# Oponentský posudek dizertační práce

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Název práce: Spectroscopic study of the dynamical behavior and interactions in supramolecular and macromolecular systems

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The thesis deals with synthesis and investigation of several types of thermoresponsive polymer solutions and hydrogels including the interpenetrating (IPN) and semi-interpenetrating (SINP) networks. The theoretical part is worked out clearly with a sufficient amount of literature references to describe the state of art of the topic of smart gels. The Experimental section is divided into four parts focused to (i) poly(vinyl methyl ether) (PVME) water solutions, (ii) the effect of additives in PVME solutions, (iii) IPNs and SIPNs of poly($N$–isopropylacrylamide) (PNIPAm), poly($N$–vinylcaprolactam) (PVCL) and polyacrylamide (PAAm) swollen in water and (iv) IPNs and SIPNs of poly($N,N$–diethylacrylamide) (PDEAAm) and PAAm. The thermally induced phase transition in these polymer systems was studied by using NMR, DSC, optical microscopy and by swelling experiments.

The effect of polymer concentration, presence of additives and composition of IPNs and SIPNs, on phase transitions was determined. The size of cooperativity domains, participating in phase transitions, was evaluated and discussed.

**I have the following comments and questions.**

Synthesis of polymer systems
Why different types of initiation were used for the polymerization? Photoinitiation for the linear PNIPAm, thermal initiation using azo-initiator for linear PAAm, thermal-UV initiation for PVCL/PNIPAm IPN and redox initiation for IPNs PNIPAm/PAAm.

Different types of initiation and possible different concentration of initiators (the data are missing) could result in different polymer characteristics as well as in different thermosensitive properties or heterogeneity formation.

p.37
Very interesting is the determination of a size of domains undergoing the cooperative process during phase transition. It is evaluated by comparing the van't Hoff enthalpy of the phase transition determined by NMR and calorimetric enthalpy of the endo- and exothermal processes evaluated by DSC. The author concluded that „ *For PVME solutions with c = 1–30wt.% the size of domains agrees quite well with average degree of polymerization (DP ~348) so showing that in*

*this case the cooperative unit is the whole polymer chain.*" The average number of units in the cooperative domain roughly equals the DP, supposing thus „ all-or-none" process.

**In fact, DP(PVME) ~1000 (Mv=60500) and thus the cooperative unit is always smaller than the chain length.**

The determined size of the cooperative domain decreases at a high polymer concetration, c=50-60%. (Table 5.1). "*This tendency to form smaller domains could follow from more significant influence of interchain interactions as well as from the occurrence of non-hydrated PVME units in solutions with higher polymer concentrations.*"
Also, the small size of cooperativity domains in polymers with additives – PVME+TBMK, PVME+TBOH, corresponds to microscopically determined smaller polymer aggregates with respect to other systems (Fig.6.6).
In contrast, however, the size of polymer aggregates- globules, determined by microscopy in PVME solution, c=20-50%,  is much larger than in 5% solution (p.34, Fig.5.7).

**Consequently, is there any relation between the size of polymer aggregates (globules) and cooperativity domains ?**

p.52     (Table 7.3)
„  *.. the enthalpy values recalculated per gram of dry polymer significantly depend on IPNs composition as well as* **on the order of components during preparation** *for PNIPAm/PAAm and PAAm/PNIPAm samples...ΔH values for IPN PNIPAm/PAAm 69/31 sample are three times larger than values for IPN PAAm/PNIPAm 42/58 with similar composition but reversed order in the synthesis procedure.* "
This is not a proper argument for an effect of order of components at synthesis. In the latter case, there is a much higher PAAm fraction  (42 % vs. 31%) preventing the phase transition. Rather another argument should be used. The Fig.7.6 shows a strong phase transition in PAAm/PNIPAm=42/58, while no transition in the case of the gel *PNIPAm/PAAm=60/40* of a similar composition but prepared by the reverse order of components.
        Moreover, obviously, the phase transition in *PNIPAm/PAAm~60/40*  is more pronounced in a solution than in a gel. In contrast to the gel, there is a strong phase transition observed in solution *PNIPAm/PAAm=58/42* (Fig. 7.6). However, in the neat system PDEAAm the calorimetric enthalpy of transition is higher in the gel than in the solution (Table 8.2.).

**Is there any explanation for this difference ?**

p.35  Figs.5.2 ,5.3, 5.4
The difference between onset or peak temperatures from heating and cooling DSC scan is interpreted as a result of different time scale of processes during formation (heating) and dissolving (cooling) of mesoglobules. This difference also depends on concentration of the polymer because the size of globules are much larger in case of higher polymer concentration and the penetration of large agglomerates takes much longer time.

The results are well interpreted. Have you tried to apply different rates of cooling/heating to prove this hypothesis ? At decreasing rate of cooling/heating, the difference between peak temperatures at cooling and heating would decrease as the experimental rate approaches to the time scale of formation and dissolving of globules.

p.41    The NMR spectrum in Fig.6.1. is not quite clearly described. The signal of globular units between 4-5 ppm is not obviously observed and hence also the effect of additives on this peak is not well seen.

Tab.7.2 Could you comment why the swelling ratio in PNIPAm/PAAm at T<LCST decreases with increasing PAAm content ?

Some formal comments**.**

p.50     In the text, $m_T$ is used instead of $w_T$ as in eq.4.4.

p.66     The transition temperatures are shifted to a higher value in the solution (Table 2) and not to a lower one as it is given in the text.

      As a conclusion, one could state that the research met the goal. The candidate prepared a series of thermoresponsive polymer systems and contributed to fundamental understanding of the parameters affecting the volume phase transition. The thesis is of a high scientific quality and in addition, M. Radecki is an author or co-author of 6 papers and delivered 10 contributions (lectures or posters) on both national and international conferences. Consequently, the author showed an ability to carry out an independent research and I recommend the thesis to the defense.

V Praze, 3.9.2018

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