Abstract

In this doctoral thesis, a system for the photoinduced ring-opening polymerization (ROP) of *N*-carboxyanhydrides (NCA) was developed for the preparation of cross-linked polypeptide gels, with the ultimate goal of developing a three-dimensional (3D) printing method based on vat photopolymerization. A key objective was to enable both the initiation and inhibition of polymerization using light in order to achieve spatial and temporal control over the reaction, thereby allowing the preparation of polypeptide gels with complex, predefined shapes without the use of molds. In the first part of my doctoral research, a system for the photoinduced initiation of the ROP of γ-benzyl-L-glutamate (BLG) NCA was developed. Since NCA monomers are not photoactive, a photoactive catalyst, i.e., a photobase, is required to trigger ROP upon light irradiation. The photoinduced ROP of NCA was investigated in different solvents using photobases from two different groups: quaternary ammonium salts and carbamate-based photobases. The selection of a suitable photobase was crucial for achieving temporal control over the reaction. The photobase had to remain inactive in the absence of light while enabling rapid ROP upon irradiation. The most suitable photobase was found to be 2-nitrobenzyl dibutylcarbamate (PB-DBA), which releases dibutylamine upon irradiation of 365 nm. The approach was extended to the preparation of cross-linked gels, thereby introducing spatial control over the polymerization. Photoinduced ring-opening copolymerization of the monofuncitional BLG NCA and the bifunctional cross-linker L-homocystine (HCys) NCA was performed using PB-DBA as the photoactive catalyst. To further improve spatial control, an acidic inhibitor was added to suppress polymerization outside the irradiated area caused by the diffusion of active species into the surrounding unirradiated regions. Excellent two-dimensional spatial control over the reaction was achieved, as demonstrated by gel formation exclusively within the irradiated area, while the unirradiated area remained liquid. In the second part of the doctoral research, a system for the light-induced inhibition of NCA ROP using a photoacid was developed. The most suitable was a merocyanine-based photoacid, which successfully inhibited the ROP of BLG NCA upon irradiation at 470 nm. However, its main limitation was its activation by 365 nm light, the wavelength required for the activation of the photobase. In the third part of the doctoral research, 3D printing was performed using digital light processing (DLP). The printing parameters required for successful printing were optimized, including those ensuring adequate adhesion of the gel to the build platform and the formation of gels with the desired dimensions. Based on the optimized parameters, an object of 6 layers of polypeptide gel was successfully printed. Overall, the developed photochemical approach provides a foundation for the integration of synthetic polypeptides with 3D printing based on vat photopolymerization.

Keywords: *N*-carboxyanhydride, ring-opening polymerization, synthetic polypeptide, photobase, photoacid, 3D-printing