

Confinement of Structural Isomers in MCM-41-SIL Matrix as Seen by Extrinsic Probes via ESR and PALS: *n*-Butanol vs. *t*-Butanol

J. Bartoš,^{1*} O. Šauša,^{2,3} M. Vyroubalová,⁴ I. Maťko,² H. Švajdlenková¹

¹*Polymer Institute of SAS, Dúbravská cesta 9, SK-845 41 Bratislava, Slovakia*

²*Institute of Physics of SAS, Dúbravská cesta 9, SK-845 11 Bratislava, Slovakia*

³*Department of Nuclear Chemistry, Faculty of Natural Sciences, Comenius University, Mlynská dolina Ilkovičova 6, SK-842 15 Bratislava, Slovakia*

⁴*Institute of Macromolecular Chemistry of CAS, Heyrovského square 2, CZ-162 06 Prague, Czech Republic*

*E-mail: Jozef.Bartos@savba.sk

The structural-dynamic states of *n*-butanol (*n*-BuOH) and *tert*-butanol (*t*-BuOH) isomers as representatives of a *linear* or *globular* protic polar medium in the bulk and confined in *MCM-41 matrix* obtained from the free volume and phase behaviour using positron annihilation lifetime spectroscopy (PALS) or differential scanning calorimetry (DSC), respectively, together with the spectral properties and related mobility and interaction of the *spin probe TEMPO* using electron spin resonance (ESR), are presented. In the bulk *t*-BuOH, the typical τ_3 vs. T response for strongly crystallizing *globularly*-shaped organics with a stepwise effect in the vicinity of T_m is found. On the other hand, the bulk *n*-BuOH exhibits a complicated course depending on the thermal cycling due to the distinct crystallization ability of the *linear* constituents due to their intermolecular H-bonding. Under confinement, both *n*-BuOH and *t*-BuOH media in the *MCM-41-SIL matrix* were amorphized and heterogenized with larger mean free volume sizes and strong broadening of their dispersion with respect to the corresponding bulk states. In addition, very distinct temperature dependences in τ_3 vs. T/T_g plots with some anomalous effect in a sub-plateau region of the *linear* isomer correlating with the DSC response are observed.

In the ESR experiment, the drastic difference in the most pronounced characteristic ESR temperature marking a transition from slow to fast motion regime with the following relations: $T_{50G}(b) \cong T_m^{DSC}(b)$ for *n*-BuOH against $T_{50G}(b) \ll T_m^{DSC}(b)$ for *t*-BuOH, where $T_m^{DSC}(b)$ is the respective melting point, was found. Further, several changes in the *TEMPO* mobility in both *BuOH media* are related to the numerous *dynamic* and *thermodynamic* transitions as obtained from measured DSC, PALS and literary viscosity data. Finally, the changes in hyperfine splitting constants of *TEMPO* sensitively reflect the *altered* structural-dynamic relationships in both of the confined *BuOH isomers* with close coincidences between all the three characteristic PALS and ESR temperatures indicating the same origin of the underlying processes behind the changes in *spin probe* mobility or the free volume expansion, respectively.