

Interactions in solutions and gels of stimuli-responsive polymer systems investigated by NMR spectroscopy

by Mgr. Rafał Łukasz Konefał

submitted to the Faculty of Science of the Charles University, Department of Physical and Macromolecular Chemistry

The submitted thesis consists of an introduction chapter and a core part summarizing the author's results. The introduction chapter of the thesis is divided in two parts, the first one introducing NMR spectroscopy as a technique the autor used for studies described in the thesis, the second focusing at polymers sensitive to external stimuli as a subject of the study. Special attention is paid to temperature sensitive polymers such as polyalkyloxazolines or poly(N-isopropylacrylamide).

The core of the submitted thesis is a discussion of the author's contributions to 11 papers in international journals. Mr. Konefał is a co-author of all those papers and the first co-author of two of them (*Eur. Polym. J.*, *Colloid Polym. Sci.*).

I have no general objections to the contents of the thesis except for the language which, in my opinion, would deserve a more careful revision (e.g. p. 15 "experimental technics", p. 18 "pH responsive acidic group constitute polymers with carboxylic, sulfonic acid, phosphoric acid, aminoacid and boronic acid groups", p. 25 "can be provide", p. 30 "cross-peaks intensities decreases", many instances of missing articles).

As the thesis is basically a summary of the author's contribution to the published papers, I would like to ask the author to comment on two points that concern the presented papers rather than on the thesis itself. I have chosen the papers of which Mgr. Konefał is the first co-author.

- 1) *Eur. Polym. J.* **2018**, *100*, 241–252: In this paper, light scattering intensity is measured at a single scattering angle ($\theta = 90^\circ$) to determine the cloud point of the solution. Did you consider multiangle static light scattering measurements to determine the gyration radius of the particles? Having R_g/R_H values would be a good measure of the compactness of the nanoparticles.
- 2) *Colloid Polym. Sci.* **2016**, *294*, 1717–1726: Multiangle light scattering measurements can be important also in DLS because in polydisperse systems, z-averaged diffusion coefficients are obtained by the extrapolation to the zero scattering vector magnitude. In this article, the apparent hydrodynamic radii obtained from intensity autocorrelation functions measured at $\theta = 90^\circ$ are used to calculate the Brownian tumbling correlation time τ_C . The obtained changes with the temperature are too low to explain the changes of NMR signals. I wonder if this discrepancy could be a result of taking the apparent R_H at 90° for the calculation instead of using the R_H based on the z-averaged diffusion coefficient. Could you comment on this problem?

My general opinion is that the work of Mgr. Konefał described in his thesis represents a significant contribution in the field of stimuli-responsive polymers. In summary, I fully recommend to accept the submitted thesis for the defense.

Prague, April 26th, 2018

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