

**Referee's review of the PhD Thesis
of Daniel Gromadzki entitled „Synthesis and self-assembly of amphiphilic
functional block and graft copolymers”**

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The submitted work deals with the synthesis of several block and graft copolymers, their molecular characterization and their self-assembly.

The Thesis consists of seven published papers, accompanied by a 100-pages text with the conventional structure of introduction, experimental, discussion, conclusions, literature and references.

New copolymers were (a) sulfonated commercial copolymer Shellvis polystyrene-hydrogenated polyisoprene, (b) block-random polystyrene-poly(styrene-acrylonitrile) prepared by nitroxide-mediated radical polymerization and (c) graft copolymers with variable grafting density prepared by combined nitroxide-mediated radical polymerization and photoinduced iniferter technique. The molecular parameters, i.e. chemical composition, molar mass, molecular size, polydispersity, grafting density) of the copolymers were determined by NMR, GPC and light scattering.

The major part of the work is devoted to self-association of the copolymers and characterization of the resulting supermolecular structures in solutions and in solid state. A series of methods have been employed, like static and dynamic light scattering (SLS, DLS), small-angle X-ray scattering (SAXS), transmission electron microscopy (TEM) and atomic force microscopy (AFM).

The submitted Thesis contains original experimental data. All synthetic steps leading to copolymer samples are described in detail, results are well presented in figures and tables and interpreted on expected level.

Comments, which do not demand answers:

- (a) The text is too lengthy. Some parts should have been shorter, e.g. DLS is much longer than other methods and contains equations not used in the text.
- (b) The aim of the thesis is ten pages long and contains a literature review which belongs to Introduction.

(c) The Conclusions (almost four pages) should not contain any citation history or even reviewers' comments.

(d) A list of symbols and abbreviations of the copolymers would be helpful.

Questions and remarks which should be answered:

(a) What are the H and π copolymers on p. 11?

(b) What is the form factor of lamella on p. 46? What does a lamellar "particle" look like? Was it ever established experimentally?

(c) I could not find any SLS experimental data. Could Mr. Gromadzki show some Zimm plots? Radii of gyration, R_g , higher than 15 nm should be seen quite clearly here.

(d) Values of R_g were mostly determined from SAXS or calculated from GPC. Were the results from both methods the same or similar?

(e) The author had many co-authors in his papers and he acknowledged help of many colleagues. It is not clear from the Thesis, how substantial was his own contribution.

The papers published in reviewed journals, amount of experimental data, their interpretation and a thorough discussion allow me to recommend the Thesis to be accepted as a ground for awarding Mr. Gromadzki the Ph.D. academic title.

Prague, February 3, 2010

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