

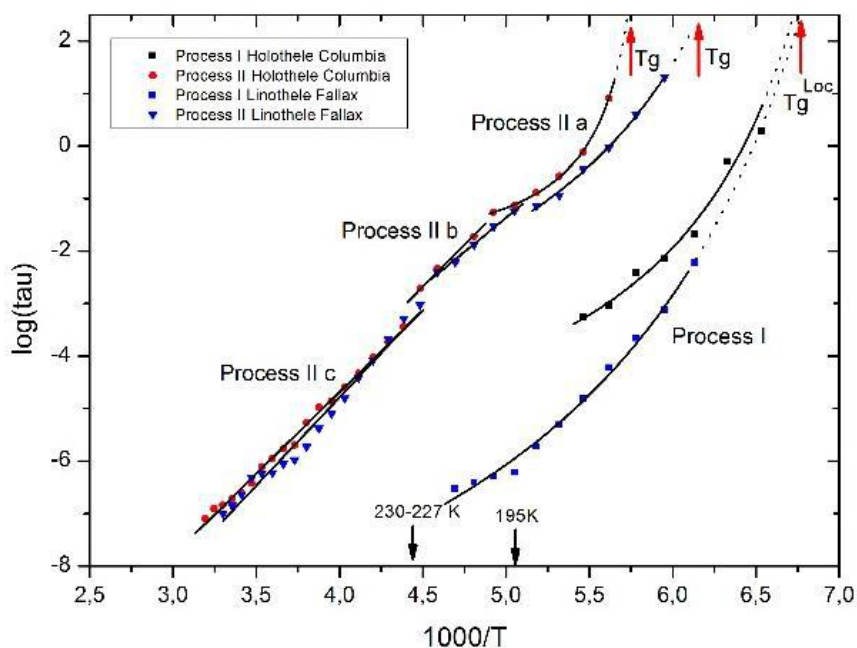
## DIELECTRIC SPECTROSCOPY STUDY OF NATIVE SPIDER SILK: PHASE TRANSITIONS IN PROTEIN CHAINS

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The study of dynamic properties of proteins and water-protein interactions is currently a hot-point for understanding the functionality of protein macromolecular systems. Over 400 million years, spiders have been living on their webs using them as a hunting tool. The vitality of spider silk is ensured by unique composition of repeating amino acids molecules such as glycine, alanine, serine and  $\beta$ -sheets forming nanofibers, followed by self-assemble microfibers. Flexibility and extensibility of spider silk are provided by water molecules confined in silk fibroin act as a plasticizer. In the present investigation, the molecular dynamics of native spider silk have been studied in a wide temperature range using broadband dielectric spectroscopy in the interval of  $10^{-2}$ - $10^9$  Hz for the first time. The water-protein interactions were performed by the temperature-dependent FTIR spectroscopy. It has been found that the water confined in the web plays decisive role in the physical properties of silk fibroin. There are at least two kinds of bonded water in the water-protein chains of fibroins: i) the tight-bond water with amide groups and ii) weakly bond water forming a hydration shell in nanofiber.

The temperature dependence of real part of permittivity exhibit three main anomalies at  $\sim 190$ K,  $\sim 225$ K and  $\sim 315$ K indicating that phase transitions are associated with a change in dipole moment in the water-protein chains. The transition in the region of 190K is associated with a partial softening of protein chains due to the local melting of tetrahedral water molecules confined in the hydration shell. Increasing dipole contribution to the  $\epsilon'(T)$  occurs due to dipolar reorientations as a result of thawing of protein chains.

A considerable change in the  $\epsilon'(T)$ , namely a triggering of strong dispersion, was found in the region of 220-230K in all studied samples of spider silk. This phenomenon indicates that the dipolar water-protein chains at different lengths appear in the silk fibroins at  $T > 220$ K. The temperature dependence of the relaxation times of water-protein molecules have been obtained from the spectra of  $\epsilon''(T)$  using Havriliak-Negami fitting formula (figure). The slowing down of the cooperative motions of water-protein dipoles is associated with glassy dynamics and it results the glass transition temperature ( $T_g$ ) of water-protein molecules at  $\tau = 10^2$ s in low temperature part. Cooperativity of molecular motions break down in the region of 190K due to melting of nano-confined water. Two parts of Arrhenius evolution of relaxation times separated at  $\sim 225$ K have different activation energies. The observed Arrhenius behavior is the evidence of unconstrained molecular motions at  $T > 190$ K. Thus, the acquiring of the structural plasticity and the enhancement of the functionality of webs occur due to the violation of hydrogen bonds of water shell and bonding water at LDL-HDL transition in the physiological temperature range of spidroins.