Gaining control of the free-radical polymerization via chemical or physical modification of the macro-radicals has undoubtedly become one of the greatest scientific achievements in the chemistry of polymers of the last twenty years. For this purpose, controlled polymerization techniques (CRP) that give it pseudo-living polymerization features, including stable free radical-mediated polymerization (SFRP), atom transfer radical polymerization (ATRP), and reversible addition-fragmentation chain transfer (RAFT) have been developed. Currently, the dominant trend in CRP methods is striving to reduce and/or eliminate the disadvantages and limitations appearing in them, including the necessity of using toxic reagents in catalytic systems, e.g. organometallic compounds. Recently, photo- and photochemically initiated polymerizations have become the most rapidly developing methods of CRP in response to the growing demand for non-toxic reagents. Due to their versatility, the most important were photo-ATRP and photo-RAFT, which have been successfully adapted for the synthesis of well-defined polymers. Nevertheless, a significant limitation of CRP methods hindering the synthesis of polymers of very high molecular weight is the low concentration of radicals affecting the low reaction rate. In addition, from a wide range of monomers can be distinguished so-called "Less activated monomers" (LAMs), which include i.e. N-vinylpyrrolidone (VP) or N-vinyltriazole (VTA). These monomers, due to their chemical structure (unconjugated vinyl group) are characterized by lower activity and polymerizability in comparison to those with higher activity (MAMs). The above properties make polymerization of LAMs towards classical free radical polymerization (FRP) and CRP difficult, and often it is impossible to obtain high conversions of monomers as well as well-defined polymers with high molecular weights. It is worth mentioning that polymers based on LAMs constitute an interesting group of materials of great importance in biomedical sciences (e.g. poly(N-vinylpyrrolidone), PVP) or electronics and optoelectronics (e.g. poly (N-vinyltriazole), poly(N-vinylcarbazole). It turns out that the increase in the conversion and polymerizability of monomers, including those with steric hindrance, is due to the compression of the system. Moreover, conducting the reaction at elevated pressure greatly increases its rate. In addition, high-pressure methods contribute to a considerable simplification of the reagents, which makes it possible to carry out the reaction without the need for solvents and catalysts. They also allow to limit the kinetic and thermodynamic limiting factors found in CRP methods and to produce polymers of very high molecular weights.

To respond to the expectations of this project, we propose the use of an innovative initiated by light polymerization method including high-pressure classical and controlled radical polymerization of selected LAMs, additionally having steric hindrance and /or existing in the form of monomeric ionic liquids. The selection of the monomers was dictated by their specific physico-chemical properties and potential use as special materials in the biomedical sciences (the polymeric binder of medicament based on PVP) and electronics (conductive polymers based on poly (N-vinyltriazole), where the use of macromolecules with well-defined structure is required. This method is based on the use of high pressure-catalyzed photopolymerization, which has not yet been described in the literature. The main objective of the project will be to determine, based on kinetic data, the most optimal conditions for high-pressure, photo-and photochemical initiated polymerization of selected N-vinyl monomers leading to the production of ionic and non-ionic macromolecules with strictly defined parameters. The project also aims to investigate the effect of high pressure on the polymerizability of monomers containing sterically hindered functional groups and on the physico-chemical properties of resulting polymers. The preparation of polymers of the desired characteristics such as the assumed molecular weight and low dispersity is particularly important in the case of physico-chemical or rheological properties of polymers. It is worth noting that the implementation of the project will allow for the creation of direct relationships between the polymer parameters, e.g. molecular weight and glass transition temperature, conductivity, stress relaxation. An important element of the project will also be the pre-qualification of polymers based on the obtained results as potential special materials for biomedical and electronic applications.