

Reviewer's Report on PhD. Thesis of Sabina Jolanta Horodecka MSc.

"Oriented copolymers with liquid crystalline building blocks"

The research reported in the submitted PhD. Thesis is an original contribution to scientific advances in the field of preparation and characterization novel reversibly crosslinked polymers.

Reversibly crosslinked polymers represent a very promising class of materials which combine material properties of the polymer networks with the processability and recyclability of the thermoplastics. These polymers have recently attracted much attention from the standpoint of processability, chemical recycling as well as self-healing materials. In this thesis S. J. Horodecka, MSc. described novel non-covalently and reversibly crosslinked elastomeric copolymers of polydimethylsiloxane (PDMS) with liquid crystalline (LC) nano-building blocks as physical crosslinking agent with thermotropic properties.

The thesis is focused on evaluation of effect of polymer architecture and structure of LC mesogenic unit structure on properties of reversible physical networks. Three different copolymer architectures (i) LC-grafted PDMS; (ii) LC-end-capped linear PDMS and (iii) linear 'infinite' LC-PDMS copolymers (with alternating LC and PDMS segments) were synthesized via hydrosilylation coupling of vinyl-functional polyaromatic mesogens with Si-H-functional polydimethylsiloxane of different lengths. Six vinyl-functional polyaromatic mesogens of azo type and azo-free type were used as physical crosslinkers. Properties of prepared copolymers were characterized by numerous methods: (i) chemical structure and molecular masses were verified using NMR spectroscopy, FTIR, SEC and MALDI-TOF; (ii) thermotropic phase behaviour was characterized by DSC, X-ray diffraction, polarized light microscopy, thermomechanical analysis and (iii) complex viscoelastic and rheological properties of copolymer in the molten as well as in the rubbery state were determined by dynamic-mechanical thermal analysis, microtensile tests, advanced mechanical analyses and rheology measurements.

This PhD. thesis is consisting of Introduction part providing comprehensive and detailed information on liquid crystals with emphasis on polymer liquid crystals, polydimethylsiloxane polymer and its derivatives, hydrosilylation coupling and reversibly crosslinked polymers. Experimental part is covering description of experimental procedures for synthesis of physical networks based on polydimethylsiloxane chains with LC crosslinker and methods of characterization of the prepared copolymers. This chapter is clear and reproducible. Results and Discussion of this PhD. thesis is a summary of a large amount of data concerning comprehensive characterization of the prepared copolymers and clarification of influence of different LC-copolymer architecture as well as thermotropic properties of crosslinking agent on

thermo-mechanical behaviour and rheological material properties of physically crosslinked copolymer. Each chapter and the dissertation as a whole are logically organised.

The research reported meets internationally recognized standards for doctoral research in its field. This conclusion can be documented by the fact that results obtained during the doctoral study have already been published in 3 articles in international peer-reviewed journals with S. J. Horodecka, MSc. as leading author. She also demonstrated knowledge of the relevant literature, and the ability to exercise critical and analytical judgment of that literature. Her research is satisfactory in its methodology and in its scholarly presentation and format.

My comments and questions are minor and do not affect the overall very high rating of this thesis.

Comments:

1) Some formal typographical errors occur in the work, e.g. copolymer (p. 109), 'infinite' (quotation marks are missing Contents 5.1.5.3, 5.15.4, p. 143, p. 123, Figure 10) ...

2. On Fig. 30 WAXS patterns of copolymer M32-co-H11 at 23 °C are shown, while WAXS patterns of neat M32 and copolymer M32-co-H21 are shown at 25 °C. I don't think a difference of 2 °C would have a dramatic effect on results, but I assume that all samples were measured at the same temperature.

Questions:

- a) The mesogens used for the coupling reaction to prepare linear 'infinite' LC-PDMS copolymers are referred to as aromatic polyethers. What was the reason for calling them polyethers when aromatic rings are linked by ester bonds. Moreover, in the Experimental part they are referred to as polyether-type, while in the part Results and Discussion part as azo-free polyaromatic mesogens. For easier orientation of the reader, it would be more appropriate to unify names of these mesogens.
- b) Do you have any explanation for differences of the achieved nominal molecular masses (according to polystyrene standard) for the azo-free linear "infinite" LC-PDMS copolymers and the analogous azo copolymers?
- c) The LC-grafted copolymers, which are described to possess LC-quartets at the grafting positions, are sometimes depicted with LC units in the quartets aligned in one direction, and

sometimes with LC units with alternating opposite alignment. What is the true alignment of the LC units in the quartets?

- d) The LC-end-capped copolymers were shown to display a distinct lamellar supramolecular structure, in contrast to all the other copolymers. Do you have an explanation for this special aggregation behaviour of the LC-end-capped copolymers?

Conclusion: I would like to state that Sabina Jolanata Horodecka, MSc. met all legal requirements relating to Doctoral degree graduates. I recommend this thesis for her PhD. defence and as a base for awarding of the candidate by the degree of Doctor of Philosophy.



Zdeňka Sedláková, PhD.

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