FROM RING-OPENING POLYMERIZATION OF *N*-CARBOXYANHYDRIDES TO USING LIGHT FOR PREPARATION OF SYNTHETIC POLYPEPTIDES

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Ring-opening polymerization (ROP) of α-amino acid *N*-carboxyanhydrides (NCAs) provides a highly modular platform and expedient route for the preparation of synthetic polypeptides. Light is an attractive trigger for polymerization as it can be controlled both temporally and spatially, and photoinduced polymerizations have become an important technology for advanced manufacturing of polymers.

In this work, we show two different approaches for the preparation of synthetic polypeptides using light. In the first approach, we prepare a polypeptide macromonomer by ROP of NCA and functionalize its chain ends with photoresponsive groups (Figure 1A). In this way, we cross-linked allyl-functionalized poly(γ-benzyl-L-glutamate) (PBLG) 3-arm star macromonomer with trimethylolpropane tris(3-mercaptopropionate) in a high internal phase emulsion by thiol–ene photopolymerization under UV irradiation [1]. By combining the PBLG macromonomer with an allyl-functionalized 3-arm star poly(ε-caprolactone) macromonomer, we obtained polypeptide–polyester materials with tunable termomechanical properties and a polypeptide–polyester bilayer material. The second approach uses light to trigger the ROP of the NCA monomers (Figure 1B). For this purpose, we used photocaged amines that release basic catalysts upon illumination. We investigated the polymerization of γ-benzyl-L-glutamate NCA triggered by the photoreleased catalysts and shed the light on photochemistry of the NCAs.

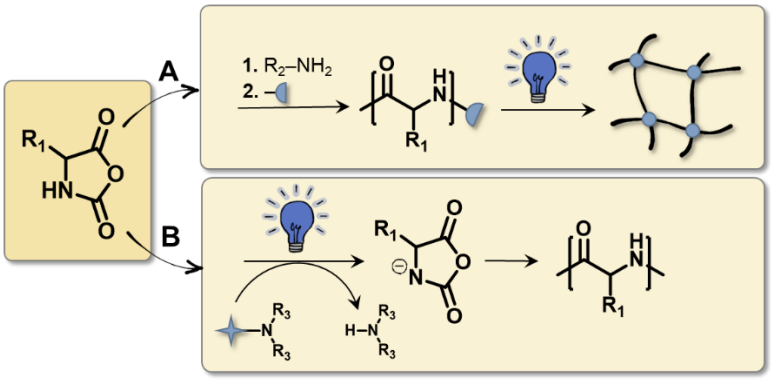

Figure 1. Using light for preparation of synthetic polypeptides. (A) Photocross-linking of chain end functionalized synthetic polypeptide prepared by ROP. (B) Photoinitiated ROP of NCA using a photocaged amine.

References

1. P. Utroša, Š. Gradišar, O. C. Onder, E. Žagar, D. Pahovnik, Macromolecules, 55, 5892–5900, 2022.