

POLY(p-NITROPHENOL) DERIVATIVES AS OPTICAL pH SENSORS

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Optical pH sensing is often based on colorimetric or on luminescent indicator molecules. The changes of their optical properties are depending on the hydrogen-ion concentration of the sample solution. Because of the proton uptake or release during operation the indicator molecules become charged, that makes them more soluble; therefore their immobilization is a crucial problem of the sensor development. Usually indicator molecules are immobilized into (e.g. via long hydrophobic groups) or onto the surface (e.g. by covalent bound) of a polymeric sensing layer that is in contact with the analyte. In this work 4-nitrophenol group containing polymers were synthesized and tested as promising colorimetric and refractometric pH sensitive materials.

The acid-basic property ($pK_a \sim 7.2$) of 4-nitrophenol (p-NP) makes it useful for many sensing applications: e.g. pH sensing in biological samples, or the construction of optical CO_2 sensors. The visual transition interval lies pH 6-8, its color changes colorless to yellow (max. at 420-430 nm), when deprotonating. However the molecule is readily soluble in water, therefore it was considered to synthesize i) a phenol-formaldehyde (novolak type) polymer and to nitrate it partly in a second step making it pH-sensitive in the proper range; ii) to synthesize p-NP-formaldehyde resin (PPNP) directly, where all of the segments of the polymer are pH sensitive, theoretically.

Two methods were used to prepare the sensing layers: first the pH sensitive polymers were dissolved in ethanol or ethanol/THF mixture and casted on a glass support. According to the second method the polymers were dissolved and mixed with a solution of hydrogel and the layers were made by spin coating. The colorimetric response of the pH sensitive layers were tested by using simple absorbance/reflectance measurement setup where the sensors (placed in a flow through cell) were connected to a fiber optic photometer. To improve the response time thin layers were prepared and measured in ATIR mode (also carried out in a flow through cell), coupling the light in and out by rectangle prisms. The sensing layers were also characterized by using different refractometric fiber optic sensor configurations.

The pK_a of the polymers show a slight decrease comparing to the monomer p-NP. They are practically insoluble in water when protonated, however they become more soluble in alkaline solutions where a poly-anion is formed. The absorption maxima for both polymers found to be similar to p-NP (around 430 nm), while in case of PPNP two new bands appeared at 675 and 750 nm, respectively. Layers prepared with hydrogel showed no leaching when exposed the sensors to alkaline buffers. Among the common sensor properties, such as response time, dynamic range, detection limit, etc., the effect of the polymer to hydrogel ratio and the thickness of the layer on the refractive index changes were also measured and discussed.

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