Synthesis and Self-assembling of Zwitterion Containing Photozymes
Iva Pashkuleva,1 Johan Benesch,1 Ventsislava Toncheva,2 George Georgiev,2 Rui L. Reis1
Corresponding Author: pashkuleva@dep.uminho.pt
13B’s Research Group, Department of Polymer Engineering, University of Minho, Braga, Portugal and
2Laboratory of Water-Soluble Polymers, Polyelectrolytes and Biopolymers, Faculty of Chemistry, University of Sofia, Bulgaria

Introduction
Photozymes (PZ) are copolymers consisting of hydrophobic co-monomers with chromophoric groups and hydrophilic co-monomers, which impart water solubility [1]. While the chromophoric units determine the light responsiveness of PZ, their amphiphilic nature can be associated with eventual self-organisation resulting in various aggregates. Therefore, the aim of the herein reported studies was to investigate if and how the PZs self-assembled. The influence of different parameters such as PZ polarity and concentration, solution ionic strength and pH on the assembling process in aqueous media was examined.

Materials and Methods

Two photozymes, obtained by random copolymerisation, were used for these studies: NZ (n=0.3; m=0.7; l=0) that does not contain zwitterion and ZI (n=3; m=0.65; l=0.05) with zwitterion unit. The synthesised PZs were characterised by elemental analysis (EA), Fourier transform infrared spectroscopy (FTIR) and size exclusion chromatography (SEC). Their assembling ability was evaluated by Dynamic Light Scattering (DLS) at different aqueous environments (concentrations, pH and ionic strength). Atomic Force Microscopy (AFM) was additionally used to analyse the formed structures.

Results
The FTIR spectra and EA confirmed the success of the copolymerization process and the ratio between the included monomers for both ZI and NZ. No homogeneous size distribution was observed in water solution of NZ. The introduction of zwitterion units (ZI) in PZ macromolecule resulted in formation of aggregates with size of about 30 nm (AFM, DLS). When ionic strength was increased (0.25% KCl), individual macromolecules with an average size of about 10 nm (DLS) were found for both ZI and NZ.

Fig. 1. AFM images of ZI and NZ deposited on mica from solutions with different ionic strength.

Discussion and Conclusions
The obtained results showed that the assembling process for ZI is driven by dipole-dipole intermacromolecule interaction, while hydrophobic assembly interactions are dominant in the case of NZ. In the presence of low molecular weight ions (K⁺ and Cl⁻), a screening effect occurs which disrupts the dipole-dipole interactions between the PZ co-ions (Fig. 2).

Fig. 2. Drawing explaining the concept of reversible destruction of the intermacromolecular zwitterionic dipole–dipole knots.

The assembling process is not influenced by the pH but exposition to light for 1 hr was enough to disrupt the formed knots.

References

Acknowledgments
The authors acknowledge EU support through the project PhotoNanoTech (Contract Number: 033168).