【別紙２】

論文名：**Control of the helical sense without chiral sources and by achiral factors in helix-sense-selective polymerization (HSSP) and characterization of the resulting polymers by highly selective photocyclic aromatization (SCAT) - Absolute HSSP, reversal HSSP and SCAT analysis-**（要約）

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　Yin　Guanwu

（以下要約を記入する）

Contents

Chapter 1

Guanwu Yin, Toshiki Aoki, Takashi Namikoshi, Masahiro Teraguchi, Takashi Kaneko, *Chemical Science*, Submitted for publication.

Chapter 2

Guanwu Yin, Geng Zhang, Toshiki Aoki, Masahiro Teraguchi, Takashi Kaneko, *Macromolecules*, **2017**, (in press).

Chapter 3

Guanwu Yin, Lijia Liu, Toshiki Aoki, Takeshi Namikoshi, Masahiro Teraguchi, and Takashi Kaneko *Chem. Lett.*, **45**, 813-815(2016).

Chapter 4

Jianjun Wang, Yu Zang, Guanwu Yin, Toshiki Aoki, Hiroyuki Urita, Ken Taguwa, Lijia Liu, Takeshi Namikoshi, Masahiro Teraguchi, Takashi Kaneko. *Polymer*, **55**, 1385-1396(2014).

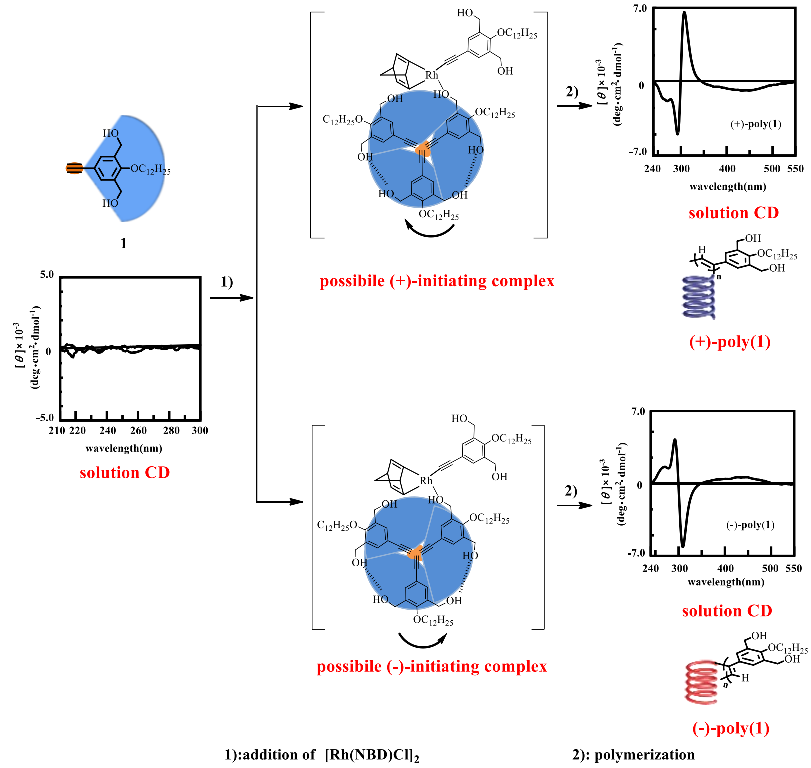
Chapter 5

Yu Zang, Guanwu Yin, Toshiki Aoki, Masahiro Teraguchi, Takashi Kaneko, Liqun Ma, and Hongge Jia. *Chirality*, **27**, 59-63(2015).

Part I： Control of the helical sense without chiral sources and by achiral factors in helix-sense-selective polymerization (HSSP)

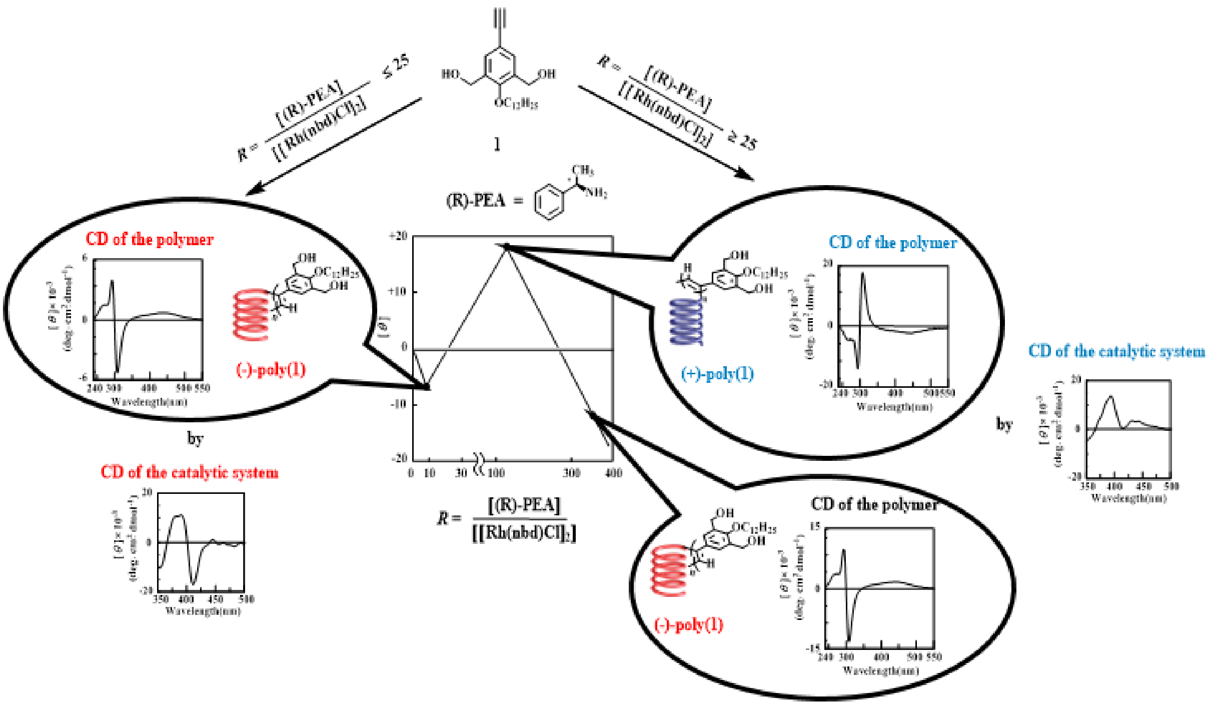
Chapter 1: Absolute Asymmetric Polymerization (HSSP) Using No Chemical and Physical Chiral Source in Solution

In chapter 1, To synthesis new chiral compounds, another chiral source compound is always necessary. Catalytic enantioselective reactions are the most valuable method to obtain new chiral compounds because a small amount of an expensive chiral compound produces a larger amount of a valuable chiral compound. However, one of the enantiomers, such as unnatural amino acids, is usually very expensive. If two enantiomers can be synthesized using no chiral compound, then we can both break the above rule and open up a more efficient route to useful chiral materials. Here we report that we have found genuine absolute asymmetric polymerization (GAAP) in catalytic helix-sense-selective polymerization of achiral monomers using not only chiral compounds as chiral sources but also circularly polarized lights (CPL). As a result, we synthesized soluble (+)- or (-)-polymers using no chiral source in solution. To the best of our knowledge, this GAAP in solution is the first example in asymmetric polymerizations.



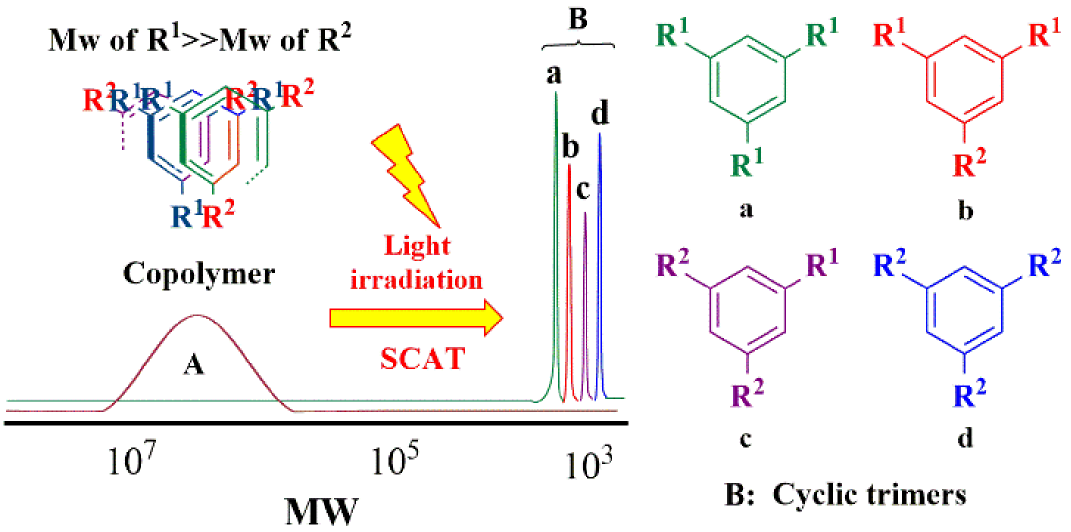
Chapter 2: Achirality to Chirality: Double Reversal of Enantioselectivity Using a Single Cocatalyst in Asymmetric Polymerization(HSSP)

In chapter 2, Chiral compounds play a vital role in our lives because we are made up of chiral polymers. A strict rule of chirality synthesis is “to obtain one enantiomer of a new chiral product, one enantiomer of a chiral source is needed”. If two enantiomers can be synthesized using a single chiral compound, we can both break the above rule and open up a more efficient route to useful chiral materials using a cheaper chiral source. Here we report the first example of double reversals of enantioselectivity in catalytic asymmetric polymerization of achiral monomers using a single isomer of simple chiral compounds as cocatalyst. Furthermore, we achieved this by changing only one achiral condition, that is, the amount of the chiral cocatalyst, without any other changes in the polymerization conditions. As a result, we easily and directly synthesized (+)- or (-)-polymer using a single chiral compound as a cocatalyst.



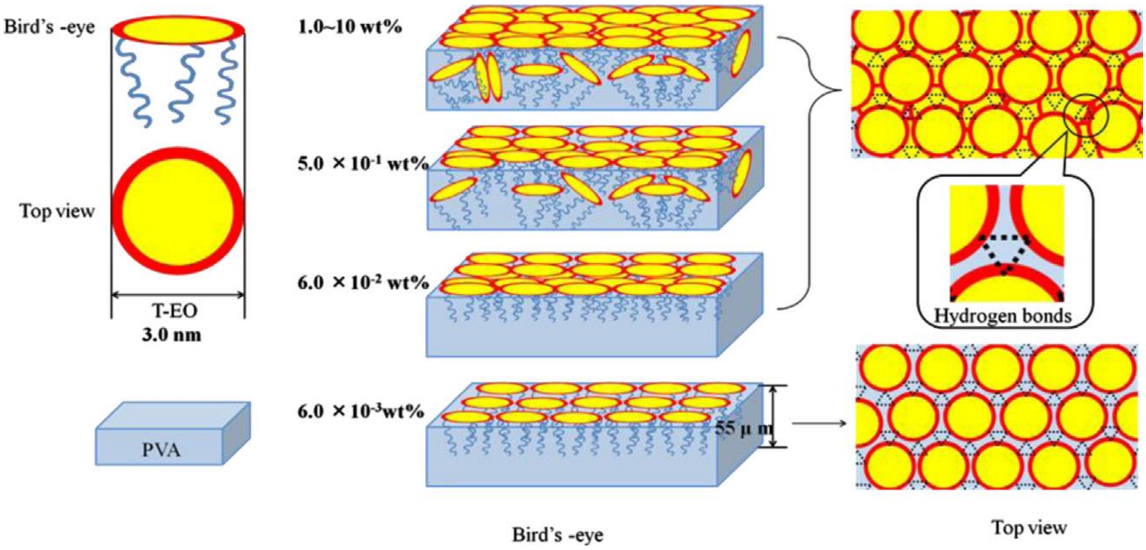
Chapter 3: Highly Selective Photocyclic Aromatization (SCAT) - GPC Method for Quantitative Determination of Microstructures of Copoly(Substituted Acetylenes) Backbone

In chapter 3. Highly selective photocyclic aromatization(SCAT) of poly(substituted acetylene)s that can quantitatively yield the corresponding 1,3,5-trisubstituted benzene derivative was applied to quantitative determination of microstructures of copoly(substituted acetylene)s. By GPC analysis of the SCAT products of copolymers of two substituted acetylenes having substituents whose molecular weights were largely different, some clear information for microstructures such as sequence (triad) distribution and composition, which could not be obtained from NMR because of their broad peaks, could be obtained successfully in a mild condition.



Chapter 4: Facile Synthesis of Five 2D Surface Modifiers by Highly Selective Photocyclic Aromatization (SCAT) and Efficient Enhancement of Oxygen Permselectivities of Three Polymer Membranes by Surface Modification Using a Small Amount of the 2D Surface Modifiers

In chapter 4. A facile synthesis of novel five 2D (planar) surface modifiers having a triphenylbenzene derivatives as a 2D structure has been achieved by the highly selective photocyclic aromatization reaction. Efficient enhancement of oxygen permselectivities through the three polymer membranes has been achieved by adding a small amount (<5.0 wt%) of the 2D surface modifiers. Among the five 2D surface modifiers, a modifier compound having oligoethylene oxide groups showed the best performance for the enhancement. These improvements were thought to be caused mainly by improvement of the solution selectivity on the membrane surface where the 2D surface modifiers were accumulated. In some of the surface modified blend membranes, their plots in the PO2 -a graph were over or close to the upper boundary line by Robeson in 1991. Since all the membranes containing the 2D surface modifiers showed better permselectivities than the corresponding substrate membranes, it is very promising for the future.



Chapter 5: Synthesis of a fluorine-containing cis-cisoidal one-handed helical polyphenylacetylene and application of highly selective photocyclic aromatization (SCAT) product on oxygen pemselective membrane

In chapter 5, A novel phenylacetylene monomer having a perfluorinated alkyl group (M-F) was synthesized and polymerized in a chiral catalytic system to yield a one-handed helical polymer. The ability and efficiency of the chiral induction of the fluorine-containing monomer in the helix-sense-selective polymerization (HSSP) was much higher than those of a monomer having the corresponding alkyl group (M-H) we reported before. The resulting polymer P-F showed cis-cisoidal one-handed helical conformation, and was suitable for highly selective photocyclic aromatization (SCAT) to give a 2D surface modifier (T-F). Oxygen permselectivity through a base polymer membrane was highly enhanced from 1.83 to 2.36 by adding a small amount (1–5 wt%) of the 2D surface modifier T-F. The improvement was thought to be caused by improvement of solution selectivity on the membrane surface which the 2D surface modifier effectively covered.

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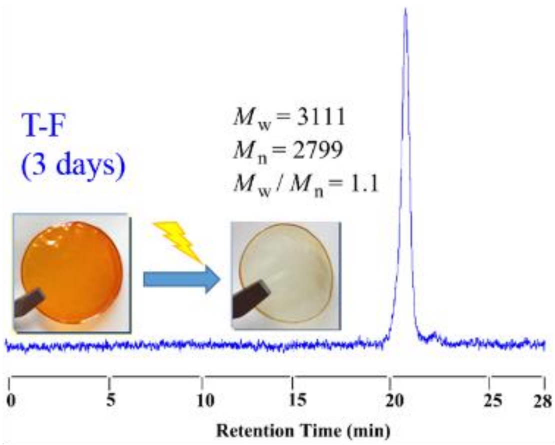
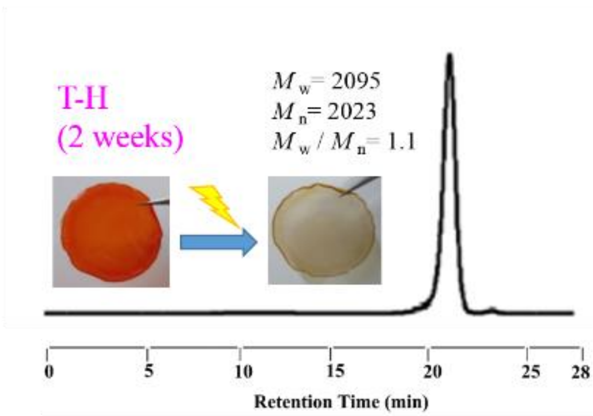

T-F
(3 days)
M_w = 3111
M_n = 2799
M_w / M_n = 1.1
0 5 10 15 20 25 28
Retention Time (min)

(a)


T-H
(2 weeks)
M_w = 2095
M_n = 2023
M_w / M_n = 1.1
0 5 10 15 20 25 28
Retention Time (min)

(b)

List of Publications and Presentations

Papers

1.Guanwu Yin, Toshiki Aoki, Takashi Namikoshi, Masahiro Teraguchi, Takashi Kaneko. Absolute Asymmetric Polymerization Using No Chemical and Physical Chiral Source in Solution. *Chemical Science*, (Article), Submitted for publication

2.Guanwu Yin, Geng Zhang, Toshiki Aoki, Masahiro Teraguchi, Takashi Kaneko. Achirality to Chirality: Double Reversal of Enantioselectivity Using a Single Cocatalyst in Asymmetric Polymerization. *Macromolecules*, (Article), **2017**, (in press)

3.Guanwu Yin, Eri Ohtaka, Toshiki Aoki, Jianjun Wang, Masahiro Teraguchi, and Takashi Kaneko. Oxygen permselectivities through supramolecular polymer membranes prepared by highly selective photocyclic aromatization. *Polymer*, **2017**, 127,232-235.

4.Guanwu Yin, Nennei Nagaoka, Lijia Liu, Toshiki Aoki, Masahiro Teraguchi, and Takashi Kaneko. A new analysis method for quantitative determination of triads of copoly(substituted acetylene)s' backbone by highly selective photocyclic aromatization. *Chem. Lett.*, **2017**, (in press).

5.Guanwu Yin, Lijia Liu, Toshiki Aoki, Takeshi Namikoshi, Masahiro Teraguchi, Takashi Kaneko. Highly selective photocyclic aromatization (SCAT) - GPC method for quantitative determination of microstructures of copoly (substituted acetylenes) backbone. *Chem. Lett.*, **2016**, 45, 813 - 815.

6.Young-Jae Jin, Hyojin Kim, Mari Miyata, Guanwu Yin, Takashi Kaneko, Masahiro Teraguchi, Toshiki Aoki, Giseop Kwak. Influence of hydrodynamic environment on chain rigidity, liquid crystallinity, absorptivity, and photoluminescence of hydrogen-bonding-assisted helical poly(phenylacetylene), *RSC Advances*, **2016**, 47, 36661 – 36666.

7.Yu Zang, Guanwu Yin, Toshiki Aoki, Masahiro Teraguchi, Takashi Kaneko, Liqun Ma andHongge Jia. Synthesis of a Fluorine-Containing Cis-Cisoidal One-Handed Helical Polyphenylacetylene and Application of Highly Selective Photocyclic Aromatization Product on Oxygen Permselective Membrane. *Chirality*, **2015**, 27, 459-463.

8.Jianjun Wang, Yu Zang, Guanwu Yin, Toshiki Aoki, Hiroyuki Urita, Ken Taguwa, Lijia Liu, Takeshi Namikoshi, Masahiro Teraguchi, Takashi Kaneko. Facile synthesis of five 2D surface modifiers by highly selective photocyclic aromatization and efficient enhancement of oxygen permselectivities of three polymer membranes by surface modification using a small amount of the 2D surface modifiers, *Polymer*, **2014**, 55,1385-1396.

Conference

1. Guanwu Yin, Toshiki Aoki, Masahiro Teraguchi, Takashi Kaneko. Spontaneous helix-sense-selective polymerization (HSSP) of achiral acetylenes in the absence of chiral sources during polymerization. Polym. Prep., Jpn., 65(2), 1ESB05.

2. Guanwu Yin, Toshiki Aoki, Masahiro Teraguchi, Takashi Kaneko. Control of the helical sense of helix-sense-selective polymerization by changing "achiral condition" using an identical chiral source and its mechanism. Polym. Prep., Jpn., 65(2), 1ESB06.

3. Yu Zang, Guanwu Yin, Toshiki Aoki, Masahiro Teraguchi, Takashi Kaneko, Liqun Ma, and Hongge Jia, "Synthesis of fluorine-containing cis-cisoid helical polymer and application of its highly selective photocyclic aromatization product on gas separation membrane", *Molecular Chirality Asia 2014*, Beijing, China(Oct. 29th – Oct.31th, 2014)

4. Hiroyuki Urita, Guanwu Yin, Jianjun Wang, Masahiro Teraguchi, Takashi Kaneko, Toshiki Aoki, and Y. Zang, "Permeation of 2D Polymer Membranes (1): Oxygen Permselectivity through 2D Polymer Surface-modified Membranes with 2D Surface Modifiers", *The 10th SPSJ International Polymer Conference*, Tsukuba, Japan (Dec.2th –Dec.5th, 2014)

5. Jianjun Wang, Hiroyuki Urita, Yu Zang, Guanwu Yin, Masahiro Teraguchi, Takashi Kaneko, Toshiki Aoki, "Efficient Improvement of Oxygen Permselectivity by the Addition of a Novel 2D Surface Modifier Prepared by Selective Photocyclic Aromatization", *12th International Conference on Polymers for Advanced Technologies*, Berlin, German (Sep.29th –Oct. 3th ,2013).