

論文名：**Optical Resolution by Circularly Polarized Light and Preparation of Supramolecular Polymer Membranes by Highly Selective Photocyclic Aromatization**

(高選択光環化芳香族化分解反応を利用した円偏光による光学分割および超分子ポリマー膜調製)

新潟大学大学院自然科学研究科

氏名： 宮田 真理

Outline of this thesis is as follows.

Chapter 1 described a general introduction of this thesis. This introduction provided some background, purpose, and contents of this thesis.

Part I that consists of Chapter 2 and Chapter 3 described photocyclic aromatization of cis-cisoidal racemic helical polymers with circularly polarized light. In Chapter 2, helix-sense-selective photodegradation of a helical poly(substituted phenylacetylene) in the membrane state was achieved by highly selective photocyclic aromatization using circularly polarized light. This is the first example of kinetic optical resolution of racemic helical polymers. In Chapter 3, it was shown that optimization and mechanism of helix-sense-selective photodegradation of racemic helical poly(substituted phenylacetylene)s by highly selective photocyclic aromatization with circularly polarized light were indicated. Improvement of the reaction rate and the selectivity of helix-sense-selective photodegradation was achieved by using photosensitizer or lowering temperature of the reaction. Helix-sense-selective photodegradation of racemic helical polymers by highly selective photocyclic aromatization with circularly polarized light was successfully achieved not only in membrane but also in solution for the first time. Furthermore, helix-sense-selective photodegradation of a racemic helical poly(substituted phenylacetylene) having conjugated imine bonds by highly selective photocyclic aromatization with circularly polarized light was achieved for the first time.

Part II that consists of Chapters 4-6 described quantitative topochemical reaction of one-handed helical polymers having rigid planar imino-linked substituents. In Chapter 4, novel substituted acetylenes having a rigid planar substituent via a dynamic covalent imino group were synthesized and subsequently polymerized by using a chiral initiator system consisting of an achiral rhodium complex and a chiral *N,N*-dimethylphenylethylamine to produce one-handed helical polymers having dynamic covalent imino groups. Furthermore, membranes could be produced from these chiral polymers that showed highly selective photocyclic aromatization and quantitative substitution of the side groups. Supramolecular polymer membranes having a high strength were obtained. Chiral polymer membranes having many different kinds of side groups were easily obtained. In Chapter 5, it has been shown that a new synthetic process to obtain new self-standing polymer. It contains two steps as follows: the first step is solid-state topochemical postpolymerization of a template polymer with polymerizable functional groups and the second step is chemical exfoliation of the resulting multi-layered polymers. In this study, a cis-cisoidal poly(phenylacetylene) having rigid planar

imino-linked substituents as polymerizable functional groups prepared by helix-sense-selective polymerization was selected as a starting template polymer which can form a columnar structure in the membrane. Presence of the best alkylene length in the diamine to proceed the topochemical postpolycondensation reaction maintaining the regular high-order structures of the starting template polymer was confirmed. Easy preparation of new subnanoporous membranes by simple membrane reaction having high conversions in spite of a heterogeneous polymer reaction was achieved. In Chapter 6, it has been achieved to obtain flexible self-supporting supramolecular polymeric membranes consisting of only 1,3,5-trisubstituted benzene derivatives prepared by highly selective photocyclic aromatization of the corresponding poly (substituted phenylacetylene)s having a columnar structure. The flexibilities of the self-supporting supramolecular polymeric membranes were enhanced by introducing hydroxyl groups, phenylene groups, and liquid crystalline substituents to the starting polymers. There were two reasons for the enhanced strength: 1) introduction of intercolumnar hydrogen bonds and 2) enhancement of the degree of intracolumnar stackings. This strength depended on the structure of the starting polymers which functioned as a template.

Finally, Chapter 7 concluded this thesis and the perspectives were described.