# Review of Andrii Mahun's Ph.D. thesis.

*Structural characterization of materials for energy applications using NMR spectroscopy.*

Andrii Mahun has worked out his dissertation thesis in the Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic under the supervision of Dr. Libor Kobera. The thesis is written in English on 96 pages and is based on 7 original papers where Andrii Mahun is either the first author or where he contributed significantly.

All seven papers are about using either liquid or solid phase NMR spectroscopy in the study of materials with high potential in the storage of electrical energy. The materials under study cover a broad range of polymer compounds like polymer electrolytes, conductive polymers and perovskites. The author was using liquid, as well as solid phase NMR spectroscopy, together with numerous other spectroscopic methods. For mastering all of these modern methods he deserves high credit.

At first look, it is obvious that the author has done huge amount of work. The thesis is written in excellent English, contains all required parts and the author has almost avoided typographical errors. I have just a couple of minor comments and notes to further improve the quality of the thesis and the impression from its reading. They are summarized further in my review. The introduction is well written and because I am not a specialist in NMR spectroscopy of materials with a potential to be employed in the field of electrical energy storage, I really appreciated the part about energy materials. The structure of the thesis, when the author has commented the results from all seven papers separately, was well chosen, making reading the thesis very comfortable and pleasant. The fact that the results described and commented in the thesis have already gone through a thorough peer reviews, makes my role much easier. Therefore, I will continue with my notes and comments followed by questions which should start a scientific debate.

Note 1: I know that the structure of the studied polymers is well known to each polymer chemist, however, when you are not a polymer chemist, you have to search for it. So, I think that putting the structural formula at the beginning of each chapter would be beneficial.

Note 2: I was missing the explanation of Figure 4.13./b.

Note 3: In the c part of the caption of Figure 4.13. there is a typo "trsndport" which should be corrected to transport.

Note 4: On page 68, there is description of the creation of the chinoid form of polypyrrol by doping it by something. From the corresponding paper one can find that the oxidative agent was ferric chloride hexahydrate, however, this is an important information and it should be mentioned also in the thesis.

Note 5: On page 71 there is a sentence: "The obtained $^{133}Cs$ spin-lattice relaxation decays show slightly accelerated $^{133}Cs$ spin-lattice relaxation time from 376 s to 281 s. It does not

make a sense to me, either the relaxation time is shortened or the relaxation rate is accelerated.

The above mentioned notes and comments do not deteriorate the quality of the thesis, they rather serve as a proof that I have read the thesis thoroughly. I have a couple of questions to the author to stimulate the scientific discussion.

Q1: One of the results of the following the reaction rate of ROx with DecOx by $^1$H NMR is that the changing ratio of ROx and DecOx affects the composition of the resulting polymers. There are detailed results for each mixture including the conclusion that the above-mentioned ratio influences the co-polymer microstructure. My question, as a layman in polymer chemistry is, whether it is possible to draw any general conclusion in terms of, for example, the bulkier side chain the more or less random co-polymer is formed, etc.?

Q2: What was the arrangement of the experiment for the test of electrochemical stability of GPEs? Was it like the cycles in batteries, i.e. with alternating charging and discharging periods?

Q3: I was missing the graph showing the fitting of the experimental data from $^7$Li-$^7$Li NMR EXSY experiment yielding the exchange rate constant. How accurate was it and what about the error of the calculated activation energy?

Q4: The question is about the structure of $Cs_2AgBiBr_6$ perovskite. You wrote that you have had a crystal structure of this molecule before you started the NMR study. $^{133}$Cs NMR spectrum indicated just one signal corresponding to one Cs atom. But in the processing of $^{133}$Cs relaxation data you used a two-atom model (two exponential functions) corresponding to Cs atoms further and closer to $Pd^{2+}$. My question is what is this approach base on? Did you have X-ray structure of the doped perovskite or any other indication that there might be two kinds of Cs atoms?

To summarize my review, I declare that Andrii Mahun has demonstrated great creative abilities in this research field and his thesis meets all standard requirements for doctoral theses at the Faculty of Science of Charles University. Therefore, I recommend Andrii Mahun to be awarded the title Ph.D. after a successful defence of his thesis.

Prague, May 24$^{th}$, 2024                                             prof. Ing. Richard Hrabal, CSc.