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Report on the PhD Thesis entitled  
**“Materials combining conducting polymers and noble metals”**  
presented by  
**Patrycja Magdalena Bober**  
to the Faculty of Natural Sciences of Charles University in Prague

The thesis of Patrycja Bober is of interdisciplinary character, combining elements of materials chemistry, polymer chemistry and materials science. More precisely, the main goal of the thesis was the elaboration of nanocomposites consisting of a conducting form of polyaniline and a percolating network of silver nanoparticles of different morphological features. The thesis could be considered as a part of a broader research program of the research group led by Jaroslav Stejskal and Miroslava Trchova from the Institute of Macromolecular Chemistry of the Czech Academy of Sciences in Prague, and directed to the elaboration of new polyaniline-based functional materials. At present, this Prague team can be considered as the most active in Europe research group working on polyaniline.

The thesis consists of six papers and a 39-page comment, written in English. In five of them Patrycja Bober is the first author, in one – the second author. In addition Patrycja co-authored four additional papers, not included into the thesis, which are related to the preparation of polyaniline-montmorillonite composites and polymerization of *p*-phenylenediimine. This record is outstanding, even taking into account that in the past two decades the number of papers published by PhD students in the framework of their dissertations significantly increased.

Large fraction of the research described in the thesis is devoted to the elaboration of the reaction medium leading to the composite of optimum morphological features and the highest conductivity. The other factors which are being taken into account are the costs and availability of the reagents and the time of reaction. First trials, although yielding promising

results, suffered from extremely long reaction times (over 2 weeks) and problems with appropriate purification of the obtained nanocomposites. In particular the nanocomposite preparations from aniline and silver nitrate in acetic acid yielded a three component mixture consisting of polyaniline, silver nanoparticles and silver acetate, whose presence was undesirable for many reasons. It quickly became clear for Patrycja that the polymerization rate is limited by the initiation step and the improvement in the kinetics can be reached only by the modification of the initiation center. She solved the problem by using a small admixtures of *p*-phenylene diamine, a compound known to promote both chemical and electrochemical polymerization of aniline. By applying this small modification in the reaction medium composition she was able to reduce the polymerization time from several days to several minutes (*Macromolecules* 2010).

In parallel she tested selected carboxylic and sulfonic acids as components of the reaction mixture. Although she obtained morphologically interesting nanocomposites in formic acid solutions, namely silver nanowires coated with polyaniline, no improvement in the reaction rate was observed and the conductivities of the resulting composites were lower than those of composites obtained in acetic acid solutions (*Reactive and Functional Polymers*, 2010). Patrycja then started to test four sulfonic acids as components of the reaction medium, namely methanesulfonic acid, toluenesulfonic acid, camphorsulfonic acid and aminosulfonic acid. Only the first one yielded composites of metallic-type conductivity, although of lower values than the conductivity of nanocomposites prepared in acetic acid solutions. The paper describing this research (*Electrochimica Acta*, 2011) presents solid research, professionally described in which the preparative work is supported by a detailed characterization of the product using several complementary techniques involving UV-vis, FTIR and Raman spectroscopies, thermogravimetry, and transmission electron microscopy. Still few points require some clarification. In Her first papers Patrycja Bober assumed that nitrate is the only anionic species compensating the positive charge in the obtained salt form of polyaniline. This was a reasonable assumption in the case of nanocomposites obtained in carboxylic acid solutions, which are weak acids. Moreover, it reasonably agreed with the results of the thermogravimetric determination of the silver content in the sample. This may not be the case for composites prepared in the presence of sulfonic acids, which are strong acids. Co-existence of two type of anions in polyaniline matrix can therefore be postulated or even the presence of sulfonic anions as the sole counterpart neutralizing the positive charge of polyaniline. Elemental analysis would be of help here since the determination of N/C and N/S ratio could shine light on the nature of the charge compensating anions in polyaniline and on

the protonation level which is of crucial importance for electrical properties of polyaniline. Moreover, it could help in clarification of the differences observed in the Ag content between the composites obtained in the presence of methanesulfonic acid and camphorsulfonic acid.

The composite obtained in a solution of aminosulfonic acid is an interesting case, although rather marginally discussed in this paper. The yield (12%) and the content of Ag (12 wt%) are drastically lower than in the three other cases. Aminosulfonic acid is rather easy to oxidize. May be its reaction with the oxidizing agent (silver nitrate) causes these differences? I propose to address this point during the thesis defence. Relatively high RT conductivity of this composite (42 S/cm) is also surprising taking into account that 12 wt% of silver corresponds to 1.8 vol% of its content, much lower than its expected percolation threshold. It is a pity that Patrycja did not profit to a larger extent from the collaboration with Dr Jan Prokes in elucidating the conductivity mechanism from its temperature dependence. It seems that the conductivity in such heterogeneous medium, consisting of two different conductors of semiconducting and metallic nature, can be described by several models eg. Sheng model, for example. Modeling could also help to explain a rather unusual temperature dependence of the conductivity in the composite obtained in the presence of 10% of *p*-phenylenediamine, where a clear minimum is observed (Figure 12 in the paper published in *Macromolecules* 2010).

Preparation of nanocomposites with the use of silver nitrate as the sole oxidizing agent always led to roughly the same content of silver in the material, with only few exceptions. To fabricate composites with varying silver content Patrycja decided to use a mixture of two oxidants in different ratios: ammonium peroxydisulfate and silver nitrate. This approach enabled her to demonstrate the electrical percolation in composites with deprotonated polyaniline phase (*Polymer*, 2011). She also compared the copolymerization and composite formation processes in liquid and frozen reaction mixtures (*Journal of Solid State Electrochemistry*). These papers contain interesting and competent discussion of the materials preparation methods and the obtained spectroscopic data. My only discomfort is caused by the molecular mass data. First, I am not sure whether the presented values are true or apparent. Polyaniline chains have a strong tendency to agglomerate *via* intermolecular hydrogen bonds since emeraldine base acts both as an H-bond donor and an H-bond acceptor. In measuring the molecular mass by size exclusion chromatography it must be assumed that the interactions of emeraldine with N-methylpyrrolidone, which is an H-bond acceptor, fully destroy this network of H-bonded macromolecules and disintegrate the agglomerates. Is this assumption valid? Second, sharp fractions of polystyrene do not seem to be an appropriate standard for

the molecular mass determination of semioxidized polyaniline whose molecules are significantly more rigid. It is known that polystyrene standards yield strongly overestimated molecular masses of more rigid polymers and this overestimation increases with increasing  $M_n$ . A comment of Patrycja concerning these problems would be welcome during the defense of the thesis. In addition I would like to discuss with Her the data presented in Table 2 of the paper published in *Journal of Solid State Electrochemistry*, 2011, which seem not totally coherent with the molar mass distribution shown in Fig. 6.

Finally some more general problems concerning the thesis should be discussed during the defence. They are listed below:

- In all preparations Patrycja uses strictly stoichiometric amounts of oxidants to yield protonated emeraldine base in acidic solutions. It is known that polymers of better chain microstructure and higher conductivity are obtained if the oxidant is taken in deficit. May be a trial with a deficit of the oxidizing agent would be worth to undertake? A comment is needed.
- In the preparation of composites with variable amounts of silver two oxidants strongly differing in their formal redox potential are used, namely ammonium peroxydisulfate and silver nitrate. It seems more advantageous to select an oxidant of the formal oxidation potential comparable to that of silver nitrate. There exists a plethora of milder than peroxydisulfate redox systems which can be used for polymerization of aromatic amines. This is especially important for copolymerization of *p*-phenylene diamine and aniline. It would also be beneficial to determine electrochemically the redox potential of aniline and *p*-phenylene diamine. A comment concerning these problems is welcome.
- I could not find in the enclosed papers any information concerning solution or thermal processability of the obtained nanocomposites. For example all conductivity measurements were carried out on pressed pellets. In principle, these composites if prepared in a colloidal form could yield free standing films or layers on an appropriate substrate *via* casting, dip coating or spin coating. Moreover, polyaniline coated silver nanowires could be blended with conventional polymers to yield conductive materials of low electrical percolation threshold. Homogenous dispersion of silver nanoparticles in a polymers matrix is extremely difficult to obtain. Polyaniline coating should facilitate such a compatibilization, especially in cases where it can form H-bonds with


the second polymeric component of the blend. Please address this point during the defense.

## **Conclusion**

The set of six papers presented as the doctoral research together with a valuable 39-page comment on the performed studies represent a very high scientific level, although maliciously speaking the papers are written in better English than the comment. The presented research contains several scientific novelty elements in their preparative part. The elaborated nanocomposites are profoundly characterized using complementary spectroscopic, microscopic and thermal techniques as well as 4-probe conductivity measurements. The results are discussed in a competent way, the clarity of the papers and their editing is above average even if the standards of international journals are considered. My slightly critical comments on few aspects of the thesis do not lower its value but rather are intended to stimulate the discussion during the defense.

To conclude, the thesis of Patrycja Bober fulfils all conditions required for a doctorate degree as far as the scientific novelty and the clarity of the written presentation are considered. In my profound opinion She should be allowed to defend it.

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