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Emerging stretched and contacted helices and its stimuli induced mutual conversion of substituted polyacetylenes prepared with an organo-rhodium catalyst

The highly stereo regular preparation of mono-substituted polyacetylenes (SPA)s as one of the π-conjugated helical polymers was performed using an [Rh(norbornadiene)Cl]$_2$-triethylamine catalyst. The SPAs are expected as new advanced materials due to semiconductivity, NLO properties, external stimulus responsibility, enantioselectivity, and oxygen permeability. These properties are related to the geometrical structure and higher-order structure of 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 has been stereoregularly 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 λ_{max} at 445 and 575 nm, 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→B), whose columnar diameter was identical to that of P(R) when heated at 80°C for1 h. These findings suggest a thermally irreversible rearrangement from a thermally unstable P(Y) with a *stretched* helix to a stable P(Y→B)with a *contracted* helix.

Biography

Masayoshi Tabata has completed his PhD from Hokkaido University, Japan and Postdoctoral studies from United Kingdom and Sweden. After that he became Assistant Professor and Associated Professors at Hokkaido Univ., and Professor of Muroran Inst.of Tech., Japan. Moreover, he also became a senior research director at National Institute of Advanced Industrial Science & Tech. (AIST) Tsukuba, Japan, and Guest Professor at Paris Univ. in France.

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