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PhD REPORT

From **Dr. Majda ŽIGON**
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On the PhD manuscript entitled:

STUDY OF MOLECULAR WEIGHT AND CONFIGURATIONAL STABILITY OF SUBSTITUTED POLYACETYLENES

Presented by **Mgr. Olga TRHLIKOVÁ**
At **Charles University in Prague, Faculty of Science, Department of
Physical and Macromolecular Chemistry**
Supervisor **Doc. RNDr. Jan SEDLÁČEK, Dr.**

The PhD thesis of Mgr. Olga Trhliková is a comprehensive review on molecular weight and configurational stability of substituted poly(arylacetylene)s. The topics associated with the work described in the PhD thesis are related to the investigation into polymerization activity of mono-substituted Rh-based complexes as catalysts for mono- and two-substituted acetylenes in different solvents and to the synthesis of poly(arylacetylene)s using Rh(cycloolefin)(acac) complexes as catalysts for polymerization to stereoregular *cis-transoid* (high-*cis*) polyacetylenes. Secondly, stereoregular high-*cis* poly(arylacetylene)s of desired molecular weights, specifically poly(phenylacetylene), PPhA, and poly[(2,4-difluorophenyl)acetylene), PdFPhA, were synthesized and their degradation in correlation to *cis-to-trans* isomerization were studied during ageing, e.g. exposition to the air atmosphere and diffused light in THF-*d*₈ solution and in the solid state.

The research work was carried out thoroughly and precisely by using diverse advanced characterization techniques such as SEC, SEC/DAD, GC-MS, NMR, EPR, and DLS, which enabled PhD candidate to find answers to the all mentioned research challenges. The conclusions are clearly stated and encompass all the addressed topics as follows:

- [Rh(cycloolefin)(acac)] complexes provided high yields poly(arylacetylene)s and not for poly(alkylacetylene)s as well as copoly(alkylarylacetylene)s. All the synthesized polymers were of prevailing *cis-transoid* configuration. PPhA molecular weight was controlled by the extent of initiation and transfer reactions. Mgr. Trhliková proposed a mechanism for the initial step of [Rh(cycloolefin)(acac)] transformation into polymerization active centres.
- Molecular weight (MW) and configurational stability in THF-*d*₈ was low for PPhA and much better for PdFPhA, ascribed to steric effect of the *orto*-substituents on the phenyl groups. Oxidative degradation and *cis-to-trans* isomerization proceeded simultaneously in

THF- d_8 . Therefore the aged solutions consisted of two fractions with different MW: high-MW fraction with high-*cis* configuration and low concentration of unpaired electrons and low-MW fraction with prevailing isomerized *cis/trans* configuration and with higher concentration of unpaired electrons. On this basis Mgr. Trhliková proposed a tentative explanation for such a behavior, namely a kind of rapid ‘domino’ effect: after the individual double bond has been isomerized, the other double bonds would isomerize more readily and the concentration of unpaired electrons, generated during the rotational scission of the main-chain double bonds, would increase, which was confirmed by EPR. The isomerized molecules are assumed to be more prone to oxidative degradation.

- Ageing of PdFPhA in the solid state showed only MW instability and did not affect (or only in minor extent) a high-*cis* configuration.

I have only minor remarks and some questions regarding the presented PhD thesis:

- a) The experimental conditions for performing the characterization of the studied polymers have to be described in such a manner that the experiments can be reproduced.
- b) Regarding the eq. 11 on p. 37, I wonder if it is possible to elaborate more in detail the correlation between fraction $f(\text{Hacac})$ and molar ratio $[M] / [I]$ to better control the polymer MW.
- c) On p. 49 a new IR band of C=O groups is mentioned as a product of oxidative degradation of polyacetylenes. Is it characteristic only for polyacetylenes?
- d) Degradation of PdFPhA in solid state (p. 72) is very slow and only MW decrease was observed, without configurational changes. What is the explanation of this kind of behavior?
- e) And the last question: would be the use of mass spectrometry as an additional advanced instrumental technique beneficial for PhD research work?

To summarize, the research achievements of Mgr. Olga Trhliková in the frame of her PhD thesis are valuable original contribution to the field of conjugated polymers, their synthesis and properties. The systematic studies resulted in new knowledge on molecular weight and configurational stability of poly(arylacetylene)s that is very important for further development of this field from both basic and applied viewpoints. The PhD work covers a broad range of topics. It is written clearly, with sufficient theoretical background, and relevant discussion and conclusions for each part. The research results were extensively published: Mgr. Trhliková is the first author of four papers related to her PhD thesis and co-author of other three papers, all published in international scientific journals.

As a conclusion, it is my pleasure to express a positive opinion for the presentation of the PhD research work by Mgr. Olga Trhliková in order to be awarded a PhD degree from the Charles University in Prague.

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