Atom transfer radical polymerization approach (ATRP) techniques are currently one of the most influential solutions in the preparation of precisely-defined polymers with a predetermined structure and specialist purposes with a wide range of potential industrial applications [1]. These methods combined with a “core-first” approach are especially privileged in the preparation of polymers with branched architecture. The phenomenon of these methods is associated with an excellent control over molecular weight (MW), narrow dispersity (MWD) of received polymers and ability to incorporate functionality in specific macromolecule place [2, 3]. The breakthrough in ATRP was the development of techniques with the regeneration of catalyst complex in the form of activator, significantly reducing the catalyst concentration to low ppm. New low ppm catalyst ATRP systems regenerate the activator by the use of a chemical reducing agent and externally controlled techniques [4]. Besides these numerous advantages of ATRP, modern polymer syntheses are searching for facile, biocompatible, cheap, and eco-friendly polymerization solutions for multidisciplinary use, thus naturally-derived substrates, in particular with unique properties, attract increasing attention in polymer sciences.

In response to that a widespread biomolecule – vitamin $B_2$ was selected to serve as a universal and cheap driving force for the synthesis of various polymers by means of variations of ATRP methods. Therefore, the main goal of the project is the investigation of riboflavin (vitamin $B_2$) as a naturally-derived substrate to create a multifunctional molecule playing a few roles simultaneously in the polymerization process, namely as an initiator, photoactivator and oxygen scavenger in the preparation of functional polymer materials with advanced architectures such as polymer brushes, copolymers and polymer stars.

The project is composed of two main concepts. The first one includes an investigation of riboflavin and modified riboflavin as an efficient photoactivator in surface-initiated metal-free atom transfer radical polymerization (rib-SI-metal-free-ATRP). It is expected that the application of “grafting from” methodology will provide an insight into the polymerization mechanism and initiation selectivity. It is planned to design a special reaction setup for rib-SI-metal-free-ATRP in microliter volumes to synthesize advanced polymeric architectures such as homopolymer, copolymer and gradient polymer brushes on flat surfaces. Such miniaturization may help to develop as a cost-effective method for synthesis of functional coatings where only 10-15 μl of polymerization solution will be used to functionalize 1 cm2 of the inorganic surface.

The other concept includes the use of brominated riboflavin as an amphiphilic ATRP initiator and the function of the unmodified isoalloxazine ring of riboflavin molecule in different ways. The main aim is to study the kinetics of various ATRP techniques in terms of a synthesis of the new types of functional brush-like polymers with riboflavin core and poly(meth)acrylates side chains. The initiation functionality of brominated riboflavin will be tested in externally controlled techniques, i.e. simplified electrochemically-mediated ATRP (*se*ATRP) and ultrasound-mediated ATRP (sono-ATRP) with parts per million (ppm) level of catalyst, and photoinduced ATRP with complete elimination of transition metal complex (metal-free ATRP). The main goal of this part is the use of biphasic conditions by using miniemulsion as a reaction medium, polymerizing both hydrophilic and hydrophobic monomer from the amphiphilic initiator, simultaneously, in open-to-air conditions. Moreover, an amphiphilic initiator may allow reduction or complete elimination of additional surfactant in reaction setup. In riboflavin-mediated metal-free-ATRP, the prepared brominated molecule will be examined simultaneously as an amphiphilic initiator and photoactivator, avoiding the use of a transition metal complex.

The project will allow creating the miniemulsion reaction setup with only the riboflavin-based molecule, monomer, and water as a solvent for simultaneous polymerization of two different monomers leading to multicomponent polymers (e.g. zwitterion molecule, pH- and temperature responsiveness in one structure, etc.). The successful project implementation will help to better understand the mechanism of ATRP techniques mediated by riboflavin as a multifunctional molecule for receiving various functional polymeric materials that are in the field of interest of the broad scientific community. It will deliver a facile, selective, oxygen tolerant, and cost-effective method for both modification of various large area surfaces with functional polymers, and preparation polymers with complex architecture.

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