

**REVIEW OF THE PHD THESIS SUBMITTED BY
MGR. RADOSLAVA SIVKOVA**

**“SYNTHESIS AND CHARACTERIZATION OF NEW POLYMERS OF SUBSTITUTED
ACETYLENES”**

The PhD Thesis of ing. Radoslava Sivkova is concerned with the synthesis and characterization of highly luminescent and soluble substituted polyacetylenes with pendant fluorophore groups, mainly of the naphthalimide type. The prepared products display a high luminescence efficiency, while the excitation of the fluorescence is possible in a broad range, due to energy transfer from the conjugated (practically non-luminescent) backbone to the pendant fluorophores, which additionally can also be excited by their own absorption. In addition to linear soluble polyacetylenes, structurally closely related rigid, non-swelling and highly fluorescent networks were obtained, which display micro- and meso-porosity.

The topic and context of the PhD Thesis is very attractive: Conjugated polymers offer a number of applications in the field of electronics, electro-optics (OLED, FET-transistors, photovoltaics), or sensors.

In the course of work on her PhD Thesis, ing. Sivkova prepared 8 new monomers based on mono- and di-substituted acetylenes, as well as a number of homopolymers and copolymers based on newly synthesized, as well as on commercial acetylene monomers. In the first stage of her work, ing. Sivkova studied catalyst selectivity (tantalum and tungsten catalysts), as well as the effects of substitution symmetry (also incorporation of structurally related but different co-monomers) on the solubility of the final products, poly(disubstituted acetylenes). The asymmetric substitution of the semi-rigid polyacetylene with bulky rigid groups led to a dramatic product solubilisation (in contrast to linear alkyl pendant groups). In some of the copolymers, aromatic fluorophores were introduced as side chains. In the second stage of the Thesis, the incorporation of a highly efficient newly synthesized naphthylimido-based fluorophore as pendant group was pursued, via post-polymerization modification of some of the soluble co-polymers prepared previously, which contained chloroalkyl side chains (as naphthylimide is not tolerated by the tantalum and tungsten catalysts). The modification proceeded via exchanging the Cl atoms for azide groups, and finally by click reaction with the (acetylene-functional) naphthylimide derivative prepared in this work. The polyacetylenes with chloroalkyl pendant groups were also modified by reaction with methylimidazole, which yielded polyacetylenes with ionic methylimidazolium pendant groups, which displayed solubility in protic solvents and also in the 1:1 methanol-water mixture. In the final part of the work, ing. Sivkova polymerized mono-substituted acetylenes using a rhodium catalyst, which is highly tolerant to pendant chemical functions, and thus was able to incorporate directly the acetylene-functional naphthylimide derivative into the polyacetylene backbone, in co-polymers which were soluble due to different substituents on the co-monomers. In a similar way, a rigid fluorescent polyacetylene network was prepared by incorporating an additional diacetylenic co-monomer. This non-swelling polymer network was found to display a considerable micro- and meso-porosity (up to 1000 m²/g), which might be of interest for potential applications in the field of sensors. The monomers and polymers were extensively characterized by SEC chromatography, ¹H- and ¹³C-NMR, IR and Raman spectroscopy, elemental analysis, as well as by recording adsorption/desorption isotherms in the case of the porous networks. The electrooptical properties were analysed by UV/Vis absorption spectroscopy and by emission spectroscopy. Among the most interesting findings of the latter methods was the proof of

efficient excitation energy transfer between the polyacetylene backbone and the pendant fluorophore groups, as well as the absence of solvatochromism in the polyacetylenes with ionic pendant groups.

As part of work on her PhD Thesis, ing. Sivkova carried out a considerable amount of synthesis work, complemented by systematic characterization. The results were published in four scientific papers which appeared in well-respected journals (2 papers as first and corresponding author, 2 more as important co-author). The Thesis is generally well-written, occasional typographic errors or stylistic imperfections can be found, but they do not cause any misunderstanding by the reader. The synthesized products are very attractive, and the conclusions concerning the synthesis chemistry, as well as the structure-property relationships in the products, are logical and well-supported by experimental evidence. The Figures and Schemes also are of good quality.

Recommendation

The submitted PhD Thesis, the results of which appeared in four papers, clearly shows, that ing. Radoslava Sivkova can work as a self-reliant and efficient researcher, and that she can resolve demanding research projects, and also successfully present her results. Hence I clearly recommend the PhD Thesis of ing. Radoslava Sivkova for defence, and as the basis for granting her the scientific title PhD.

in Praha, August 29, 2016

Dr. Adam Strachota, PhD

Comments / Questions

- 1) In view of the discussion of the polymerization chemistry of the different polyacetylenes, it would have been useful to depict more detailed schemes of the of the catalysis mechanism for the employed Ta-, W- and Rh-catalysts.
- 2) p. 25: In the case of the M0/M1 copolymerization, a maximum content of 50% (alternating) of the less reactive M1 co-monomer can be achieved. Could this be explained by Cl-W interaction (Cl from M1)?
- 3) A strong MW degradation was observed after click attachment of the naphtylimide pendant groups. What would be the eventual chemistry of degradation by Cu^+ ions?
- 4) Could you provide a tentative explanation of the blocking of Cl substitution (chlorobutyl pendant groups) by neighbouring azido groups?
- 5) Would be a click crosslinking using azido-modified polymer and the diacetylene M9 promising?
- 6) How strong was the change in the oxidation stability, when going from the Ta- and W- catalysed polymers (poly-disubstituted) to Rh-catalysed products (poly-monosubstituted)?
- 7) Does the excitation energy transfer (PA chain \rightarrow fluorophore) occur through space or via orbital overlap? Would it be possible to achieve – in continuation of this work – a white emission (e.g. multiple fluorescence peaks in block copolymers)?
- 8) Were the ionic-functionalized polymers also soluble in EtOH/water?

Technical remarks:

p.46, L.4 from bottom: “P(PN/M3)” \rightarrow “... PN1 ...”

p.56/57: text repetition: the short paragraph which crosses from p. 56 to p. 57 repeats again on in identical form on p. 57.

p.58, L.3 from top: “P(PN/M4) ... P(PN/M5)” \rightarrow “... M5 ... M6 ...”

p.60, in Table 11: all “M8” \rightarrow “M9”