

## ABSTRACT

Polymeric materials, due to their unique physicochemical properties, are widely used in many industries. Understanding their behaviour near the glass transition is of key importance, as drastic changes in the viscoelastic properties occur, and relaxation processes reflecting molecular mobility are observed. The particularly exciting group is polysiloxanes, whose backbone is based on *Si-O* bonds, giving the macromolecule a unique character. Due to the presence of numerous relaxation processes near the glass transition temperature ( $T_g$ ), they are an intriguing object of molecular dynamics research.

This doctoral dissertation presents the results of a study on the detailed analysis of the molecular dynamics of the homopolymer poly(mercaptopropylmethylsiloxane) (PMMS) and PMMS copolymers grafted with various acrylate and methacrylates via a thiol group. The main aim of the research was to elucidate the nature of the relaxation processes observed in the dielectric loss spectra and to determine the influence of the topology and architecture of the polymers on their dynamics under varying thermodynamic conditions. The study used Broadband Dielectric Spectroscopy (BDS) and complementary techniques: Differential Scanning Calorimetry (DSC) and Dynamic Mechanical Thermal Analysis (DMTA).

Based on the results obtained for the PMMS homopolymer, it was shown that the additional  $\alpha'$  process is a *sub-Rouse* relaxation, whose behaviour was similar to the dynamics of *normal-mode* relaxation. This is evidenced, among other things, by the superposition of the slower  $\alpha'$ -process and  $\alpha$ -segmental relaxation regardless of temperature and pressure conditions, as well as by the similar values of activation volume ( $\Delta V$ ) determined for both processes. This evidence provides a strong argument for classifying the  $\alpha'$ -process as *sub-Rouse*.

Studies of PMMS copolymers grafted derivatives of acrylates/methacrylates showed that steric hindrance related to the length and stiffness of the side chains significantly affects the glass transition temperature ( $T_g$ ). For methacrylate-based PMMS copolymers, we can distinguish two relaxation processes ( $\alpha$  and  $\alpha'$ ), while for acrylate-based PMMS copolymers, only one broad relaxation process ( $\alpha$ ) was present. In both cases, the  $\alpha$  process was due to segmental relaxation. The  $\alpha'$ -process, on the other hand, may correspond to partial sub-Rouse molecular movements (due to superposition with  $\alpha$ -relaxation). However, we cannot rule out the possibility that it is related to the relaxation of the stiff methacrylate side group.

On the other hand, studies of three PMMS copolymers grafted with various butyl acrylate isomers revealed that modification of the polymer structure due to grafting significantly affects the molecular dynamics. As the steric hindrance of the graft increases, the glass transition temperature and the width of the segmental process increase. The values of pressure parameters  $dT_g/dp$  and activation volume  $\Delta V$  are significantly higher than for the PMMS homopolymer, which was attributed to the increased steric hindrance. Moreover, the increasing steric hindrance from the grafted side groups limits the ability to form hydrogen bonds.

In summary, the obtained results enabled the identification of additional relaxation processes for polysiloxanes and deepened the understanding of the influence of graft copolymer architecture on their dynamic properties. The obtained results are relevant to the design of modern polymeric materials, especially in applications requiring high control over the dynamics and stability of the material under varying thermodynamic conditions.