MS024.O04

New developments in surface-enhanced solid-state NMR spectroscopy and their applications

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A key challenge in the development of modern materials and pharmaceuticals is to determine at the atomic scale their structure and dynamics. Recently, Dynamic nuclear polarization (DNP) has developed into a powerful analytical technique to enhance the sensitivity of magic angle spinning (MAS) solid-state NMR spectroscopy of materials and pharmaceuticals.1

In this presentation, we will first present some recent results, where we used molecular modelling in combination with proton NMR spectroscopy under very fast magic-angle spinning (MAS) and DNP surface-enhanced NMR spectroscopy (DNP SENS) to characterise the polymer backbone group conformations and packing arrangement in the high-mobility donor–acceptor copolymer diketopyrrolo-pyrrole-dithienylthieno[3,2-b]thiophene (DPP-DTT). We found that the bulk polymer adopts a highly planar backbone conformation with a laterally-shifted donor-on-acceptor stacking arrangement. The same planar backbone structure and intermolecular stacking arrangement is preserved in the films following solution processing and annealing, thereby rationalizing the favourable device properties of DPP-DTT, and providing a protocol for the study of other thin film materials. 2 DNP SENS NMR enabled high-quality one- and two-dimensional 13C NMR data to be obtained in a few hours for the thin-film samples.

We will then show how high DNP enhancements can be preserved at room temperature by using solvents having a high glass transition temperature. In particular, by dissolving BDPA and TEKPOL in ortho-terphenyl (OTP), enhancement factors of around 80 and 40 were obtained at 240 K (i.e. at the glass transition temperature of OTP) and of up to 10-20 were obtained in the metastable phase at ambient temperature and at both 9.4 and & 18.8 T.3 The method was successfully applied to monitor molecular dynamic transitions in pharmaceutically relevant solid samples, like Ambroxol and Ibuprofen.

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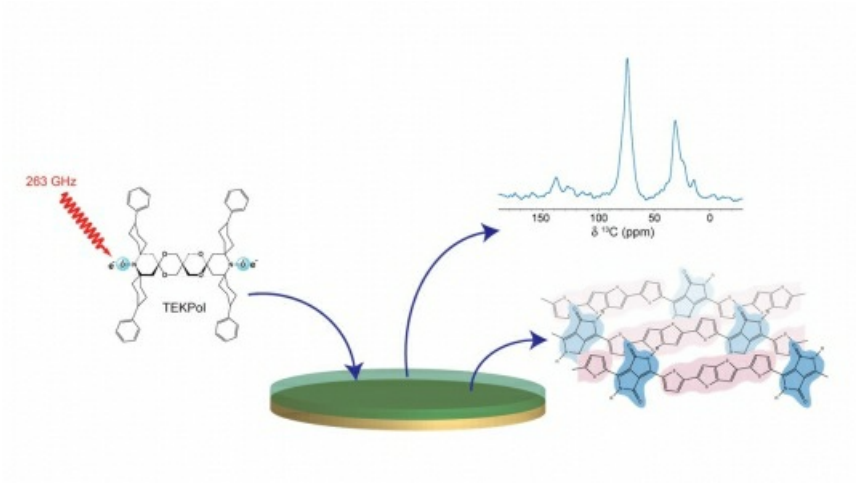

Keywords: DNP enhanced Solid State NMR, Thins films, Dynamics of Pharmaceuticals