

17<sup>th</sup> International Conference on

# Industrial Chemistry and Water Treatment

May 21-22, 2018 | New York, USA



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### Emerging $\pi$ conjugated stretched and contacted helices of substituted polyacetylenes prepared with an organo-rhodium catalyst

The highly stereo-regular preparation of mono-substituted polyacetylenes (SPA)s was performed using an [Rh(norbornadiene)Cl] 2-triethylamine catalyst to give the  $\pi$ -conjugated helical polymers, because, the SPAs are expected as new advanced materials due to semi-conductivity, NLO properties, external stimulus responsibility, enantioselectivity, and oxygen permeability. These properties are strongly related to the geometrical structure, e.g., cis or trans forms and higher-order structure, e.g.,  $\pi$  stacking along with the helical main-chain in the solid phase. Therefore, we have investigated whether the geometrical and helical structures of the SPAs can be controlled through molecular design and/or external stimuli. The p-n-hexyloxyphenylacetylene (pPA) monomer was stereo-regularly polymerized using the Rh catalyst at 25°C. When ethanol and n-hexane were used as the polymerization solvents, a yellow P(Y), and its red P(R) were obtained, respectively. The diffuse reflective UV-vis spectra of these polymers showed  $\lambda_{\max}$  at 445 and 575nm, respectively. The WAXS patterns of P(Y) and P(R) exhibited hexagonal columnar structures which were attributed to the stretched and contracted helices, respectively. Additionally, P(Y) was irreversibly transformed into a reddish-black P(Y $\rightarrow$ B), whose columnar diameter was identical to that of P(R) when heated at 80°C for 1h. These findings suggest a thermally irreversible rearrangement from a thermally unstable P(Y) with a stretched helix to a stable P(Y $\rightarrow$ B) with a contracted helix. In the case of aliphatic polyacetylene ester, the mutual helical oscillation between the contacted and stretched helices was found in the solution.

### Biography

Masayoshi Tabata has completed his PhD from Hokkaido University, Japan and Post-doctoral Fellowship from United Kingdom and Sweden. After that, he became an Assistant Professor and Associated Professor at Hokkaido University, and Professor of Muroran Institute of Technology, Japan. Furthermore, he also became a Senior Research Director at National Institute of Advanced Industrial Science and Technology (AIST) at Tsukuba, Japan, and Guest Professor at Paris University in France.

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