

論文名：3,5-ビス(ヒドロキシメチル)フェニルアセチレンのらせん選択重合と主鎖コンフォメーションに誘導された側鎖の不斉光学的性質

Title: Helix-Sense-Selective Polymerization of 3,5-Bis(hydroxymethyl)phenylacetylenes Bearing Functional Aryl Groups and Chiroptical Properties of Side Groups Related to Their Backbone Conformation

新潟大学大学院自然科学研究科（論文博士は氏名のみでも可）

氏名 時志春 (Zhichun Shi)

(以下要約を記入する)

The helix is the most basic and important conformation in biological macromolecules, such as DNA, RNA and enzyme. Importantly, the helical structure is inherently chiral, which is meaningful for generation of life in nature involving molecular recognition, replication, and catalytic activity. Chemist scientists have been engaged to develop artificial helical polymers, supramolecules and so on, aiming at not only the imitation of biological helices and functions but also their potential applications in materials, sensing specific molecules, the separation of enantiomers, and asymmetric catalysis. In this study, we will synthesis of a new RHPA monomer connected with a rigid and π -conjugated substituent, And then investigate chiroptical properties of side groups related to their backbone conformation, the helical conformation stability of the polymers related to the side chain structure for the corresponding polymers.

In chapter 1, An achiral 3,5-bis(hydroxymethyl)phenylacetylene connected with a rigid and π -conjugated substituent were polymerized using a rhodium (Rh) complex catalyst in the presence of chiral 1-phenylethylamines. The circular dichroism (CD) spectra of the polymers indicated that an excess of one-handed helical polyacetylene backbone was induced by helix-sense-selective polymerization under the asymmetric condition despite the achiral monomer. The split type induced CD signals at 300 nm were attributed to the chromophore including the conjugated side group since the signal appeared at the longer wavelength compared with the poly[3,5-bis(hydroxymethyl)phenylacetylene] without conjugated substituent.

In chapter 2, HPA monomers DBHPA connected with a rigid and linear π -conjugated terphenylacetylene were successfully polymerized with a rhodium catalyst [Rh(nbd)Cl]₂ in the presence of chiral PEA to give the corresponding polymers, and it was confirmed that HSSP proceeded for DBHPA and the terphenyl side groups were also arranged helically with preferential helical sense. Fluorescence peak of poly (DBHPA) decreased at 310 nm and increased at 390nm due to addition of a polar solvent. This fluorescence chang was induced by conformational change of backbone.

In chapter 3, 3,5-bis(hydroxymethyl)phenylacetylene (HPA) monomers DTHPA and DPETHPA connected with a rigid and linear π -conjugated oligomer were successfully polymerized with a rhodium catalyst $[\text{Rh}(\text{nbd})\text{Cl}]_2$ in the presence of chiral PEA to give the corresponding polymers. Helix-sense-selective-polymerization proceeded for DBHPA. CD, UV and WAXS spectroscopic studies revealed that the intramolecular hydrogen bonds of the polymers contributed to the stabilization of their helical conformation but the stability depended on the length of the rigid and linear π -conjugated side group.

In chapter 4, The *m*-HGHPA and *p*-HGHPA were polymerized in the presence of the $[\text{Rh}(\text{nbd})\text{Cl}]_2$ catalyst and (*R*)- or (*S*)-PEA to give the corresponding polymers. The split-type induced CD signals at 310 nm and broad signals at 400–550 nm were observed for the THF solution of poly(*m*-HGHPA), while no optical activity was observed for the poly(*p*-HGHPA).

In chapter 5, We synthesized new monomers PEHPA connected with a rigid and linear π -conjugated substitute were successfully polymerized with a rhodium catalyst $[\text{Rh}(\text{nbd})\text{Cl}]_2$ in the presence of chiral PEA to give the corresponding polymers. HSSP proceeded for PEHPA. CD, UV studies revealed that the intramolecular hydrogen bonds of the polymers contributed to the stabilization of their helical conformation but the stability depended on the length of the rigid and linear π -conjugated side group. And then investigated selective cycloaromatization (SCAT) ability of the polyphenylacetylenes related to the helical conformation stability.

In summary, we have already succeeded in synthesizing a poly(phenylacetylene) without chiral side groups, and the polymerization which had rigid and π -conjugated substitute using a rhodium (Rh) complex catalyst in the presence of chiral 1-phenylethylamines to give the corresponding optically active helical polymers. It was found that the intramolecular hydrogen bonds of the polymers contributed to the stabilization of their helical conformation but the stability depended on the length of the rigid and linear π -conjugated side group. These results suggested that the molecular design of reasonable packing of side groups to give adequate interaction between side groups would be require for the statical helical conformation of polyHPAs connected with a rigid π -conjugated substituent.

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