

The main idea of our proposal is to study the impact of high pressure and spatial confinement, implemented by application of the nanoporous materials of controlled size, geometry and functionality on:

1. Step growth polymerization involving different kinds of epoxy and amine hardeners.
2. Ring Opening Polymerization in lactones, such as ϵ -valerolactone, ϵ -caprolactone, γ -butyrolactone, γ -angelica.
3. Radical polymerization of novel, synthesized for the purpose of this project, monomeric ionic liquids.
4. Mutarotation and solid state isomerization involving reactions activated by proton transfer, cis-trans interconversion and finally racemization in selected saccharides (e.g. fructose, sorbose, ribose) and active substances (e.g. glibenclamide, omeprazole, ibuprofen).

The first part of our work is devoted to high pressure polymerization in very important class of monomers. It should be added, that due to special physicochemical properties of produced macromolecules they find application in various branches of industry. It is expected, that application of high pressure during chemical conversion of listed above compounds will enable optimization of the reaction conditions and obtainment of macromolecules of well-defined physicochemical properties, such as molecular weight, PDI, structure, dc conductivity of produced polymers, as well as concentration of isomers in the case of isomerization interconversion. In addition, we also would like to determine constant rates, activation energy and activation volume for the reactions carried out at different T and p. These parameters will be very useful to discuss the mechanism of chemical reactions occurring at high pressures. The other motivation of such studies is to propose a new theoretical model to predict constant rates and activation volume at varying pressures and temperatures. It seems to be crucial to avoid or eventually suppress side reactions and to predict the main pathways of polymerization or isomerization. For this purpose entropic Avramov model, very often used to describe molecular dynamics of glass formers at different T and p, will be applied.

The other part of our project will be devoted to studying the impact of nanoporous materials on the isomerization and polymerization. We wish to determine the influence of varying geometry, functionality and pore diameter on the kinetics and properties of formed polymers, as well as distribution of isomers in the case of polymerization and isomerization. It must be stressed, that nanoporous materials offer unique opportunity to synthesize nanofibers and nanorods of different diameters and properties. Furthermore, such materials can find numerous applications in medical, optical and electronic nanotechnologies. Our studies will be also important in the case of APIs. We would like to verify, is it possible to limit or even suppress mutarotation or isomerization in saccharides and pharmaceuticals by varying functionality and degree of confinement. The outcome of our research may contribute to development of much safer nanoformulations of drugs characterized by enhanced pharmacological parameters. The other very interesting issue we would like to address is the impact of negative pressure, which surely develops in nanoporous materials, on the progress of studied chemical reactions. It is worth mentioning, that many different mechanisms of such reaction are considered. However none of these approaches takes into account negative pressure as another significant variable in controlling progress of chemical conversion. In this context it is worth to remind, that there are reports indicating, that negative pressure inside nanoporous materials is even higher than 80 MPa. Herein one can mention, that our very recent studies on dynamics of glass formers in AAO uniaxial membranes confirm this supposition. It seems to be very important to explain the role of negative pressure on the progress of isomerization and polymerization. It will enable to revise old theories and construct new concepts of chemical conversion in pores.

The final and simultaneously the most risky point of our project concerns pioneering real high pressure studies on polymerization and isomerization under confinement. We expect, that by combination of both variables significant progress in control over chemical reactions will be gained. We are going to determine constant rates, activation energy and activation volume to elucidate the mechanism of these reactions carried out at so extreme conditions. In addition, we plan to study the interplay of both high pressure and degree of spatial confinement on the structure and morphology of recovered products. These research may lead to development of new ways of synthesis of nanopolymers with unique structure and properties.

The planned project, what is worth emphasising, has an interdisciplinary character and covers different aspects of chemistry of materials at high pressures and under spatial confinement. We are going to go much beyond the current state of the art and focus on the description of fundamental properties and mechanism of polymerization, as well as the most conventional chemical isomerization of some classical compounds, including saccharides and APIs undergoing proton activated processes. The main idea of our proposal is to gain as much control over the chemical interconversion and optimizing physicochemical properties, structure and morphology of the recovered products.

Systematic research will surely contribute to progress in basic knowledge and may be useful in synthesis of macromolecules and controlling undesired isomerization of APIs. We are also convinced, that our studies on confined systems may provide strong background to development of new ways of synthesis of polymeric nanofibers and nanowires and safe nanodrug formulations of enhanced bioavailability.