

SUMMARY

This PhD thesis contains the results of systematic research, the main purpose of which was to better understand the influence of variable thermodynamic conditions on the dynamics of glass transition and the kinetics of crystallization of low-molecular substances forming the glassy state. By variable thermodynamic conditions were understood here a modification of the thermodynamic parameters of the system as a result of compression as well as the use of spatial limitations of the order of "nano". It is worth to noting that in both cases it should expect significant changes in density of molecular packing, as well as changes in the nature of molecular interactions, which can influence in a significant way (not necessarily the same) into dynamic properties of the tested materials near the transition glassy as well as their crystallization behavior. The effects associated with density fluctuations are next to temperature effects the key to understanding the glass transition and crystallization processes, because even the phase diagrams of substances are two-dimensional (T, ρ), not one-dimensional. Thus, the application of such an approach to the performed research allowed to look at many issues related to the dynamics of glass transition and attempts to control/modify the tendency to crystallize/vitrify the tested materials in a completely new, more synthetically way.

This work is experimental in nature and is based on the results of research obtained primarily using the dielectric spectroscopy. This method is an ideal tool for studying the molecular mobility of liquids and glasses in a wide range of relaxation times as well as monitoring the kinetics of crystallization or phase transition detection. However, in the context of the conducted research, its main advantage was the relative ease of adaptation to tests conducted in the conditions of elevated pressure reaching even 1.5 GPa (!), As well as geometry limited to the "nano" scale (liquid trapped in nanoporous matrices with a pore size a dozen or several dozens nanometers).

The paper presents how the increased pressure affects the dynamics of the glass transition process and the crystallization process of two model, glass-forming substances (*i*) propylene carbonate and (*ii*) fenofibrate. The most important results that have been obtained include (*i*) showing, in analogy to temperature measurements carried out at atmospheric pressure, the important role of the compression/decompression rate on the tendency to form glassy state/crystallization in the isothermal conditions, and showing that (*ii*) through skillful controlling parameters such as temperature and pressure, or choosing the thermodynamic path is possible to directly affect on the crystallization process and the

obtained products. This will be particularly important, especially in the context of fenofibrate belonging to the group of cholesterol lowering drugs, which shows a rich polymorphism, what which can have a significant impact on the therapeutic effect. In this case, favoring only one selected polymorphic form, or in general, controlling the crystallization behaviors of glass-forming materials using compression techniques can have important application importance.

Just an interesting experimental results were provided by research conducted in limited geometry. First of all, they confirmed the latest scientific reports suggesting that the dynamics associated with the glass transition in a nanoporous medium may be subject to the same principles as supercooled macroscopic liquids. This is especially about the idea of density scaling and isochronal superposition. Nevertheless, the results of the research that was obtained as part of this doctoral dissertation call into question graded in the literature conviction that meeting one of the above rules also means fulfilling the second rule. In turn, studies on crystallization kinetics conducted for liquids trapped in nanoporous matrices showed that with the reduction of the pore size, we observe many significant changes concerning the process of the crystallization process, e.g. changes the shape of the crystallization curve from sigmoidal to exponential, decreases the value of the crystallization rate constant and the Avrami parameter, and shifts towards lower temperatures/higher sub-quench the maximum of crystallization rate constant. Thus, "confined" effects can play also an important role as pressure effects when it comes to the possibility of better and more conscious controlling of the tendency to crystallize glass forming materials.

The obtained results bring a very high cognitive value, especially due to the fact that in the literature there is a lack of such systematic research devoted to behavior of materials forming the glassy state in various thermodynamic conditions. This may be proved by the fact that some of them concerning the influence of spatial constraints on the course of the crystallization process were strongly emphasized in the recent review on the crystallization of amorphous materials by prof. Descamps from France (*Int. J. Pharm.* 542 (2018) 186–195). The results collected during the preparation of the present PhD thesis allow to look at the glass transition and crystallization processes in context of changes not only in temperature/thermal energy, but also density of packing molecules (generated using two alternative strategies, two-dimensional spatial limits of the "nano" and elevated pressure). It is worth noting that only through such a combination it is possible to obtain a coherent and complete description of both considered processes, as well as methods for controlling/modifying the crystallization behavior of materials depending on the application or future applications.