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External probing characterization in relation to relaxation dynamics:
cis-1,4-poly(isoprene)

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The structural-dynamic state of amorphous systems can be characterized directly by internal probe techniques such as diffraction, scattering and relaxation, e.g., dielectric spectroscopy. In the indirect characterization, external atomistic (o-Ps) and molecular probes may be applied by means of positron annihilation lifetime spectroscopy (PALS) or electron spin resonance (ESR), respectively. Our recent combined PALS and ESR studies on a series of organics with various intermolecular interactions (VdW- vs. H-bonding) [1] and on three cis-1,4-poly (isoprenes) (1,4-PIP) of different molecular weight [2] revealed the mutual coincidences that suggest the common origin behind the crossover effects in the corresponding PALS and ESR responses.

In our contribution we relate the annihilation behaviour of ortho-positronium (o-Ps) in 1,4-PIP 10k to the spin probe reorientation of 2,2,6,6-tetramethyl-piperidinyl-1-oxyl (TEMPO) in 1,4-PIP 10k via PALS and ESR as well as to the electric dipole relaxation dynamics of the pure medium from broadband dielectric spectroscopy (BDS). The o-Ps lifetime over a wide temperature range from 100 K up to 350 K exhibits four regions of different free volume behaviour with three characteristic PALS temperatures: T_g^{PALS}, T_{b1}^{L} and T_{b2}^{L}. These findings are in good coincidence with the characteristic ESR bend effects at T_{x1}^{slow}, T_{x2}^{slow}, T_{50G} and T_{x1}^{fast}, T_{x2}^{fast}. Next, relaxation dynamics of 1,4-PIP 10k as investigated by BDS [3] revealed that the various aspects of the structural relaxation above T_g are responsible for the PALS and ESR crossover effects. Finally, the α-relaxation can be described in terms of the two order parameter (TOP) model [4] with the mutual relationships between $T_m^{c} \cong T_{b1}^{L} \cong T_{x1}^{fast}$ and $T_A \cong T_{b2}^{L} \approx T_{x2}^{fast}$ indicating the common physical origin of the structural-dynamic changes.
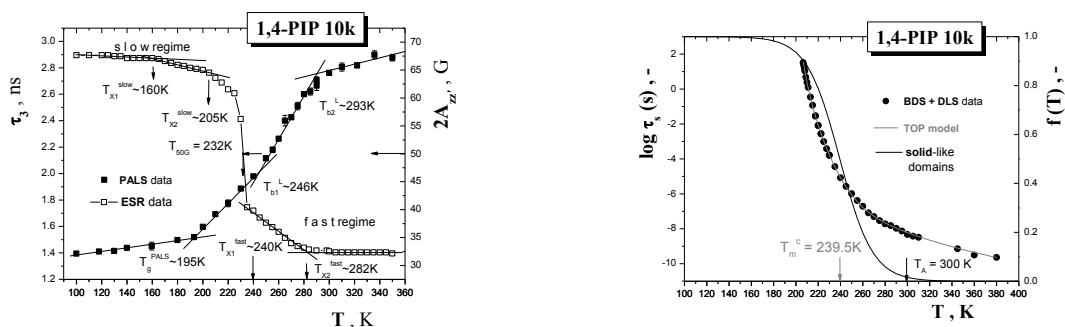

Fig.1. a) Mean o-Ps lifetime (τ_3) vs. spectral parameter of TEMPO mobility ($2A_{ZZ'}$) 1,4-in PIP 10k as a function of temperature b) Structural relaxation time (τ_α) in terms of the TOP model with its characteristics: T_m^{c} and T_A.

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