Solid State NMR Characterization of Conductive Polyanilines

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Abstract

Different forms of ring deuterated polyaniline with different conductivity have been characterized by solid state deuteron nuclear magnetic resonance.

Quadrupole echo (QE) spectra of all forms of polyaniline consist of a superposition of lineshapes for nearly rigid aromatic rings and a small fraction of rings which undergo fast 180° flips. The intensity of the fast flipping component is temperature dependent and different for conductive emeraldine salt (ES) and non-conductive emeraldine base (EB). This is a manifestation of the different structure and morphology of these polymers.

Simultaneous measurements of QE lineshapes and the relaxation time anisotropies allowed an accurate description of motion in polyanilines. Slow, small-angle libration in an asymmetric cone provided the best description for the "rigid" fractions of EB and ES. The broadening of deuteron QE lineshapes is consistent with the presence of a distribution of cone angles. Relaxation time measurements also reveal a relatively narrow distribution of librational rates for the EB sample. For ES, the magic angle spinning (MAS) spectra show the existence of two resolved signals with different relaxation rates, which are ascribed to microscopic domains with very different electrical properties. The unexpectedly short relaxation time found for nonconductive domains in ES can be explained by the presence of localized, unpaired electrons.

Spin count experiments proved that in highly conductive ES samples, loss of NMR signal intensity occurs not only because of high RF reflectance but also because of irreversible dephasing before signal acquisition due to interactions of nuclear spins with localized unpaired electrons.

Deuteron MAS spectra provided unique information about small frequency shifts. Compared to non-conductive EB, conductive emeraldine salts have an additional manifold of spinning sidebands, which is shifted ~5.8 ppm towards higher frequencies. These shifted sidebands arise from quasi-metallic regions of the sample, where deuteron spins interact with delocalized electrons (Knight shift). The experimental temperature dependence of the intensity of the shifted peak can be explained using models developed for amorphous semiconductors. The observation of a Knight shift has an important consequence for the theory of electrical conduction in polyaniline: it implies that polarons are the charge carriers.