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Review of Doctoral Thesis of

Daniel Gromadzki, MSc Eng.
entitled **„Synthesis and self-assembly of amphiphilic functional block and graft copolymers"**

Thesis advisor: Professor Petr Stepanek

Doctoral thesis prepared by Mr Daniel Gromadzki is a concise description of a subject (98 pages) illustrated with 45 figures, 14 tables and 89 references. The integral part of the thesis are 7 papers published in recognized scientific journals which are attached as appendices.

The meritorious and scientific evaluation of the thesis I will present in the following parts:

1. Timeliness of the subject
2. Elements of scientific novelty
3. Analysis of experimental techniques and methodology
4. Discussion annotations
5. Conclusions

Timeliness of the subject

Investigation of polymer composition and architecture is a subject of many research work on macromolecular systems. Since discovery of anionic polymerization, block copolymers can be efficiently prepared by sequential addition of monomers to various „living" polymer chains. Interestingly, it allows to synthesize block copolymers from two distinct and specific monomers in order to create various architectures, such as diblocks, triblocks, star and graft copolymers. The most important polymer used for the preparation of

such complex structures is polystyrene, which already had demonstrated not only tremendous interest as a model system to study molecular architecture and phase behavior in block copolymers but also showed its high potential as building unit in important industrial products known as Kraton, Styrolux or Dynaflex. These block copolymers belong to the group of thermoplastic elastomers, a unique class of materials. While macroscopically homogeneous, these polymers phase separate and forms self-assemblies on a microscopic (nanometer) scale.

Anionic polymerization allows to produce various block copolymers with well defined architectures such as graft or star copolymers. The difference in the cohesive energy densities between constituting (A and B) segments, differing in Flory-Huggins thermodynamic interaction parameters, result in microphase separation and different (micro)domain structures. These domains acts as physical crosslinks in TPEs being an amorphous glassy domains, crystalline lamella, ionic clusters, etc.

Development of controlled/living radical polymerization (CLRP) allowed further extend and design various new molecular architectures based on polystyrene and broad range of different molecules. The possibility to utilize a stable free radicals, most often a nitroxide based radical in a nitroxide mediated polymerization (NMP), allowed to obtain polymers with predetermined molecular weight, low polydispersity, and controlled composition and topography. Thus, molecularly engineered materials can nowadays be prepared by radical polymerization processes and their application is envisioned in many areas. Therefore, it can be concluded that block and graft copolymers are gaining increasing interest from the basic (molecular architecture in solution and in bulk, phase separation) and the applied research point of view, therefore the subject discussed in Mr. Gromadzki work is timely and interesting.

Elements of scientific novelty

Since discovery of living anionic addition polymerization in 1956, thousands of papers and patent applications were published on block copolymer's architectures, their undiluted (bulk) and dilute properties, the order-order transition compositions, surface behavior etc. Especially, if microphase separation is governed by ionic clusters, block copolymer ionomers can be prepared as materials highly suitable for application in separation processes or in fuel cells. Starting from chemically distinct repeat units, living anionic polymerization allows to prepare block and graft copolymers of well defined architectures. New polymerization methods such as CRP, and especially NMP, led to non-linear polymers with units randomly

distributed along the macromolecular chain and with larger than common polydispersity. This applies, for example, to random (A-*b*-B) block copolymers with variable acrylonitryle content, where microphase separation is a driving force for self-organization into ordered structures. These structures can show different behavior (conformation) in dilute solution and can affect the polydisperity. This problem can be extended to comb macromolecules (graft copolymers) which has the ability to self-organize into micells if they are dissolved in a solvent selective for one block. If graft copolymers are being concerned, the "grafting from" atom transfer radical polymerization (ATRP) can provide control over polymer structures of molecular brushes with different backbone and side chain density.

Therefore, the main objective of his work was to synthesize and characterize block and graft copolymers which showed different capability to self-assembly into functional macromolecules with controlled domain (ionic) structure, micellization behaviour and amphiphilic properties.

The Author demonstrated that with the use of advanced macromolecular engineering it was possible to prepare styrenic block ionomers with high degree of sulfonation which has a significant effect on strong microphase separation. He demonstrated also that block copolymers with random blocks {A-*b*-(A-*co*-B)} show microphase separation leading to ordered structures, where the polydispersity increases domain spacing in ordered structures of styrenic copolymers. The Author elucidated the dilute solution properties and dilute dynamics of these block copolymers. Moreover, by combining the nitroxide-mediated radical polymerization and photoiniferter process for the fist time, the Author prepared amphiphilic block copolymers with comb-like topology, thus demonstrating its high potential for grafting of many monomers (besides of styrenic and (meth)acrylic). This method enabled the preparation of well-defined hydrophobic polymeric backbone with adjustable amount of the side grafting sites and their length. The Author realized this idea with the amphiphilic molecular brushes with hydrophobic polystyrene core and hydrophilic poly(ethylene glycol) side chains.

Analysis of experimental techniques and methodology

With the use of different synthesis techniques, a candidate for doctoral degree has prepared various polymers for systematic studies on the structure and properties of block and graft self-assemblies. Nuclear magnetic resonance (NMR) and gel permeation chromatography (GPC) allowed to describe in details chemical structure of ionomers and

graft copolymers/molecular brushes. With the use of static light scattering (SLS) and dynamic light scattering (DLS) the Author was able to elucidate basic molecular parameters of macromolecules (weight-average-molecular weight, *z*-average radius of gyration and the second viral coefficient) from polymer solution as well as their diffusion processes and hydrodynamic size in solution. Since the block and graft copolymers show microphase separation, the domain size and shape was studied with small-angle X-ray scattering (SAXS) and transmission electron microscopy (TEM). An excellent visualization of domain morphology was attained not only with TEM but also with atomic force microscopy (AFM).

From that short list of methods it is clearly seen that the candidate for doctoral degree used modern and adequate characterization techniques which allowed to draw appropriate conclusions.

Discussion annotations

PhD student, Mr Daniel Gromadzki, in his doctoral thesis has addressed different issues related to synthesis and properties of block, block-random and graft copolymers. The Author was also interested in elucidation of thermoresponsive properties of cylindrical molecular brushes for potential biomedical applications as drug delivery carriers. The doctoral dissertation, and especially seven papers being an integral part of the thesis, contains enormous amount of experimental results.

Discussion of the results and conclusions are well formulated and they fully reflect the wealth of the results presented in the work.

There are some minor mistakes in the main text, for example, a wrong numbering of tables (doubled Table 1). The bibliographic style of citations makes rather difficult to quickly identify appropriate reference. Some of the figure and table legends are placed on another page than the figure/table is presented (pages 52, 59, 73). Other mistakes are the typographical errors which are not diminishing the overall value of the work.

A few questions, however, are addressed to the candidate for doctoral degree which should be answered during the defence:

1. what means the „grainy" structure and what is a difference between structure and morphology?

2. what is the mechanism of polymer staining with RuO_4?

3. It is known that the bulk block copolymers can be brought into the weak segregation regimen by decreasing either χ (Flory-Huggins interaction parameter) or N (the overall degree

of polymerization). What is the correlation between domain ordering and rheological properties of block copolymers as a function of temperature?

Conclusions

The candidate for doctoral degree had performed very large experimental program to understand the self-assembly process in amphiphilic block copolymers. The obtained results demonstrated many features of scientific novelty. The Author used the combined nitroxide-mediated radical polymerization and photoiniferter process for the first time thus producing interesting materials of well defined topology. He provided a deep insight into the physical properties of dilute solutions (both, in nonselective and selective solvents) and melt phase behavior of synthesized block copolymers. The research area explored by the Author is of great scientific interest and, obviously, of enormous practical potential.

Taking into account the original concept presented in a work by Daniel Gromadzki I strongly recommend the thesis entitled "Synthesis and self-assembly of amphiphilic functional block and graft copolymers" to be accepted as a basis for awarding Mr. Gromadzki the academic doctoral (PhD) title.

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