

PALS and ESR evidence of the dynamic crossover in the amorphous phase of the crystalline *n* - alkanes

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The *n*-alkanes form an important class of organics serving as models for polymers, surfactants and bio-systems. In spite of the simple chemical structure their thermodynamic and structural behaviors are rather very complex. The most significant complicated feature is their slight supercooling ability which leads to hardly achievable amorphous states of the *n*-alkanes. Consequently, basic descriptors of the amorphous *n*-alkanes or the amorphous states of the crystalline *n*-alkanes such as the glass-liquid transition at T_g and the dynamic crossover within the supercooled liquid at T_X require very special experimental and/or evaluation techniques. Thus, the former can be obtained by a vapor deposition technique for the shortest member only [1], while the latter follows as a parameter from the power law fit of the normal (fluid) liquid state viscosity also for the shorter members: *C3-C12* [2]. The aim of this contribution is to present a combined PALS and ESR study of both the annihilation behavior of the external atomic probe, *ortho*-positronium (*o*-Ps) and the related free volume and the reorientation dynamics of another external molecular probe, i.e., one of the smallest spin probe 2,2,6,6-tetramethyl-piperidiny-1-oxy (TEMPO) in typical even and odd *n*-alkanes: *n*-hexane (*C6*) and *n*-undecane (*C11*). In both the ESR and PALS responses, i.e. τ_3 vs. T and $2A_{zz}$ vs T plots, the main solid-liquid phase transition at T_m and for *C11* also the solid-solid phase transition at T_{ss} are confirmed in accord with the two *n*-alkanes studied by this combined approach so far: *n*-tridecane (*C13*) and *n*-hexadecane (*C16*) [3,4]. In addition, both PALS and ESR provide the corresponding evidences indicating the presence of amorphous domains within the crystalline phase of *C6* and *C11* and supporting the existence of the suggested crossover at T_X within the supercooled liquid state of the crystalline *n*-alkanes.

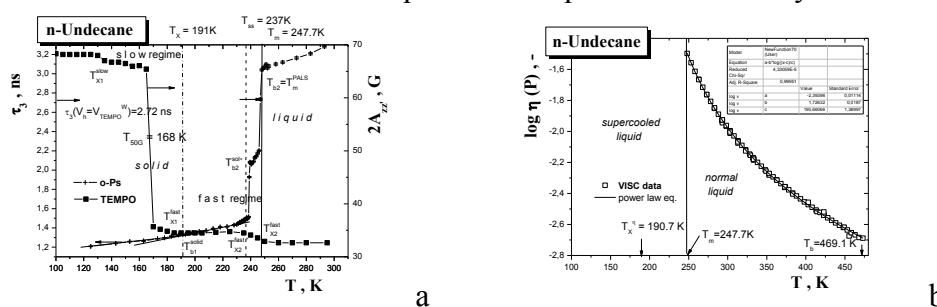


Fig.1. a. Comparison of ESR and PALS responses ; b. Power law fit of the liquid viscosity of *C11*.

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