

SEC/DAD AND ¹H NMR STUDY OF MOLECULAR WEIGHT AND CONFIGURATIONAL STABILITY OF HIGH-CIS POLY(PHENYLACETYLENE) AND POLY[(2,4-DIFLUOROPHENYL)ACETYLENE]

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High-cis poly[(2,4-difluorophenyl)acetylene] (PdFPhA) and poly(phenylacetylene) (PPhA) were prepared by polymerization of respective monomers with [Rh(diene)acac] catalysts and the molecular-weight (MW) and configurational stability of these polymers were studied by SEC/DAD and ¹H NMR techniques. Polymers dissolved in THF-d₈ and exposed to the atmosphere and daylight at room temperature were found to undergo simultaneously proceeding cis-to-trans isomerization and oxidative degradation. The rate of these processes was considerably lower for PdFPhA compared to PPhA. Partly aged PPhA and PdFPhA were revealed to contain two microstructurally differing fractions: deeply isomerized macromolecules (lower-MW fraction) and microstructurally unperturbed high-cis macromolecules (higher-MW fraction). The SEC/DAD technique provided a high chromatographic separation and spectral distinction of these fractions in the case of partly aged PdFPhA and SEC/DAD was demonstrated as a very powerful tool for the characterization of polydisperse conjugated polymers. The hypothesis was postulated explaining the non-uniform distribution of high-cis and isomerized trans-rich macromolecules along the MW distribution of partly aged PPhA and PdFPhA. The hypothesis particularly assumed the acceleration of degradation of polymer chains by simultaneously proceeding cis-to-trans isomerization due to which the unpaired electron content was enhanced on the isomerized chains.

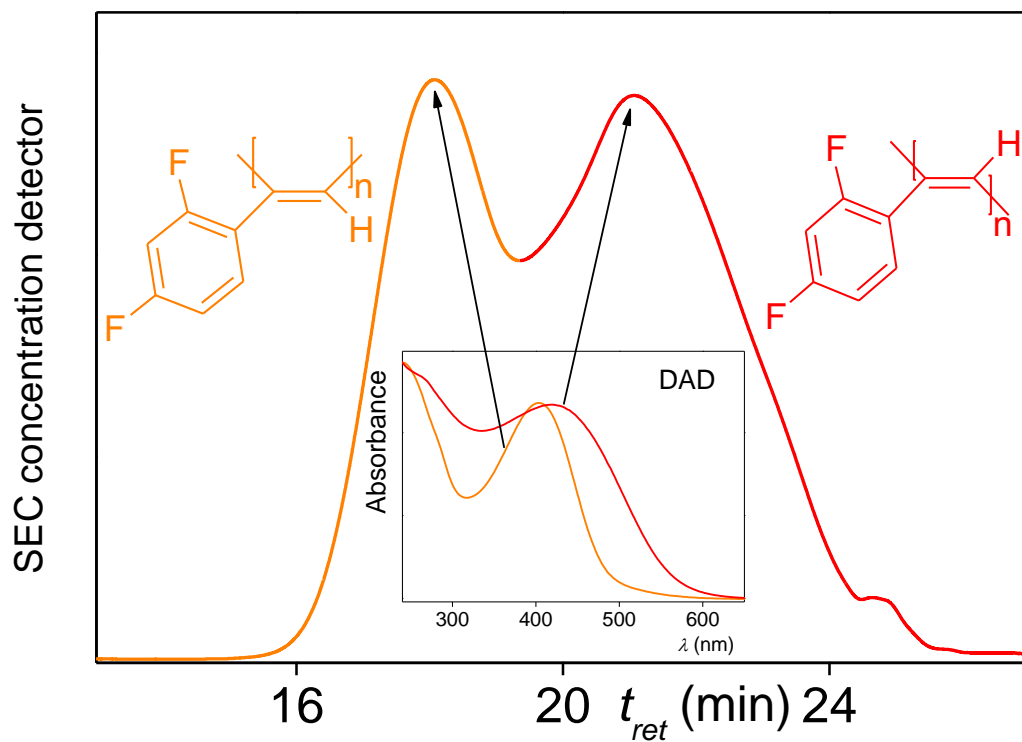


Figure: SEC/DAD chromatogram of PdFPhA aged in THF- d_8 for 337 hours. The solution was kept in contact with the atmosphere and diffuse daylight at room temperature. Corresponding UV vis spectrum is shown for each maximum of SEC/DAD chromatogram.