Ph.D. Thesis Evaluation Report

Author: Mgr. Nadiia Velychkivska
Title: Investigation of external stimuli-influenced temperature-sensitive polymers behavior studied by spectroscopic methods
Reviewer: Mgr. Viktoria Poterya, Ph.D.

The PhD work is dedicated to research in the field of stimuli responsive polymers, or so-called smart materials. This fast-developing field opens up an access to a variety of applications in nanomaterial science. The polymer-solvent interactions play an important role on the phase separation process. The ternary systems containing additives such as cosolvent represent another systemы where phase separation effects can be enhanced. Different factors such as nature of the solvent and additive can have a dramatic effect on phase separation process, the structure of the newly formed agglomerates and their stability. The presented research conducted during PhD is important and brings new knowledge into the field of stimuli responsive polymers.

The clarity and language level of the work is at a very good level. Author consistently introduces the reader with stimuli responsive polymers, presents the obtained results with their comprehensive interpretations and makes clear conclusions. The goals of the thesis are clearly defined and the content of the thesis meets the set goals.

The thesis is composed of four sections.

In the Introduction author describes the temperature sensitive polymers, and the experimental methods which are used to investigate their properties. The phase separation phenomenon is explained in detail. The current stage of research for the samples proposed for the PhD investigation is provided in subsections 1.1.1-1.1.3.

In the second chapter the goals of the thesis are described.

The third chapter is devoted to the description of the chemical procedures for samples preparation. The PVME and PNIPAM polymers were mixed with four different additives. Porphyrin-PNIPAM conjugates were synthesized with two different average molecular weights to study also the size effect on the phase separation temperature.

The last chapter presents the results of the research conducted during the PhD study. The effect of several hydrophobic additives to PVME and PNIPAM on phase separation temperature was studied using NMR spectroscopy. It was found that t-BuMK additive has the biggest effect on phase separation temperature, Tp, for both studied polymers. The dependencies on the additives basicity and hydrophobicity were investigated to explain the observed results. From the experimental data the thermodynamic parameters such as enthalpy and entropy were determined. Time-resolved H NMR spin−spin relaxation experiments were used to reveal the stability of the phase separated globule structures. The experimental results showed that even small concentrations of hydrophobic additives can drastically change the temperature response of the PVME and PNIPAM polymers and improve the structure stability. The more complex Porphyrin-PNIPAM conjugates with two different average molecular weights were investigated using three experimental techniques: NMR, DSC and SAXS. Research was quite extensive and provided the interesting results. It was found that critical temperature can be tuned by varying the length of PNIPAM chains. SAXS technique provided the information about the structure of polymers before and after the phase separation.

The list of literature is large enough to show that author is aware of the scientific developments in the field.

The thesis is well written and scientifically sound. Considering that the English is not the author's mother language, I have to admit that there are no gross grammatical errors. Since English is also not my first language, I cannot correct grammar in a thorough manor. Although I can suggest some small improvements.

Suggested revisions

Grammer:

- Abstract: "Of the polymers with a phase separation…" should start with Among the polymers.
- p. 21 "In order to tilt the magnetization radio-frequency pulse perpendicular to z-axis has to be applied at the resonance condition close to Larmor frequency" change the words order to Radio-frequency pulse perpendicular to z-axis has to be applied at the resonance condition close to Larmor frequency in order to tilt the magnetization.
- P. 34 "A study the influence" should be A study of the influence…
- p.55 "We supposed that $(CH_3)_3$ groups… " change to We suggested that $(CH_3)_3$ groups…
- p.59 "From the data shown in Fig 4.2.8 follow" should be From the data shown in 4.2.8 it follows
- p.60 first paragraph "anime" should be amine.
- p. 71 "Slight differences…" change to Small/minor differences.
- p. 84 "The co-nonsolvency effect of PNIPAM is the strongest at… " should be The co-nonsolvency effect of PNIPAM is strongest at… Also this sentence is rather long and it would be better for the reader to split it in to two. Second would start with: This is very close to the point where the largest ….

Pictures:

- It would be preferential for some pictures to have a better resolution since upon zooming of the pages the blurring of the lines becomes noticeable (Fig. 1.3 and 1.4).

Content:

- p. 47 "Basicity of studied additives increases in the following order:" Instead of the sign bigger > the opposite < sign has to be there, the arrow sign can be also possible.
- p. 58 "…is represented in the following order starting from least to most hydrophobic *t*-BuAM > *t*-BuMK" sign again should be reversed. The same has to be corrected for the pKa dependence in the last sentence of p. 58.
- Fig. 4.2.4 could have been described in more details. The dependencies of T_{width} for some additives are not straightforward, it seems that at concentration at 5% there is change in the behavior for several additives.

Summary

The candidate for PhD degree, conducted a thorough and comprehensive research. The obtained results were novel and they bring new insight into the field of stimuli responsive polymers. It is confirmed by the publication of experimental findings as peer reviewed journal articles. Author participated in seven scientific conferences and was a part of scientific international collaborations. Author demonstrated an ability for independent work. Thesis fully satisfies the requirement for obtaining a PhD degree.

I recommend the PhD thesis of Mgr. Nadiia Velychkivska, entitled “Investigation of external stimuli-influenced temperature-sensitive polymers behavior studied by spectroscopic methods” for the defense.

Questions on author

1. Author described many sophisticated techniques which were used during the PhD time. Which one of the experimental methods was used by the author personally?
2. On page 46 the stabilizing effect of t-BuAM on T_p was explained such as “Most probably it is the interaction between NH2 group of t-BuAM and etheric oxygen from PVME”. But down in the text on page 48 it was written: “Whereas in the case of t-BuAM additive, HDO and t-BuAM molecules interact only very weakly with PVME, which indicates no substantial binding to polymer globules.” It is a little bit confusing to me and so I would be glad if author would clarify the way the t-BuAM interact with PVME.
3. The t-BuMK additive showed the largest effect on the Tp of PVME- prominent Tp decrease (Fig.4.1.4). Further in the thesis the spin-spin relaxation method was used to study the stability of equilibrium structure. Fig. 4.1.6 and 4.1.7 show the results for two additives: t-BuAM and tBuOH, but not for tBuMk. Was there any special reason to show data only for these two additives? Further in the conclusion part, it was stated that tBuMk behaves similarly to tBuMk. I suggest to mention the spin-spin relaxation results for tBuMk since it had the largest effect on Tp.
4. In the studies of T_p dependences of PNIPAM on the concentration of additives the biggest effect on Tp was shown for *t*-BuMK. This was explained by formation of *t*-BuMK cage around hydrophobic groups of PNIPAM. Since in the studies with PVME the similar effect was observed, can the suggested explanation for PNIPAM be applied to PVME with *t*-BuMK as well?
5. The studies of Porphyrin-PNIPAM conjugates were very detailed and provided a lot of information about phase separation behavior and structure. The formation of cooperative domains upon phase separation showed very interesting phenomenon. Both conjugates at similar concentrations initiate formation of cooperative domains which contains approximately the same number of monomeric units. Is there any plausible explanation for such a behavior?

14.09.2020

Opponent Mgr. Viktoriya Poterya, Ph.D.