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PhD REPORT

From	**Prof. Majda ŽIGON**
Position	**Scientific Counsellor**
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On the PhD manuscript entitled:

MATERIALS CONTAINING CONDUCTING POLYMERS

Presented by	**Ms. Natalia BLINOVA**
At	**Charles University in Prague, Faculty of Science, Department of Physical and Macromolecular Chemistry**
Supervisor	**Jaroslav Stejskal, PhD.**

The PhD Thesis of Ms. Natalia Blinova focuses on the preparation of various morphologies of conducting polymers, preferentially polyaniline (PANI), the control of conductivity, and the understanding of the chemistry of aniline oxidation. Intrinsically conducting polymers such as PANI, polypyrrole (PPy), polythiophene and their derivatives are among the most important and widely studied conducting polymers due to a good combination of properties, relatively simple and inexpensive synthesis, and many potential applications in various fields. PANI probably has the best combination of properties such as conductivity and stability, however, a serious shortcoming is poor processability due to its insolubility and infusibility what makes its application difficult. This weakness can be somewhat overcome by preparation of better soluble substituted PANIs, colloidal dispersions or preparation of nanostructures. This PhD Thesis is devoted to better understanding of various effects on the synthesis of PANI of various morphologies as well as of their specific properties important for potential applications.

The contents of the PhD Thesis is divided into three parts. The first one (A) is devoted to the synthesis, i.e. the preparation of PANI in aqueous solutions of phosphoric acid at various experimental conditions, a comparative study of the preparation of PANI and PPy, and the oxidation of aniline by silver nitrate producing PANI/Ag nanocomposites. The second part (B) reports on a new approach to the synthesis of PANI with reactants separated either by semipermeable membrane or gel to demonstrate the concept of coupled PANI-assisted redox reaction by means of transport of electrons and protons through conducting PANI membrane. Similar approach was used to modify polystyrene latex with a surface PANI layer. The third part of the PhD Thesis (C) comprises the systematic studies of PANI properties such as conductivity, thermal and chemical stability, doping with iodine etc.

In the first part Ms. Blinova first systematically studied the synthesis of PANI with various concentrations of phosphoric acid, from 0,2 to 4 M (A1). The highest conductivity of PANI, 15.5 $S \cdot cm^{-1}$, was obtained at 1.0 M concentration. Possible explanations for higher

content of phosphoric acid in PANI and its lower conductivity at higher concentrations of phosphoric acid are the protonation of both imine and amine nitrogens, the formation of polyphosphate counter-ions, or adsorption of phosphoric acid in PANI. FTIR spectrometry was used to analyze the molecular structure, which was independent of the concentration of phosphoric acid. Thin films were prepared on the glass substrate while colloidal dispersions were produced in the presence of PVP in 0.2 – 3 M of phosphoric acid.

Comparative study of the preparation of PANI and PPy (A2) was performed in 0.2 M hydrochloric acid and in different concentrations of phosphoric acid with an oxidant ammonium peroxydisulfate (APS) and showed similarity in chemistry. Optimum stoichiometry between oxidant and monomer was 1.25 in both cases, however, the oxidation of pyrrole was faster and without an induction period, typical of aniline oxidation. Both PANI and PPy were protonated by partly by sulfuric acid originating from APS and partly by phosphoric acid. The extent of the latter increased with its increasing concentration. The conductivity of PPy ($10^{-2} – 10^{-1}$ S·cm^{-1}) was for one to two orders of magnitude lower than that of PANI (10^{0} S·cm^{-1}) and was the highest at the oxidant-to-monomer ratio 1.1, while conductivity of PANI was the highest at the ratio 1.3. Conductivity of PANI was contrary to PPY practically independent of the acid concentration while that of PPy decreased with increasing concentration of phosphoric acid.

The use of silver nitrate as an oxidant for aniline oxidation has not been reported yet. It was performed in aqueous nitric (A3) and acetic acid (A4) and resulted in PANI/silver composites with around 70 wt% Ag. However, the reaction time was long, at least two weeks, and, as suggested by FTIR and TGA, mainly oligomeric species were formed, especially at high acid concentrations. When prepared in nitric acid, Ag was in the form of nanoparticled about 50 nm in size, and flakes, while in acetic acid it was in the form of clusters of nanoparticles (30-50 nm), nanowires or nanorods coated with PANI, or marble-like textures. In the first case, PANI exhibited nanofibrilar morphology, i.e., nanofibers that constitute elongated brushes, and also some nanotubes with inner cavities of various diameters. The conductivities of composites ranged from 10^{-1} to 10^{3} S·cm^{-1}, and were related to the presence of various morphologies of PANI and Ag.

The second part of PhD thesis (B1 – B3) focuses on the synthesis of PANI with reactants separated by a semipermeable barrier (PANI membrane, gelatin gel, PANI surface layer on polystyrene latex particles). These experiments are based on the concept of coupled PANI-assisted redox reaction. By formation of PANI without a direct contact of reactants they give evidence of transport of electrons, protons and ions through a semipermeable barrier. Molecular structure, molecular weights and conductivities were similar to PANI prepared by conventional procedure.

The third part of PhD thesis (C1 – C4) encompasses the research work of the candidate by systematic studies of PANI properties, important for potential applications, such as stability of PANI dispersions (C1), control of conductivity and contact angles by partial protonation (C2), doping with iodine (C3), and mixed electron and proton conductivities of PANI films in aqueous solutions of acids (C4).

Although a very detailed work has been done some questions still arise that can be resolved during continuation of this research. (i) The preparation of PANI/Ag composites is a novel approach; it still needs optimization of experimental parameters to obtain well defined morphologies and properties. (ii) Determination of PANI molecular weights would be advisable. (iii) In the part B model experiment(s) could be done to support the proposed explanations. (iv) What was the morphology of semipermeable PANI membrane?

In summary, research achievements of Ms. Natalia Blinova in the frame of her PhD Thesis are valuable contributions to the field of conducting polymers. The systematic studies result in new knowledge that is interesting from both basic and applied viewpoints and is very important for further development of this field. The original contribution of the presented research to the field of polymer science is crucial in designing the tailor-made polymers and polymeric materials for specific applications. Though the PhD work covers a broad range of topics it is written clearly, with sufficient theoretical background, and relevant discussion and conclusions for each part. The research results were extensively published: nine papers were published in international scientific papers, one paper has been accepted for publication and one manuscript was submitted.

As a conclusion, it is my pleasure to express a positive opinion for a presentation of the doctoral work by Ms. Natalia Blinova in order to be awarded a PhD degree from the Charles University in Prague.

Ljubljana, September 16, 2009

Prof. Majda ŽIGON

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