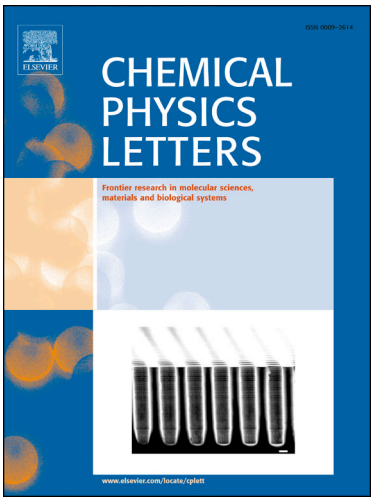

Research paper

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ESR and PALS detection of the dynamic crossover in the supercooled liquid states of *short* and *medium*-sized *n - alkanes*

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Abstract:

A joint study of the spin probe *TEMPO* dynamics by ESR and the annihilation rate of *ortho-positronium* by PALS in four *short*-and *medium*-sized *n-alkanes* is presented. In addition to the usually observed changes in both the reorientation dynamics and size of free volumes at the temperature of melting, T_m, and solid-solid phase transition, T_{ss}, an additional coincidence between the characteristic ESR and PALS temperatures $T_{X1}^{fast} \cong T_{b1}^{sol} < T_m, T_{ss}$ was found. The phenomenological analysis of the viscosity data of *n-alkanes* using the power law equation indicates a presence of locally disordered regions in which the dynamic change occurs at the crossover temperature $T_X \cong T_{X1}^{fast} \cong T_{b1}^{sol}$.

Key words: *n-alkanes*, spin probe dynamics, ESR, ortho-positronium annihilation, PALS, viscosity, dynamic crossover

Introduction

Despite rather simple chemical structure of *n-alkanes*, they exhibit very rich and complex structural-dynamic behaviors consisting in, e.g., the well-known zig-zag trend in the temperature of *solid* to *liquid* transition at melting point T_m^{DSC} with increasing chain lenght ***n.*** On the contrary, to the analogous course of the *solid-solid* transition at T_{ss}^{DSC} is continuous. The *n-alkanes* have been studied extensively in the bulk solid and liquid states by means of variety of standard experimental approaches [1] such as thermodynamic[2], structure-diffraction [3] and structure-molecular spectroscopy [4] as well as various dynamic techniques [5,6] utilizing different macroscopic and microscopic internal probes. The structural-dynamic state of the *n-alkanes* in both the *solid* and *liquid* phases can be also investigated from the microscopic viewpoint via external probing techniques. Two promising ones are based on using atomic-sized probe such as *ortho-positronium* (*o-Ps*) by means of positron annihilation lifetime spectroscopy (PALS) [7-11] and appropriate molecular one such as *nitroxide spin probes*, e.g., *2,2,6,6-tetramethyl-piperidinyl-1-oxy* (*TEMPO),*via electron spin resonance (ESR) [12-14]. The PALS studies have been focused on various free volume aspects of the