

Abstract

New procedures for preparation of polyacetylenes with highly luminescent naphthalimide groups that might be potentially utilized in optoelectronics and sensors are developed within the framework of present doctoral thesis. The procedures provide luminescent *a)* linear polyacetylenes that can be processed from solutions, and *b)* mesoporous network polyacetylenes with high pore volume.

Two paths to soluble polyacetylenes are used: *(i)* copolymerization of ethynyl-functionalized naphthalimide (monomer **PN**) and a monoethynyl aromate catalyzed with [Rh(nbd)acac], and *(ii)* modification of poly(disubstituted acetylene)s carrying ω -chloroalkyl pendants involving the exchange of chlorine atoms for azido groups and subsequent “click”-reaction of Huisgen type of azido groups with ethynyl groups of **PN**.

The **PN** does not homopolymerize but copolymerizes with ethynylaromates. The highest possible molar fraction of the **PN** units in copolymers is of 0.5, which suggests the absence of **PN** dyads or longer sequences in copolymers and the alternating arrangement of **PN** units in the copolymers of the composition of 0.5. Surprisingly, ethynylarenes that give insoluble homopolymers gave soluble copolymers with **PN**.

The modification procedure requires knowledge on the effect of the monomer structure symmetry and substituent bulkiness on its polymerizability and solubility of resulting polymer. This study made with new diarylacetylenes revealed negative effect of the structure symmetry on the solubility of linear polydiarylacetylenes that can even cancel solubilizing effect of the attached alkyl groups. Therefore, the soluble luminescent polymers have been exclusively prepared by modifications of polymers of asymmetric monomers carrying 4-chlorobutyl pendants. These precursor polymers were also modified by the reaction with *N*-methylimidazole giving novel conjugated polyelectrolytes that are soluble in green solvents, including aqueous methanol (50 % by vol.), but not in pure water. Although the modification procedure is more work-demanding, the resulting polymers have the advantage of higher stability in air compared to the copolymers of monosubstituted acetylenes.

The luminescent mesoporous networks prepared by copolymerization of **PN** and 4,4'-diethynylbiphenyl with [Rh(nbd)acac] catalyst shows a very high specific surface of ca 1 000 m²/g (BET).

All prepared copolymers show luminescence emission originating from **NP** type units which proves the excitation energy transfer from their main chains onto pendent naphthalimide moieties. Extremely high Stokes shift (up to 13 700 cm⁻¹) is observed if the luminescence is excited with the light beam absorbed by polymer main chains.

Keywords: conjugated polymer; coordination polymerization; modified polymer; luminescence; naphthalimide; network polymer; polyacetylenes; polyelectrolytes.