Review of Ph.D. Thesis

Mgr. Olga Trhlíková: "Study of molecular weight and configurational stability of substituted polyacetylenes"

The scope of the Thesis is the chemistry related to the stability and degradation of the substituted polyacetylenes.

The theme of the Thesis is interesting and important because substituted poly-acetylenes are conducting polymers with possible applications.

Special attention in the Thesis is paid to the configurational stability behaviour of poly-acetylene derivatives and on the degradation mechanism of poly[(2,4-difluoro-phenyl)acetylene (PdFPhA) and poly[(fluorophenyl)acetylene]. There are some interesting points to clear:

From the theory it follows that the linearity of the plot of reciprocal number-average molecular weight, $1/X_n$, vs time, t, is a criterion of the random chain-scission [Ref. 120 and Ref. 1-7 therein]. The replacement of X_n with the molecular weight of the apex of the size exclusion chromatography (SEC) elution curve (EC, Cf. Equations 5 and 7, pp. 20, 21) is a quite crude approximation considering the fact that the SEC EC (Fig. 22, p.67) utilized for the construction of the $1/X_p$ vs t plots (Fig. 25, p. 70) for PdFPhA-(H), -(M), (L) show heavy tailing, especially fractions -H for 0 hours (non-degraded sample), which is critical for the M_n value. The degraded fractions show even multiple maxima, e.g., the curve for PdFPhA-(H) shows two big ones and one small. It should be explained why only X_p can be reliably obtained from SEC measurements (above Equation 7, p. 21). Was the SEC system calibrated? (In paper IV, the plot $1/X_p$ vs t is used without any discussion.) In fact, the chain scission of PdFPhA is not random because the dispersity of PdFPhA with the degradation time t increases to a maximum of $M_w/M_n \approx 7$ and goes back to $M_w/M_n \approx 2$ (Fig. 13, p. 55) which seems to be a consequence of the isomerized fractions differing in the speed of scission (p. 49). Randomness of the scission of the isomers is a difficult question because of the transitions and/or equilibrium between the isomers.

The Thesis is founded on several published papers, it is well written and the literature survey is exhaustive.

The Thesis fulfills all requirements and is recommended for the defense.

Prague, 16 August 2013   RNDr. Miloš Netopilík, CSc.