

## **POLYMER INSTITUTE**

SLOVAK ACADEMY OF SCIENCES Dúbravská cesta 9 845 41 Bratislava SLOVAK REPUBLIC

## Referee's comment of PhD thesis submitted by Patrycja Magdalena Bober entitled "Materials combining conducting polymers and noble metals"

Submitted doctoral thesis of **Patrycja M. Bober** contributed to traditional research of conducting polymer based materials and hybrids at Institute of Macromolecular Chemistry, AS CR, in the group of Dr. Jaroslav Stejskal. The thesis deals with the preparation of polyaniline (PANI) - silver hybrids when aniline monomer was oxidized with silver nitrate in acidic aqueous medium producing polyaniline—silver composite. The influence of different organic acids on yield and structure of prepared materials was studied, because the oxidation of aniline with silver nitrate is slow and takes over several months to get a reasonable yield. An addition of a small amount of *p*-phenylenediamine, or co-oxidizing agent, ammonium peroxydisulfate, was studied with the aim to accelerate the polymerization reaction and preparation of materials with high electrical conductivity.

From this point of view is the topic of PhD thesis actual, and can bring new knowledge, or it can be inspiration for the work of other group, as shown already by citations of published papers by P. Bober et al. The topic is rather complex, because the most efficient methods for obtaining composites on the base of PANI-Ag has to be find.

Theoretical introduction of the thesis is written clearly and provides information about the most studied conducting polymers, especially about polyaniline, its synthesis, with the summarization of its oxidation and protonation forms. Synthesis of polyaniline is described in details and application of this conducting polymer as well as applications conducting polymer-noble metals composites is summarized. The author cited 121 original scientific papers published in the last decade, but I will appreciate to cite some important review papers about PANI synthesis, properties and application.

The **Chapter 2 Aims of the study** is clearly written with detailed description of the thesis aims.

I have also some comments and questions to PhD thesis.

- 1. Part 3. Experimental techniques for characterization of polyaniline—silver composites, usually type of equipments are also added into this part.
- 2. In the part 1.3. **Conducting polymers-noble metals composites** you mentioned, that conducting polymers—noble metals composites can be prepared by five basic ways. Which one from these possibilities is the most suitable for preparation of PANI-Ag composites with the highest conductivity? Can you also compare their advantages and disadvantages?

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- 3. Your conclusion concerning the polymerization using acetic and formic acids solutions as reaction media is that PANI–Ag composites are inhomogeneous. Explain this more exactly, it was only mixture of small and big Ag particles you found? Are Ag particles visible in the sample?
- 4. The oxidation of aniline with silver nitrate is slow and takes several months to obtained reasonable yield. You used chemical ways for the acceleration of this reaction. Can you compare your approach and results with the other techniques as mentioned in literature, heating, ultrasound, or UV-Vis irradiation?
- 5. From obtained results you know how to prepare hybrid materials with desirable conductivity, morphology, amount of silver, etc. As shown from TEM study, prepared materials are in the form of nanoparticles or microparticles. Did you measure their specific surface area? Will you use these PANI-Ag hybrids for future study sensoric properties, or for other application?

## Conclusions

The aims of submitted PhD thesis have been fulfilled. New types of "Materials combining conducting polymers and noble metals" were developed and discussed in the context of nowadays knowledge.

The author of submitted thesis published six publications in international scientific journals with high impact factor, and other four papers were not included in the thesis. She presented outcomes of her research also in various international conferences. She showed that is able to carry out the research in specified direction, to work within international community, but also to evaluate results and create corresponding conclusions.

Therefore, after answering questions and successful defence of the thesis, I recommend to award **Patrycja Magdalena Bober** the degree

"Philosophiae doctor".

Bratislava, April 29, 2013

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