CONDUCTING MATERIALS: STRUCTURE AND PROPERTIES OF POLYANILINE INTERACTING WITH H-PHOSPHONATES

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Polyaniline (PANI), one of the most intensively studied conducting polymers, represents rather a class of materials than a single compound. It is usually prepared by chemical oxidative polymerization. PANI is conducting when it is doped, typically with an inorganic acid. However, such acids are not the only species able to dope PANI. H-phosphonates, $HPO(OR)_2$, are diesters of phosphonic acid and, in contrast to the phosphorus oxoacids and theirs esters previously used for doping of PANI, there is no OH group in their structure and consequently no acidic hydrogen available for interaction with PANI. Even though it is possible to find information that dialkyl H-phosponates act as very weak P–H acids, pK_a values reported to be equal or higher than 20 do not promise ability to interact with non-conducting PANI base form as typical acid. Nevertheless, interaction of PANI base with H-phosphonates proceeds and conductive adducts are formed.

In this contribution, we present that non-conducting PANI base powder interacts with dimethyl H-phosphonate (DMPH), diethyl H-phosphonate (DEPH), dibutyl H-phosphonate (DBPH), and diphenyl H-phosphonate (DPPH) and yields conducting adducts; the highest conductivity 0.23 S cm^{-1} is observed for DPPH. The samples were analyzed by FTIR, Raman, solid-state ^{13}C and ^{31}P NMR, and EPR spectroscopies. We show that the doping of PANI with H-phosphonates is only partial and at least part of DEPH and DPPH molecules preserves the H-phosphonate structure, in contrast with DMPH and DBPH. Information on polaron delocalization and mobility obtained from Raman and EPR spectra correlates: polarons in the PANI adduct with DEPH and DPPH are of higher mobility.