PHOTOCROSSLINKING OF COUMARIN-MODIFIED POLY(2-OXAZOLINE)S

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Upon irradiation of coumarin moieties with UV light above 300 nm, [2+2] cycloaddition of ethylenic groups occurs, leading to a formation of coumarin dimers.[1] A reverse reaction, known as a photocleavage is observed while irradiating the coumarin dimers with UV light with shorter wavelengths around 250 nm.[2] Polymers containing coumarin moieties have been widely applied for the preparation of crosslinked networks. Since no photoinitiator is needed for crosslinking, such polymers are attractive especially for biomedical applications, e.g., for hydrogel formation.

Hydrogels containing coumarins have been prepared by e.g. polycondensation of polyethylene glycol with coumarin containing a chain extender [3] and radical copolymerization of N,N-dimethylacrylamide and monomers with coumarin derivative as a pendant group.[4] The photogelation properties and its reversibility were examined by varying the coumarin content and the molar mass of the prepolymers.

Interestingly, only one report so far describes the preparation of poly(2-oxazoline)-based hydrogels crosslinked by coumarin dimers,[2] although this class of polymers has been increasingly gaining research interest over the last decades. Poly(2-oxazoline)s have already been employed in biomedical applications due to their biocompatibility, well-defined structure and chemical versatility. In addition, poly(2-oxazoline)s with shorter side chains are water-soluble, what makes them ideal candidates for hydrogel formation.

This work focuses on the synthesis of a series of partially hydrolyzed poly(2-ethyl-2-oxazoline) differing by degree of hydrolysis and the polymer chain length. These polymers were further modified with (4-methylcoumarin-7-yloxy)acetic acid by using N,N'-dicyclohexylcarbodiimide for activation. The modified polymers were used for the preparation of UV-crosslinked hydrogels. The influence of the degree of modification and of the polymer chain length on the material properties was investigated, the gelation was studied via photo-rheology under UV light. Authors would like to acknowledge Austrian Science Fund (FWF): M 2805-N (Meitner Programm) for financial support.

[1] Trenor S., Shultz A., Love B., Long T., Chemical Reviews 2004 104 (6), 3059-3078

[2] Chujo Y., Sada K., Saegusa T., Macromolecules 1990 23 (10), 2693-2697

[3] M. Nagata, Y. Yamamoto, React. Funct. Polym. 2008, 68, 915–921.

[4] Kabb C., O'Bryan C., Deng C., Angelini T., Sumerlin B., ACS Appl. Mater. Interfaces 2018, 10, 16793–16801.