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Opponent review of the Ph.D. thesis submitted by Nadiia Velychkivska

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The Ph.D. thesis is entitled “Investigation of external stimuli-influenced temperature-sensitive polymers behavior studied by spectroscopic methods “, and it consists of 5 major chapters: Introduction, Aims, Experimental Part, Results and Discussion and Conclusion. It is complemented with 3 published papers. The thesis thus keeps more or less a classical structure, and the published papers are not integral part of the thesis. The size of the thesis is about 100 pages, the formal structure is logical and proportional, and it includes all necessary components, namely, bibliographic sources are properly cited.

The goals are clearly stated in “Aims of the thesis” and they include investigation of the phase separation phenomena of 3 polymers – PVME, PNIPAM, and porphyrin-PNIPAM conjugate dissolved in various (mixed) solvents. The main experimental method is NMR spectroscopy, which smartly complemented with SAXS, DLS, DSC, optical spectroscopies, etc. I have a formal comment here, the goals specification might be better given in a very beginning of the work rather than being partly hidden after the theoretical part.

The introductory theoretical part (“Introduction”) provides brief but generally sufficient basic description of the studied systems, their thermodynamics, experimental methods and description of data processing in order to derive the requested parameters. I appreciate the chapter 1.2.2, which provides derivation of all the needed relations between observables and the characteristic thermodynamic parameters. This concept is further worked out in the discussion part concerning the porphyrin-PNIPAM conjugate project by incorporation of the Flory-Huggins theory.

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The experimental part provides all the necessary specific details on the syntheses, sample preparations and experiments carried out.

The “Results and Discussion” chapter describes in detail the 3 projects. The first two follow a similar scheme – influence of a given set of additives on the coil – globule transition of the given polymer PVME or PNIPAM. The results are documented by typical NMR spectra and graphs documenting the phase transition as well as the graphs of dependencies of major thermodynamic parameters on temperature and the system composition.
It is interesting to note that ordering of the projects is clearly chronological, and the thesis perfectly document growth of the candidate as for variety of experimental methods and approaches used, the level of theory applied and the depths of primary data interpretation. Thus, the last project concerning the phase transition in porphyrin-PNIPAM conjugates is the most interesting for a reader. The experimental approach includes NMR p-factor and DSC temperature and concentration dependencies, phase diagrams, SAXS, pH dependence, optical spectroscopy, and combinations of these approaches. This project constitutes the best part of thesis and, in fact, the thesis would be good enough, if based solely on this project.

My comments to the thesis and questions to the candidate:

1) The level of the data analysis is significantly improving in the chronological sequence. In fact, I have some comments to presentation data of the PVME and PNIPAM projects: the graphs contain experimental data points, but the connecting lines are rarely fitted according to any physical model. I suggest to be careful about this type of presentation and to avoid it if possible. Alternatively, it should be clearly stated in the caption. This point is also related to experimental errors specification. More care should be taken establishing errors of observables and their propagation to the resulting thermodynamic parameters.
2) Use of NMR relaxation: I am missing specification of relaxation mechanisms of the transverse relaxation: do they involve dipole-dipole interaction, chemical exchange, and what about the fluctuations of the magnetic field due to local inhomogeneities caused by the phase microseparation? I am not completely sure about the short-hand relation – “the faster relaxation – the slower motion” without a detailed specification of the relaxation model, especially in the cases when proton/water chemical exchange cannot be excluded by comparison with relaxation of the methyl groups.
3) Fig. 4.1.7 is a bit too artistic, it would be better, if it is supported by more quantitative basis (e.g., clearly, the concentration of chains in the second row should be twice as the first one).
4) Description of NMR basis in the introductory part (1.2.1) is composed in the style of the most simple textbooks. I would prefer that this is avoided. The two-cone figure is inherently incorrect from the quantum mechanical point of view.
5) It is generally stated that candidate’s contribution to the projects is in the range of 40-65 %. Could the candidate provide a more detailed specification of her contributions to the individual projects and papers?

To conclude, despite of a few comments and suggested improvements, the thesis contain fairly large amount of original data and interpretations. The 2 projects were already published as 3 papers in respected journals, and last project, which has not been published yet, is found far the best, and it documents major progress the candidate has made. The candidate has clearly manifested her scientific and creative abilities, and the submitted thesis meets the general requirements imposed on the dissertation thesis in the field of physical and macromolecular chemistry and it presents a solid basis for awarding candidate with Ph.D. degree upon a successful defense.

Jan Lang