

**Report on the Ph.D. thesis of Ms Natalia Blinova:**

***"Materials containing conducting polymers"***

presented to Faculty of Science, Charles University in Prague,

The Ph.D. thesis prepared by Ms N. Blinova is related to one of the most important groups of materials discovered in recent years - conductive polymers. During last two decades these materials found many applications in electronics and photonics, and they become extremely important with a recent concept of "plastic electronics" that allows to combine properties of polymers (low cost of production, easy processing, capability of tailoring for particular application, good mechanical properties, low weight, *etc.*) with electronic and photonic functionality.

Particularly, polyaniline (PANI) seems to be an important candidate for large scale industrial applications due to its good chemical stability and high electrical conductivity. Indeed, there are an increased number of applications in which PANI is used, as electrodes, electrical sensing, electromagnetic shielding or corrosion protection. Although this polymer is known for more than 100 years and its preparation seems to be relatively simple, the mechanisms behind the synthesis are very complex and the polymerization chemistry deserves extended research. Better understanding of the polymerization mechanisms is needed in order to better control the polymer morphology and related electronic properties. From this point of view the submitted work is very actual and the reported results have a crucial importance and major potential impact on possible applications.

The work is focused on three major topics: (i) systematic study of synthesis of various morphological forms of PANI (powders, colloidal dispersions and thin films), (ii) synthesis of PANI in conditions of spatially separated reactants, and (iii) study of physical properties of PANI related to potential applications. Some achievements reached within this work have a principal scientific value for the subject. Particularly, I find extremely interesting the results on the polymerization with separated reactants, the developed procedure of precise control of polyaniline conductivity and contact angles by partial protonation, and the oxidative polymerization of PANI using silver nitrate with simultaneous formation of Ag nanoparticles/PANI nanocomposite.

The submitted Thesis consists of nine published papers, additional one paper accepted for publication and one just submitted, and it is accompanied by an extensive part with summary, comments and discussion of the results. Besides two papers on measurements of physical properties of PANI, in all other publications Ms Blinova is listed as a first author. Hence, her major contribution to the work may be assumed. The shown papers appear in high quality international journals, most having high impact factor, and they were subjected to a review process. That proves an excellent quality of the performed work. The comments are written clearly in a very readable way and, as far as I can judge, with a very good English style. This part contains rather brief introduction, the results are well summarized and discussed with a references to the most relevant papers known from the literature. Certainly, detailed description of experiments can be found in the enclosed copies of the author's papers.

From the formal point of view I found only few grammatical or spelling errors and one major mistake in the misleading reference to the proper Figure 18 on the page 29.

There are following questions and comments to the work:

1. On the page 11 there is written that the template added to the reaction mixture affects the polymerization through changes of pH. How can it be explained?
2. The polymer shown in Fig 12 was directly polymerized on the TEM grid? If not, how was it deposited?
3. The effect of conjugation length and defects concentration on one side, and degree of crystallinity on the other side, on the interchain and intrachain mobility is primarily just reversed than described on page 14, although both effects are mutually interconnected.
4. The term "hopping" is not generally equivalent to "phonon-assisted tunneling" as it is claimed erroneously on page 15.
5. The silver nanoparticles content in the Ag/PANI composites is probably well below the percolation threshold. On the other hand, the electrical conductivity of composites reported on page 30 is relatively high and even showing a metallic behavior. Is there any explanation of this behavior? It could be perhaps explained by an inhomogeneous distribution of Ag nanoparticles and formation of conductive pathways already at very low Ag concentrations.
6. The effect of daylight on the oxidative polymerization of aniline was reported (Polymer 50, 2009 p. 53). What is the mechanism of this phenomenon? Does light affect the polymerization from the beginning of the reaction or it is observed later when some nanoparticles with metallic behavior are already created. Was any photoinduced charge transfer observed in the system or reported in the literature?
7. The stability measurements of polyaniline dispersion in water reported on page 41 was performed at 105 °C. What was the boiling point of the mixture? Was any increased pressure applied or a salt added to the system for the stability measurements?

I can conclude that the reviewed thesis contains interesting and valuable new results, properly described and deeply analyzed by the author. The high level of the research performed by Ms Blinova is documented by the number of her papers accepted in recognized international journals and the comments shown above should not decrease the evaluation of its quality.

I fully recommend to accept the submitted work of Ms Blinova in its present form as her PhD thesis for the defense examination.

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