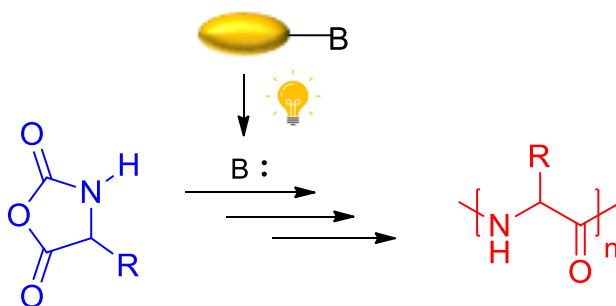


Figure 1: Photoinduced ROP of NCA monomers catalysed by a photoreleased base.