Macromolecules with branched architecture, especially brush-like polymers, due to their unique properties compared to their linear counterparts, have many potential biomedical applications. However, the key problem that scientists are struggling with, considering the synthesis of branched systems for medical industry is the cost of synthesis of functional structures, which is generated by the need to receive ultra-pure products, and thus the effective and simple methods in the preparation of polymer systems in environmentally friendly conditions, using biocompatible naturally-derived substrates are sought. The next important issue considering the application in biomedicine is the synthesis of precise polymer structures with predetermined molecular weights and thus strictly defined properties.

Atom transfer radical polymerization (ATRP) is a process belonging to the versatile reversible-deactivation radical polymerization (RDRP) procedures. The essence of ATRP is formation of an equilibrium between a low concentration propagating radicals and a larger number of dormant species. Compared to conventional free radical polymerization the step of radical generation is reversible and occurs by a dynamic redox mechanism. Furthermore, polymers and biopolymers prepared by ATRP are characterized by narrow molecular weight distributions (MWDs) and control over molecular weights (MWs). Moreover it allows site incorporation of functionalities and preparation of well-defined hybrid composites. This technique has had a significant impact on the development of various branches in biotechnology, mostly because of its extensive applications in the preparation of biomaterials based on polymers. The use of ATRP makes it possible to control polymer topology and obtain various structures, ranging from linear chains, stars, cycles, combs and brushes, up to regular networks. This technique also allows preparation of polymers with controlled composition such as block, graft, gradient and periodic copolymers.

ATRP technique combined with a “core-first” approach is especially privileged in the preparation of architecture polymers from polyphenol compound as naturally-derived cores. “Core-first” utilizes substrates with ubiquitous functional hydroxyl groups prone for modification by appropriate initiator – halogen atoms in the case of ATRP method. Troxerutin, as a polyphenol structure is an excellent candidate for simple modification with polymers using ATRP according to a “core-first” method.

The headline aim of the research project is the optimization of the synthesis of novel naturally-derived stimuli-responsive polymer brushes using low ppm ATRP techniques based on continuous regeneration of catalyst complex, starting from supplemental activation reducing agent (SARA) ATRP utilizing copper as a reducing agent in organic solvent, moving to more environmentally friendly reaction medium – miniemulsion, using activator regeneration by electron transfer (ARGET) ATRP and external stimuli to regenerate catalytic complex, including ultrasonication-induced ATRP (sono-ATRP) in which, under the ultrasonic waves in the aqueous environment, hydroxyl radicals are created constituting the factor leading to the regeneration of Cu (I), without necessity of introducing any additional chemical compound making this technique extremely pure in context to current art of state in low ppm ATRP techniques.

The realisation of the project in particular relies on kinetic analysis of the electrochemical catalytic process (EC’) during reduction of the regenerated $Cu^{II}Br_2$/TPMA in the presence of the received ATRP troxerutin-based macroinitiator (Trox-Br_{10}) and subsequently detailed cognition of mechanism and kinetics of polymerization processes with the use of that brominated macromolecule. In connection with the innovation nature of the synthesized biopolymer and also providing novel information related to mechanism and kinetics of conducted reactions, the realisation of the presented project will certainly lead to development of important scientific domain such as Polymer, Biopolymer Chemistry being a part of the domain of scientific research ST - Science and Technology.

It is assumed that these troxerutin-based brushes will be ensure flow control of substances in and out in connection to significant pH response due to anionic poly(acrylic acid) (PAA) segments and cationic poly(2-dimethylaminoethyl methacrylate) side chains, additionally the macromolecules are nontoxic and biocompatible properties, which undoubtedly allow for wide potential application in medicine as stimuli-sensitive drug carriers. Taking into account the fact that troxerutin is used as a vasoprotective, this modified structure can improve its activity or be a carrier for this structure.