

## ABSTRACT

(Doctoral Thesis, 2016, Mgr. Tomáš Faulkner, IONIC POLYACETYLENE TYPE POLYMERS AND POLYMER NETWORKS BY CATALYST FREE QUATERNIZATION POLYMERIZATION)

The composition and structure of a series of ionic  $\pi$ -conjugated poly(monosubstituted acetylene)s prepared via catalyst-free quaternization polymerization (QP) of 2-ethynylpyridine (2EP) activated with equimolar amount of alkyl halide [RX = ethyl bromide, ethyl iodide, nonyl bromide and hexadecyl (cetyl) bromide] as a quaternizing agent (QA) have been studied in detail. The performed QPs gave ionic polymers well soluble in polar solvents, with approximately half of pyridine rings quaternized, which implies that also non-quaternized monomers were involved in the process of QP. The configurational structure of polyacetylene main chains was suggested based on  $^1\text{H}$  NMR, IR as well as Raman (SERS) spectral methods. The QPs in bulk gave more expected irregular *cis/trans* polymers while the QPs in acetonitrile solution gave high-*cis* polymers.

A series of prepared symmetrical bi-pyridylacetylene based monomers has been polymerized via QP approach resulting into a series of new ionic  $\pi$ -conjugated poly(disubstituted acetylene) type materials. It is therefore obvious that the mechanism of quaternization activation frequently applied on monosubstituted pyridylacetylenes is efficient also for the polymerization of disubstituted bi-pyridylacetylenes. The structure of resulting materials can be easily tuned via the selection of QA. When monofunctional benzyl bromide was applied the linear ionic  $\pi$ -conjugated polyacetylene type polymers were obtained. When bifunctional 1,4-bis(bromomethyl)benzene was applied, the ionic polymer networks were obtained. The network structure is formed by interconnected  $\pi$ -conjugated polyacetylene type chains and the ionic alternating chains. The degrees of quaternization of prepared materials ranging from 0.27 to 1.20, which implies that (i) also non-quaternized bi-pyridylacetylene monomers are involved in the QP process and (ii) the structure of monomer (mainly the positional isomerism of N atom of pyridyl groups) as well as structure of QA affect the resulting degree of quaternization. Owing to the ionic nature, all linear polymers were well soluble in common polar solvents. Both linear polymers and polymer networks exhibit photoluminescence, furthermore, polymer networks prepared from *para*-pyridyl based monomers strongly emit in visible region. Due to the highly cross-linked structure, polymer networks also shown moderate  $\text{CO}_2$  adsorption capacity up to  $13.6 \text{ cm}^3 \text{ g}^{-1}$  (STP) and exceptionally high ethanol vapor capture capacity up to 24.5 wt% (293 K).