Contribution

Recent Researches on Construction of Artificial Helical Polymers
Practical Molecular Design Methodology by the Factors for Inducing and Maintaining Helical Structures on the Basis of Classification of Main Chain Skeletons

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Abstract

Recently, demand of high-functionality for artificial polymers increases more and more in the various fields of materials such as optics-photonics and electronics. Especially, development of synthetic processes for the polymers having clear helical structure attracts large interests from the viewpoint of not only for creation of novel functionality and functional materials but also for elucidation of fine functionality displayed by helical biopolymers. In this review, recent research development and trend of artificial helical polymers and supramolecules are categorized and discussed focusing the relation between the fundamental molecular structure and capability of achieving induced/fixed helical conformation.

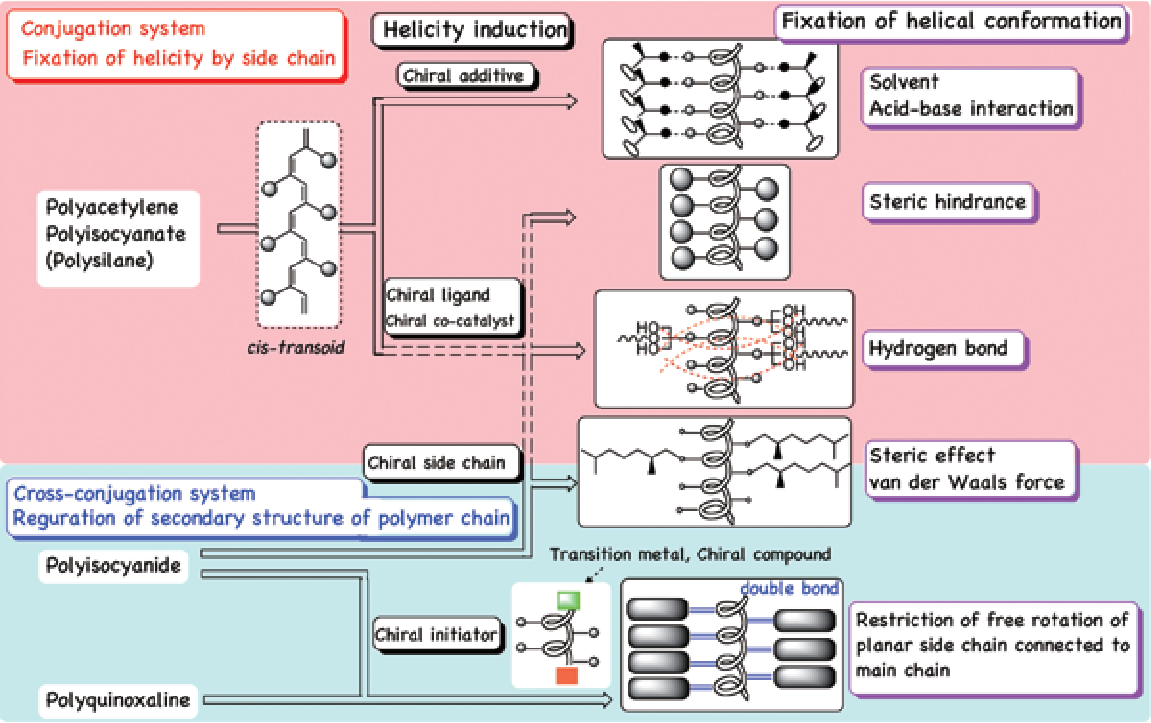


Figure 0-1. Outline

1. Introduction

1-1. Short History of Synthetic Helical Polymers[1a,b]

Studies on helical structures of macromolecular compounds have started at the almost same period about independent types of polymers, i.e., helical structure of proteins (Pauling, 1951), double helical structure of DNA (Watson, Crick, 1953), and 1/3-helical structure of isotactic polypropylene (Natta, 1955) have been clarified during a few years. Especially, Natta's finding of isotactic polypropylene has an advanced technological meaning that helical structures of polymers can be constructed artificially via minute control of stereoregularity in design of the polymer structures and the corresponding monomers and achievement of fine synthetic reaction. Afterward construction of synthetic helical polymers having bulky substituents has been studied to generate various kinds of this type of polymers such as polyisocyanates,[2a,b] polyisocyanides,[3] polychloral,[4] poly(alkyl methacrylate)s,[5] polysilanes,[6] polyacetylenes,[7a-d] polythiophenes[8] (Fig. 1-1). The rigid to semi-rigid polymer main chains of these polymers are explained to maintain the helical conformation of the polymers.

As an outstanding work for synthesis of helical polymers, Okamoto and the coworkers reported asymmetric polymerization of acrylate.[5] In this polymerization system, the screw-sense of the helical conformation is controlled by the chirality of asymmetric ligand composing of the initiator of the addition polymerization. In general, polymers having flexible main chain backbone cannot maintain the helical conformation in solution as the polymer main chain rotates without strong restriction. Hence, for the sake of the maintenance of the helical conformation of polymers, introduction of bulky side chain pendant was undertaken to make the polymer main chain practically rigid employing their steric hindrance. For examples, poly(triphenylmethyl methacrylate) takes stable helical conformation (Fig. 1-2), in contrast to random coil conformation of poly(methyl methacrylate) in solution. In a natural consequence, determination of the direction of winding of the polymer main chain means the designation of the screw-sense of the polymer helical conformation. The synthetic polymers derived from vinyl monomers have polymer main chain of repeating sequence composed of sp^3-carbons. So helical polymers of this type, i.e. those without effective interacting functional group need sufficient magnitude of van der Waals interactions to keep the helical conformation. Contrarily, the helical conformation of biopolymers such as polypeptides is induced and maintained by both hydrogen bonding and van der Waals force. Especially, inter- and intramolecular hydrogen bondings contribute to the secondary structure of the polymers. However, the appropriate alignment of hydrogen bondings in synthetic polymers is difficult to be constructed. Therefore, there are rather scarce reports except for synthetic DNA or synthetic polypeptides.

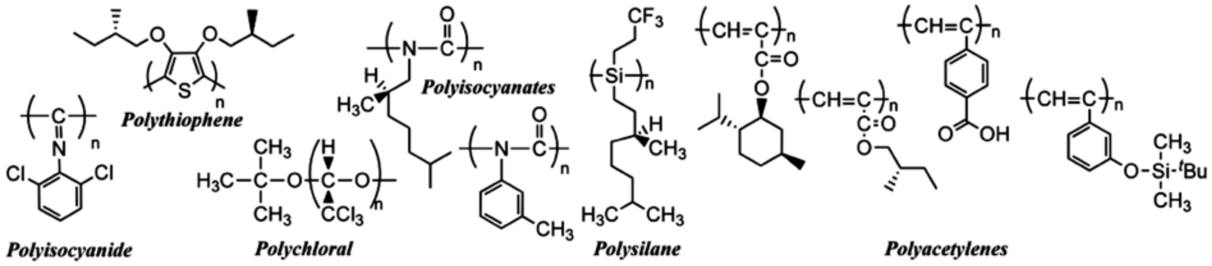
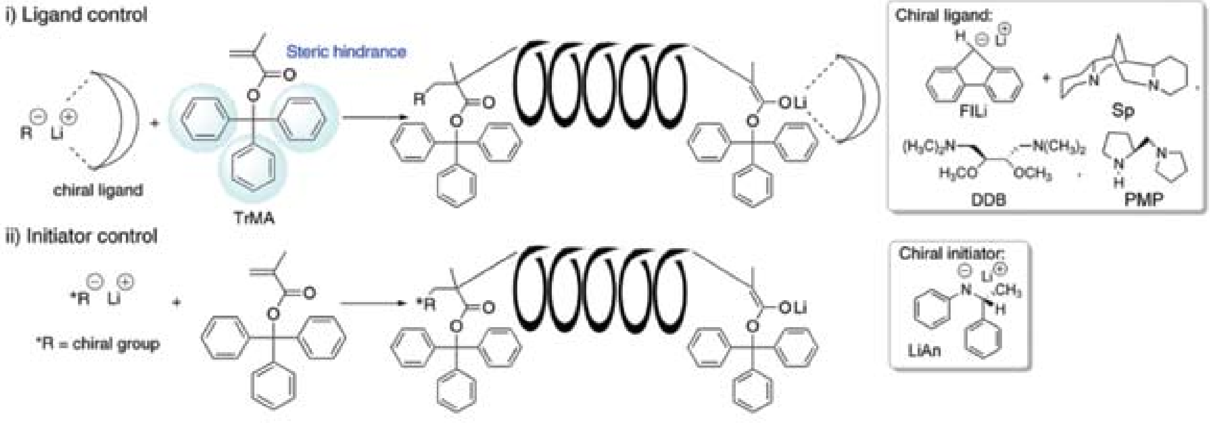


Figure 1-1. Artficial helical polymers



Nakano, Okamoto in *Controlled Polymerization, KIKAN KAGAKU SOSETSU*, No. 18, ed. by Nihon Kagakukai, 1993.

Figure 1-2. First example of helix-sense-selective polymerization

1-2. Overview of Recent Researches

The optically active polymers investigated on synthetic aspect are roughly classified into two types having chiral center in the repeating unit or not. As an example for the former, introduction of asymmetric center of the monomer molecule into the polymer main chain is of the most employed methods such as polymerization of optically active monomers represented by binaphthyl (Habaue–Okamoto[9],Tsubaki[10]). In addition to this, the synthetic approaches with control of chirality of the repeating unit in the main chain, i.e., helix-sense-selective type conformation of asymmetric polymerization of achiral monomers (Okamoto[11], Nozaki[12]) and asymmetrically monomer-selective polymerization of racemic monomers (Kakuchi[13]), are undertaken presently. On the other hand, approaches for the latter method, the induction of anisotropic arrangement of atomic groups, i.e., chirality, and the stabilization of the resulting helical conformation of the semi-rigid main chain with the aid of asymmetric source situated inside or outside of the monomers are attempted, represented by screw-sense-selective polymerization of polyacetylenes and polyisocyanates. These optically active polymers having induced axial chirality without asymmetric atom in the polymer main chain are roughly classified into sp^3–sp^3 type and sp^2–sp^2 one, according to the fundamental structure of polymer main chain. Furthermore, optically active polymers of sp^2–sp^2 type polymer main chain are further divided into conjugated and cross-conjugated main chain polymers (Fig. 1-3).

The helical polyacrylates of early ages described above are classified as one of the helical polymers having sp^3–sp^3 main chain and the stabilization of the conformation is largely attributed to the structure of alkyl group of the ester moiety. The substitution of alkyl group brings about large difference in degree of stabilization of helical structure. Though polypeptides are essentially classified as a type of sp^3–sp^2 main chain polymers, planar nature with bond angles of 120° of peptide bond due to the resonance of amide moiety affords the polymer feature as partially rigid polymer structure. The screw-sense of α-helical conformation is determined by the chirality of α-carbon and the intramolecular hydrogen bond strongly stabilize the conformation. Afterwards the trend of development of optically active polymer has been shifted to that deals with polymers having sp^2–sp$^\alpha$ ($\alpha = 2, 3$) type main chain repeating units. Polyacetylenes and polyisocyanates are the polymers having conjugated sp^2–sp^2 type main chain feature, in which the side chains bonded via sp^2–sp^3 linkages induce, stabilize, and fix the chirality. On the other hand, polyisocyanides are the polymers having cross-conjugated sp^2–sp^2 type main chain structure, in which the side chains bonded via sp^2–sp^2 linkages control the chirality. For this type of polymer synthesis, variety of stereo-controlling techniques of covalent and non-covalent methods are investigated. This type of optically active polymer receives large interests, and various controlling techniques are proposed and studied especially from the point of flexibility in designing and synthesis of the artificial polymers of helical conformation.

2. Induction and Stabilization of Helical Structure

This review introduces the recent works on the synthesis of artificial helical polymers focusing those on the synthetic helical polymers having neither asymmetric centers nor asymmetric axes in the repeating units according to the classification of the synthetic methods into following three categories, 1) fixation or stabilization of helical conformation, 2) asymmetric induction of polymer main chain conformation by molecular asymmetric factors of outside of molecule, and 3) asymmetric induction of polymer main chain conformation by intramolecular asymmetric factors.

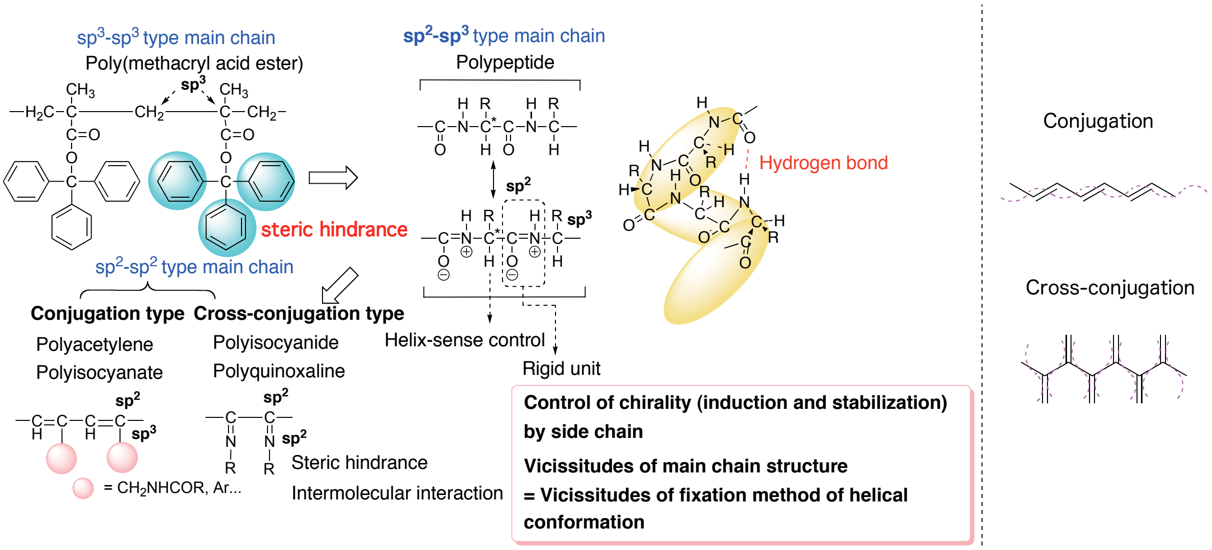


Figure 1-3. Vicissitudes of molecular design of main chain structure and control of chirality of helical conformation in synthetic study on optically active polymers comprised of repeating unit without asymmetric atom

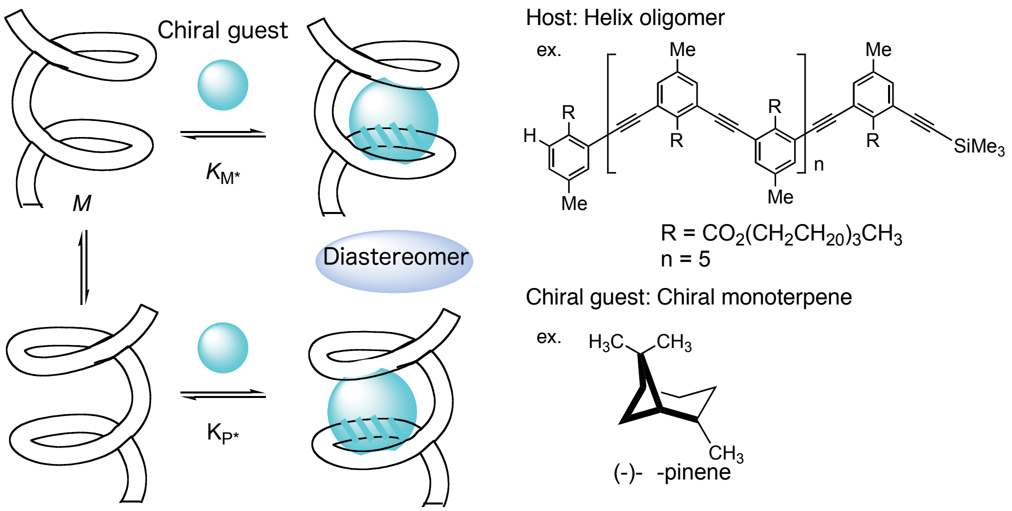
2-1. Fixation Methods for Helical Conformation of Polymers

This section deals with the practical methods for maintaining the helical conformation of polymers together with helix-sense-selective induction. There are several methods for this purpose as follows: 1) intermolecular host–guest interaction, 2) coordination or chelation of metal ion, 3) van der Waals force (interaction), 4) acid–base interaction, 5) hydrogen bondings, 6) steric effect of bulky pendant groups, and so on.

Moore and the co-workers have reported the fixation of helical conformation of *m*-phenylene ethynylene oligomer (as a host) through formation of 1:1 complex with chiral monoterpene (as a guest) in acetonitrile solution (Fig. 2-1).[14] Inouye and the co-workers have revealed the induction of helical conformation of poly(*m*-ethynylpyridine) (as a host) through hydrogen bonding with saccharide template.[15] In this system, the helical conformation is fixed by intermolecular hydrogen bonding and rigid main chain structure.

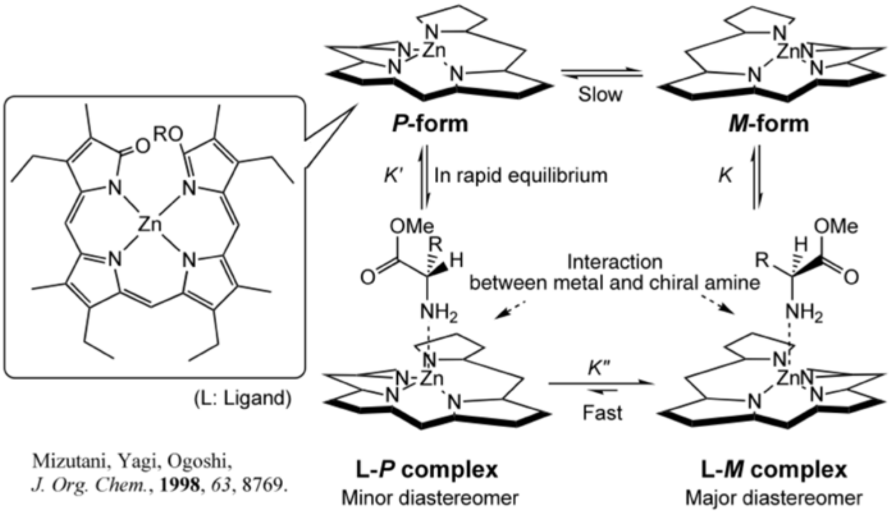
Ogoshi and the co-workers[16] and Shinkai and the co-workers[17] have achieved induction of helical conformation of polyaromatic compounds by chelation to Zn or Cu and fixation of the one screw-sense of helical conformation by the intermolecular interaction with chiral additive molecules (Fig. 2-2). The screw-sense of the helix depends on the structure of the added chiral molecules. Furthermore, Ishimaru and the co-workers retained the one screw-sense of helical conformation of porphyrin dimer induced as follows: the racemic porphyrin dimer coordinated with Zn(II) was treated of chiral amine to induce helical conformation by the aid of chiral amine–Zn interaction followed by removal of the chiral amine and coordination of Ba^{2+} ion to crown ether moiety.[18]

Fujiki and co-workers have succeeded in the synthesis of various helical polysilane homologues with the aid of Wurtz coupling. The polysilane having long alkyl chains bearing trifluoromethyl group at the end site induces and maintains its helical conformation by the aid of weak Si---F–C interaction. They intended to develop the functional materials utilizing such weak intermolecular van der Waals force. This work is described later in detail as the Topic 1: Chiroptical transfer and amplification.[19]



Prince, Barnes, Moore, *J. Am. Chem. Soc.*, **2000**, *122*, 2758.

Figure 2-1. Helicity induction by host−guest intermolecular interaction



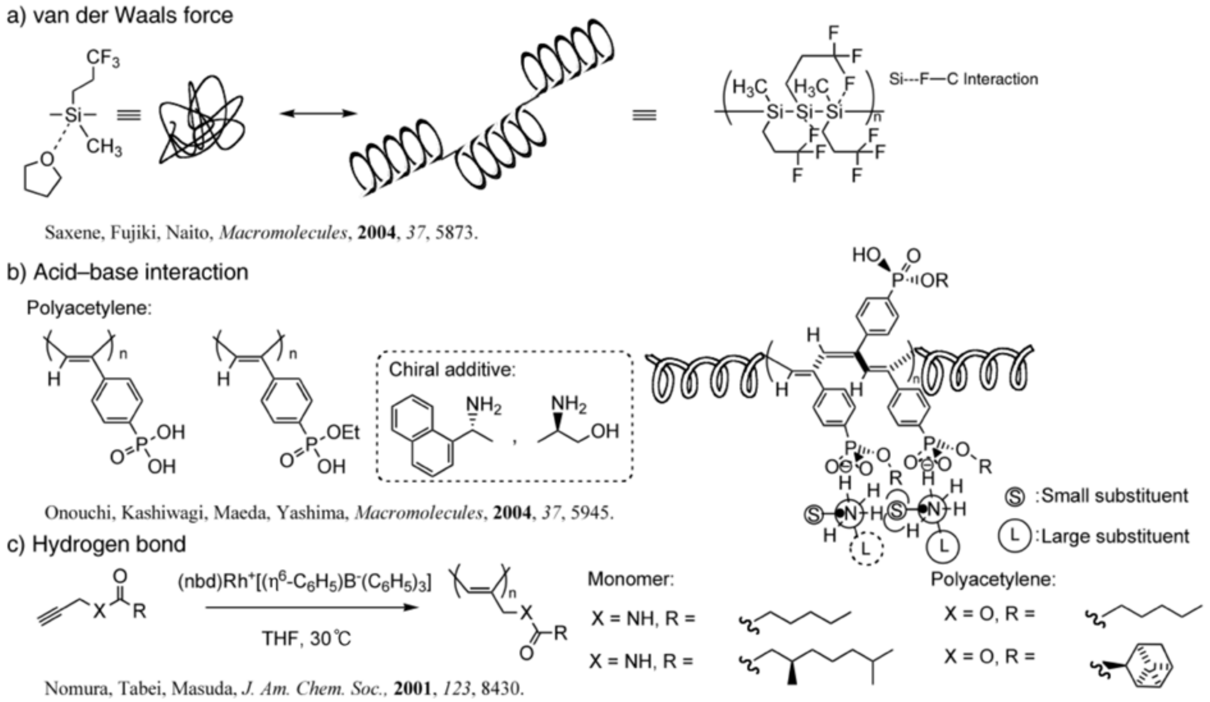
Mizutani, Yagi, Ogoshi, *J. Org. Chem.*, **1998**, *63*, 8769.

Figure2-2. Helicity induction by coordination formation of metal complex

Yashima, Okamoto, and the co-workers have achieved induction and maintenance of one screw-sense helical main-chain conformation of polyacetylene derivatives having side chain carboxylic acid moiety or phosphoric acid moiety. They utilized the acid–base interaction between acidic side groups on the polymer main chain and the chiral amine additives to induce the one screw-sense helical conformation and demonstrated that the one screw-sense conformation was also retained even after replacement of the chiral amine with an achiral alcohol. This work is also described later in the Topic 2: Chiral memory.

Masuda and the co-workers reported induction of helical conformation of poly(*N*-propargylamide) of *cis-transoid* structure having bulky and chiral side chains and maintenance of the helical conformation by the aid of hydrogen bonding between the side chains (Fig. 2-3c).[21]

Aoki and the co-workers demonstrated the distinct approach compared to those of the researches described above. In the syntheses of polymers having helical conformations reported by Yashima's group and Masuda's team, presence of achiral alcohol or chiral side chain is indispensable for maintenance of helical conformation. On the contrary, Aoki and the co-workers demonstrated the maintenance of one screw-sense helical conformation of polymer without use of asymmetric source except for chiral co-catalyst of (*R*)-/(*S*)-phenylethylamine (*R*/*S*-PEA) (Fig. 2-4).[22,23] This is attributed by the suitable design of the alignment of the substituents on the monomer molecule in which the hydrogen-bonding interaction and the repulsion of the bulky pendant groups presumably function most effectively between the corresponding units.

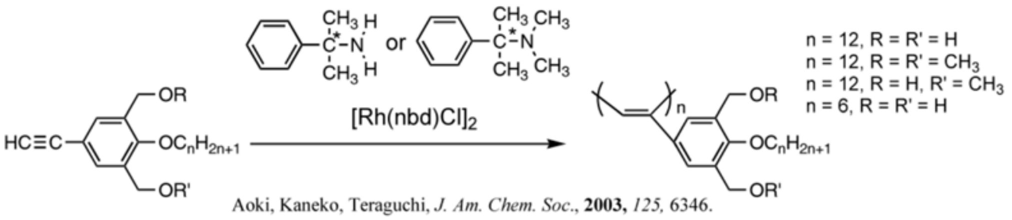


Saxene, Fujiki, Naito, *Macromolecules*, **2004**, *37*, 5873.

Onouchi, Kashiwagi, Maeda, Yashima, *Macromolecules*, **2004**, *37*, 5945.

Nomura, Tabei, Masuda, *J. Am. Chem. Soc.*, **2001**, *123*, 8430.

Figure 2-3. Helicity induction by intermolecular/intramolecular interactions



Aoki, Kaneko, Teraguchi, *J. Am. Chem. Soc.*, **2003**, *125*, 6346.

Figure 2-4. Helicity induction by steric hindrance of side chain

2-2. Asymmetric Induction by the Use of Asymmetric Source of Outside of the Molecule

In this section, asymmetric induction of helical conformation of polymer having no asymmetric factors on the main chain repeating units or side chain moieties is described. The induction was performed by the aid of asymmetric factor outside of the monomer/polymer molecules.

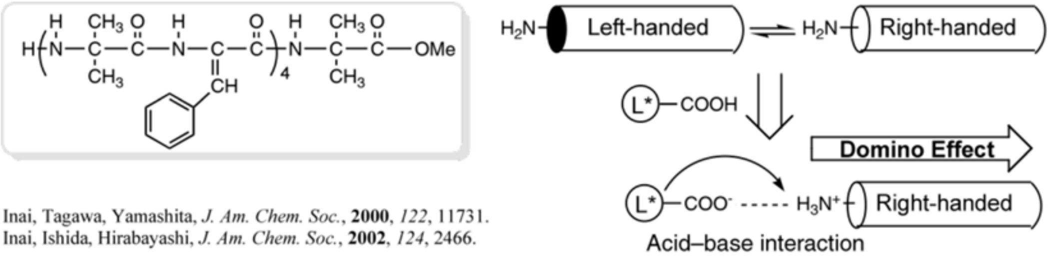
Green and the co-workers reported that poly(hexylisocyanate) shows a Cotton effect in a chiral chloroalkane solvent due to the helical conformation. Yamashita and the co-workers reported a successful induction of a helical conformation with the aid of intermolecular interaction of chiral additive molecules and polar side chains of the polymer. For example, induction of helical conformation of polyisocyanide through acid–base interaction between chiral amine and hydroxycarbonyl side chain[25] and that of poly(phenylacetylene) through capture of chiral additive molecules by the crown ether side chain.[26] As one of the applications based on this methodology, they demonstrated the preparation of helical conformation of polymer electrolytes.[27]

Fujiki and the co-workers reported that induction of helical conformation of polysilane proceeded through addition of chiral alcohols.[28] Furthermore, Masuda and the co-workers reported induction of one screw-sense helical conformation of achiral *N*-propargylamide through hydrogen bonding between the amido side groups and the added chiral alcohol or amine molecules.[1b] Inai and the co-workers have found that one screw-sense helix of whole molecule of polypeptide chain is induced simply by acid–base interaction between the *N*-terminal of the polypeptide and the added chiral carboxylic acid depending on the absolute configuration of the chiral carboxylic acid (Domino effect) (Fig. 2–5).[29]

On the other hand, there have been several examples where helical induction is observed without the use of chiral additives or chiral solvents. Okamoto and the co-workers reported the achievement of asymmetric induction of polythiophene with the aid of addition of methanol or Cu(II) ion, which shows no induced CD in good solvent such as $CHCl_3$.[30] The investigation was extended to development of chiral supramolecules having switch-function. For achievement of the switching function, the finding that polythiophene handly undergoes doping with Cu(II)–bipyridyl complex in chloroform–acetonitrile mixed solvent has been utilized.

On the basis of development of novel chiral catalysts and initiators, there have been a lot of works on the choice of catalysts or initiators according to the combination of adjustment of the flexibility of the main chain of the resulting polymer and the bulkiness of the side chain in the monomer. The control of the chirality in polyacetylenes and polyisocyanates is undertaken by the side group attached via single bonding with an sp^2–sp^3 manner to the conjugated polymer main chain (Fig. 2–6). Therefore, the researches have been intended to develop the chiral catalysts to control the conformation of the polymer main chain.

The transition metal complex catalysts composed of Rh or



Inai, Tagawa, Yamashita, *J. Am. Chem. Soc.*, **2000**, *122*, 11731.
Inai, Ishida, Hirabayashi, *J. Am. Chem. Soc.*, **2002**, *124*, 2466.

Figure 2-5. Helicity induction by noncovalent chiral domino effect

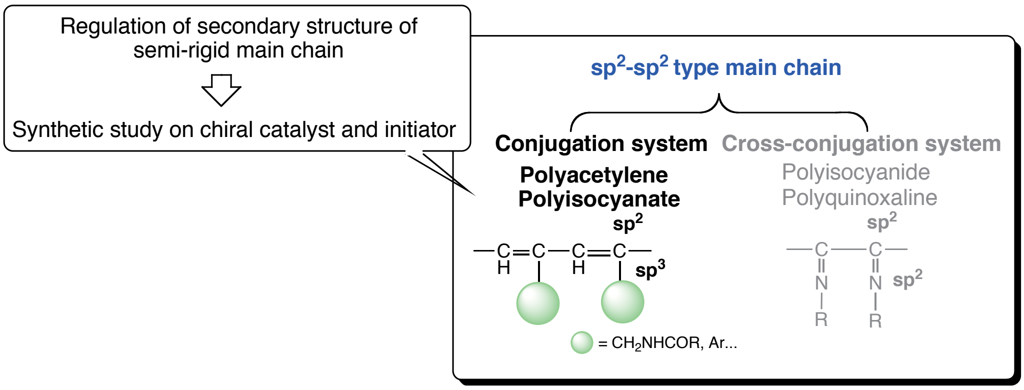


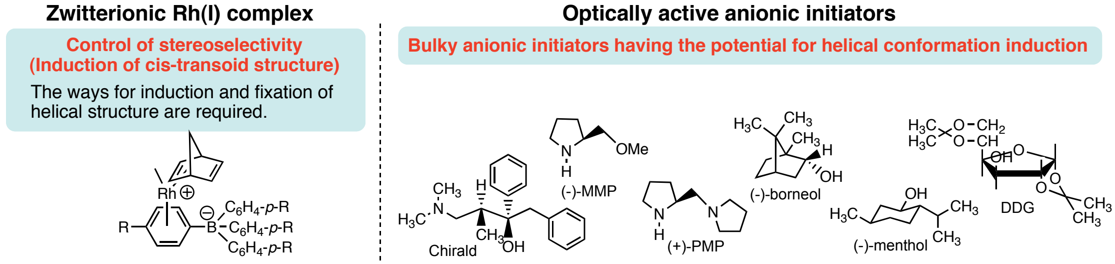
Figure 2-6. Abstract: Synthetic study on conjugated polymers ~Polyacetylene and polyisocyanate~

Mo have been employed for the purpose of conformation control of the main chain of polyacetylenes. Especially, [(nbd) RhCl]$_2$ and MoCl$_4$–^{n}Bu$_4$Sn have been recognized as effective catalysts for induction of *cis-transoid* conformation. Noyori and the co-workers have found that the kind of the diene ligand of Rh$^+$(diene)[(η^6-C$_6$H$_5$)B$^-$(C$_6$H$_5$)$_3$] type dipolar ionic Rh(I) complex affects largely on the polymerization reactivity.[32] Furthermore, they have succeeded to synthesize the polyacetylene having one screw-sense helical conformation from chiral monomer bearing long alkyl side chains by the aid of Rh$^+$(nbd)[(η^6-C$_6$H$_5$)B$^-$(C$_6$H$_5$)$_3$] initiator (Fig. 2-7, left). The initiator, which is free from halogen atoms, is able to afford high-molecular-weight polymer under the mild reaction conditions such that the reaction temperature is below room temperature. On the other hand, Okamoto and the co-workers reported that anionic initiator such as lithium salt of (-)-menthol or (*S*)-(+)-2-(1-pyrrolidinylmethyl)pyrrolidine can afford one screw-sense helical conformation of aromatic polyisocyanate (Fig. 2-7, right).[2b]

Polyisocyanides and polyquinoxalines are classified as the polymers having cross-conjugated main chains. The control and governing of the screw-sense of helical conformation of polyisocyanides essentially depend on the side groups attached via double bonding manner (sp^2–sp^2) to the main chain. It has aroused great interest to the substituent effect on monomers in the course of investigation of the chiral initiators (Fig. 2-8).

Nolte and the co-workers synthesized polyisocyanides with selectivity in screw-sense of helical conformation by treatment of an achiral isocyanide bearing bulky substituent with an initiator composed of (*R*)-(+)-/(*S*)-(-)-(1-phenylethyl) methylamine and nickel(II) tetrakis(*tert*-butylisocyanide).[3]

On the other hand, Takahashi and the co-workers achieved a one screw-sense helical conformation of polyisocyanide obtained from chiral and achiral isocyanides by the aid of platinum–palladium binuclear complex catalyst and the oligomeric initiator (Fig. 2-9).[33] The copolymer has the same screw sense of helical conformation with that of the homopolymer of the chiral isocyanide monomer. In this system, the presence of random copolymer sequence of the oligomer is essential where the chiral monomer governs the screw-sense of helix through thermodynamic control like Sergeants and Soldiers rule. In the essentially same fashion, Drenth and the co-workers achieved the synthesis of polyisocyanide and the induction of the one screw-sense helical conformation of the polymer through copolymerization of achiral isocyanides and chiral isocyanide with bulky side chains.[34] However, the screw-sense of the helix has turned opposite to that of the homopolymer synthesized solely from the monomer having chiral side chains (Fig. 2-10, left). This unexpected result is interpreted as follows: The polymerization of achiral isocyanide gives the even amounts of right-handed and left-handed screw-sense helical polymers resulting in formation of a racemic mixture (conglomerate) of helical polymers. On the other hand, polymerization of optically active (chiral) isocyanide monomer affords only one of the two screw-sense helical conformations. Furthermore, polymerization of optically active isocyanide monomer proceeds slower than that of achiral one. The chiral monomer, of which propagation of polymerization is far slower, is able to react at the propagation terminal of the helical polymer yielded from achiral isocyanide monomer. However, the difference in the rates of the reaction of the chiral isocyanide monomer at two helical polymers derived from achiral



Kishimoto, Itou, Noyori, *Macromolecules*, **1995**, *28*, 6662.

Okamoto, Matsuda, Yashima, *J. Polym. Sci.: Part A*, **1994**, *32*, 309.

Figure 2-7. Initiators and catalysts for regulation of main chain structure

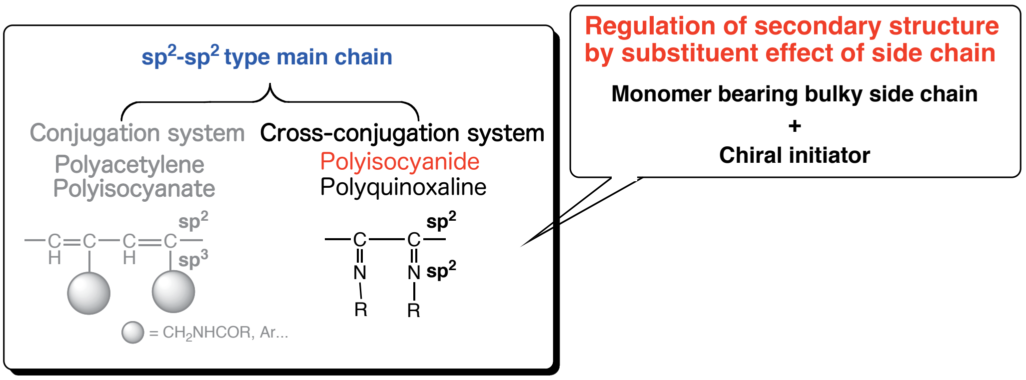
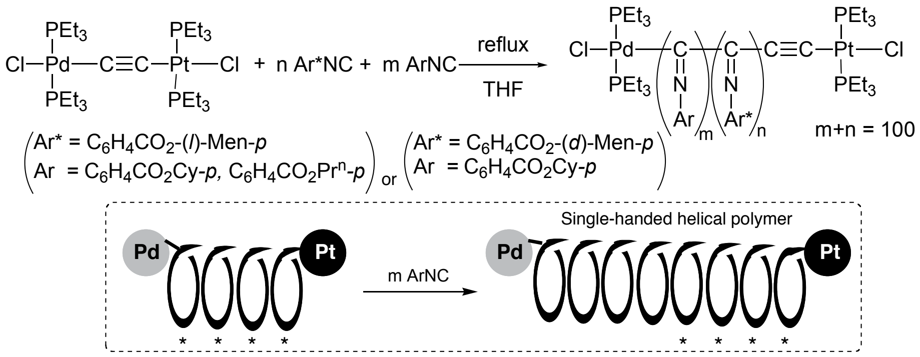


Figure 2-8. Abstract: Synthetic study on cross-conjugated polymers ~Polyisocyanide~

isocyanide monomer is significant to allow only the reaction with the end of one of the helical polymers of achiral isocyanide monomer, of which direction of helix is the same with that the chiral isocyanide monomer would afford. Furthermore, the polymer chain terminal where the chiral isocyanide monomer attached is apt to resist the next reaction. In this accordance, the formation of one of the two screw-sense of helical polymers are strongly restricted to allow the reaction at the polymerization terminal of the other screw-sense of helical polymer to yield preferential formation of this screw-sense of helical polymer (Fig. 2-10, right).

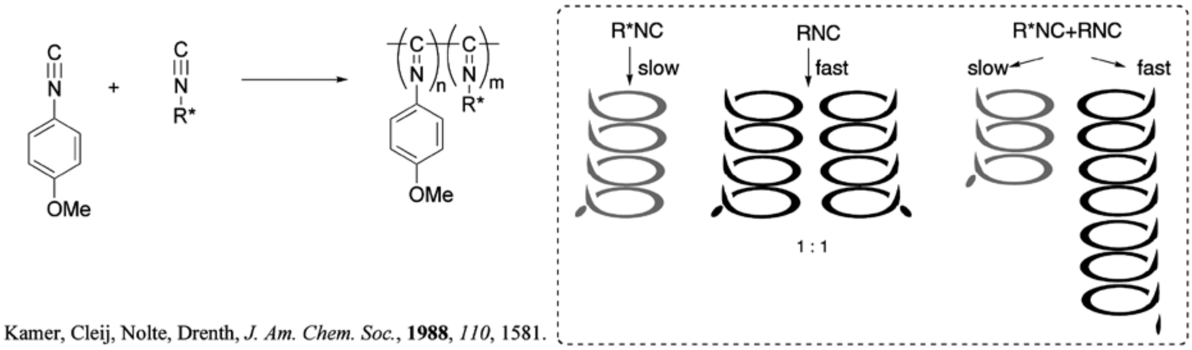
Contrary to the "independent" control and government of the screw-sense of helix of polyisocyanides polymer backbone by side chains, C=N bond pairs incorporated in a quinoxaline hetero aromatic ring form planarly extended side chain to fix the polymer chains effectively. In a natural consequence, a series of helical polymers have been developed by utilizing such characteristics of quinoxaline unit that is incorporated in the polymer main chain and then undergoes the polymer chain elongation along with induction of helical conformation (Fig. 2-11).

Ito and the co-workers reported the polymerization of 1,2-diisocyanoarenes by the aid of Pd(II) complexes.[35] They reported that with the aid of Pd(II) complex having chiral phosphine ligands rather low selectivity for one screw-sense helical structure was yielded against the polyquinoxaline obtained[36] whereas high selectiveness for screw-sense of helix was achieved by the aid of optically resolved quinoxaline



Takei, Onitsuka, Takahashi, *Angew. Chem. Int. Ed. Engl.*, **1996**, *35*, 1554.

Figure 2-9. Screw-sense-selective polymerization of isocyanides by initiator comprised of dinuclear Pt-Pd complex and chiral oligomer



Kamer, Cleij, Nolte, Drenth, *J. Am. Chem. Soc.*, **1988**, *110*, 1581.

Figure 2-10. Screw-sense-selective polymerization of isocyanides by inhibiting the growth of one enantiomer of a racemic pair of polymer helices

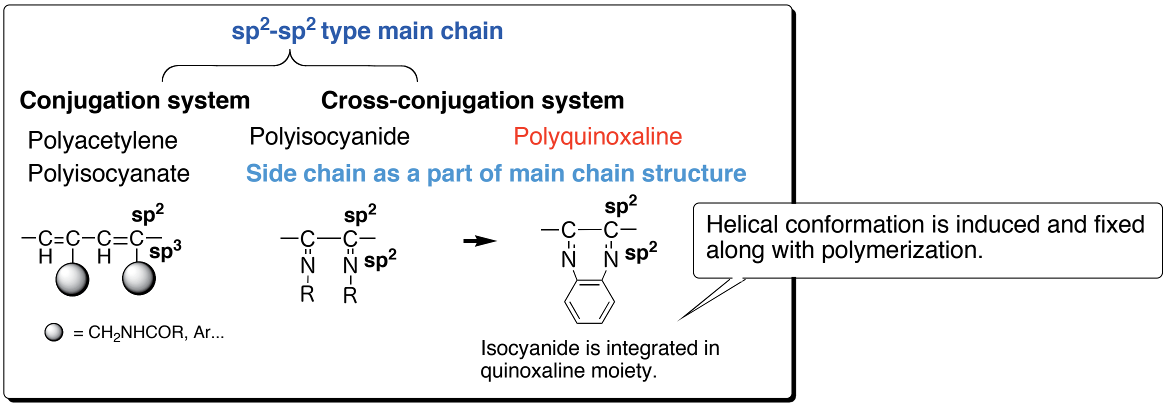


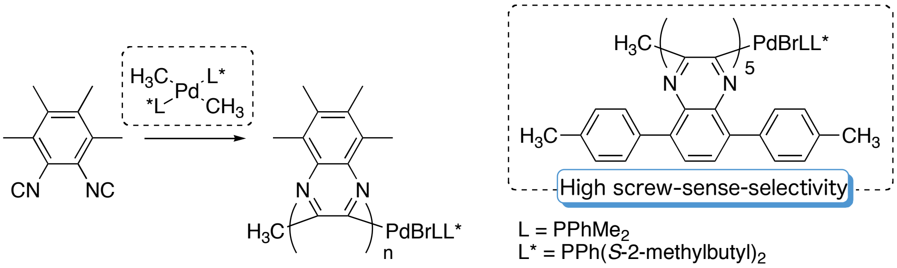
Figure 2-11. Abstract: Synthetic study on cross-conjugated polymers ~Polyquinoxaline~

pentamer-Pd(II) complex (Fig. 2-12).[37] Furthermore, on the basis of a separate examination, the achieved screw-sense-selectivity has proved not to depend on the type of substituents on the phosphine ligands.[36] It means that the selectiveness in screw-sense of helix by Pd(II) complex is interpreted not due to the chirality of phosphine ligands but attributed to the secondary structure of the polymer. On the basis of such consideration, Suginome and the co-workers have succeeded the helical screw-sense-selective polymerization of 1,2-diisocyano-3,6-di-*p*-toluoylbenzene by the aid of a Pd(II) complex composed of rather simple asymmetric source of 1,1'-binaphthyl.[38] This successful induction of screw-sense-selective helical structure is deeply attributable to the preceding formation of helical conformation of initiator itself with high screw-sense-selectivity for helical conformation. Accordingly, the choice of the substituent on the binaphthyl core determines the screw-sense-selectivity for helical conformation in the polymerization.

2-3. Induction of Screw-Sense of Helix by the Use of Asymmetric Source of Inside of the Molecule

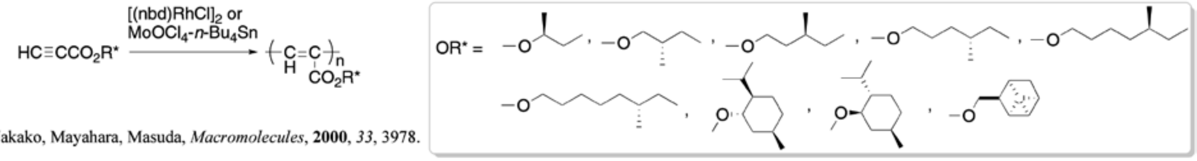
In this section, some examples of induction of screw-sense of helix by the aid of asymmetric source of inside of the monomer are introduced. About this category of approaches, simple polymerization of monomers having chiral side chain and polymerization under the specific circumstance controlled by the chiral side groups such as intermolecular interaction or spatial repulsion between the side groups were reported. Masuda and the co-workers synthesized the series of polyacetylenes having chiral side chains of different length or bulkiness and evaluated the effects of the substituents on specific rotation (Fig. 2-13).[6b] They concluded that selectiveness of screw-sense of helical conformation tends to descend awing to interference by steric hindrance due to the short length and also awing to disturbance by preferential formation of random coil due to the long chain length of alkylene spacers. Against the bulkiness of the substituents, it has been revealed that configuration of the γ-carbon affects on the secondary structure of the polymer main chain in a more determining fashion.

As another type of approach, Koe and the co-workers reported the synthesis of polysilanes composed of both achiral side chains of different alkylene length and/or substitution position and chiral side chains (Fig. 2-14).[39] All of the CD spectra of the polymers in THF show the positive Cotton effect with almost equal intensity. In the UV spectra of the polymers, the wavelength for the maximum absorption (λ_{max}) is almost unchanged. This suggests that the optical properties of single helix of polysilane depend on the secondary structure of the polymer main chain. On the other hand, when the polymer is dissolved in the good solvent such as THF or isooctane followed by dilution with poor solvent such as methanol or ethanol, the screw-sense of the formed aggregation of the helical polymers shows the dependence on the substitution position of alkyl group on the benzene ring. Furthermore, the intensity of CD depends on the good solvent–poor solvent ratio. This fact indicates that the substituent effect of achiral side chains or the polarity of the solvent is the determining factor for the pitch or the diameter of the aggregation of the helical polymer.



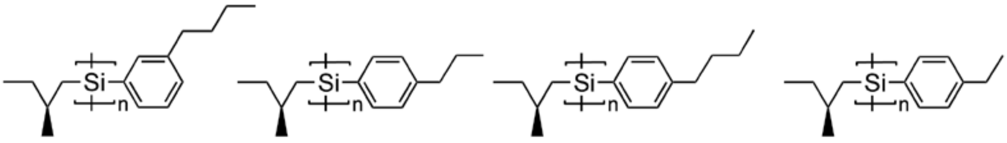
Ito, Kojima, Murakami, *Tetrahedron Lett.*, **1993,** *34*, 8279.

Figure 2-12. Screw-sense-selective synthesis of polyquinoxalines with bulky oligomeric initiators



Nakako, Mayahara, Masuda, *Macromolecules*, **2000**, *33*, 3978.

Figure 2-13. Chirality inducing polymerization controlled by chiral side chain



Peng, Motonaga, Koe, *J. Am. Chem. Soc.*, **2004**, *126*, 13822.

Figure 2-14. Polysilanes bearing chiral and achiral side chains

In the recent years, many reports of this research field display the results of copolymerization of chiral and achiral monomers referring to the corresponding information of the synthesis of homopolymer purely prepared from chiral monomer solely. The achievement of the helix induction is estimated as the non-linear relationship of the optical property between the monomer and the polymer by the aid of circular dichroism measurement. The aim of these works is considered to confirm Majority effect or Sergeants and Soldiers rule by the addition of small amount of chiral monomer (Fig. 2-15).

Takahashi and the co-workers reported the non-linear relationship between the specific rotation and the molar ratio of the monomer bearing the chiral side chain in the repeating unit for the random copolymer obtained by the polymerization of chiral and achiral monomers with the aid of the oligomeric initiator,[33b] which is mentioned previously in section 2.2. On the other hand, the relation shows linearity in the corresponding block copolymer. These facts demonstrate that many factors such as the control of the distribution of the repeating units originated from the monomer bearing chiral side chains in the copolymer catalyst, the adjustment of the required amount for the essential additives, and so on, affect competitively in these polymerization reaction. Masuda and the co-workers reported the copolymerization of *N*-propargylalkylamide and monomers bearing chiral side chains.[1a] In this case, amplification of optical purity was observed when *N*-propargylalkylamide bearing β-branched alkyl chains was employed as the monomer.[1a] Yashima and the co-workers investigated the steric effect of the achiral substituent on the monomer molecules in the copolymerization of a monomer having chiral carbamoyloxy group and achiral one in the presence of [RhCl(NBD)]$_2$.[6d] They reported that the copolymer obtained from an achiral comonomer having *p*-*tert*-butyldiphenylsiloxy group and a chiral comonomer bearing *p*-carbamoyloxy group has specific rotation value of double the magnitude against that for the homopolymer obtained from the monomer having chiral side chains. Furthermore, the helix of the copolymer is proved to opposite in screw-sense against that for the homopolymer synthesized from the monomer having chiral side chain solely. Consequently, the steric effect of bulky pendant group on the achiral comonomer predominates over the thermodynamic control of chiral side chain in this case.

In this manner, information about the novel helical polymers obtained from acetylenes bearing aliphatic substituents or disubstituted acetylenes are of great vale from the synthetic aspects. Kondo and the co-workers achieved the copolymerization of two acetylene monomers having 11-dodecyn-1-ol group and cholesteryl 3-butynylcarbonate moiety, respectively, in the presence of Rh(nbd)[B(C$_6$H$_5$)$_4$] (Fig. 2-16a).[40] The copolymer is composed of *cis* configurated molecular structure of repeating units having one screw-sense helical conformation, which is stable enough under air circumstance. In addition, the Cotton effect of the induced circular dichroism is affected by the amount of choresteryl moiety involved. Masuda and the co-workers succeeded the synthesis of disubstituted polyacetylene via polymerization with satisfactory induction of one screw sense helical conformation by the aid of introduction of bulky pinanyl group as a side chain (Fig. 2-16b).[41] Tang and the co-workers reported the synthesis of series of disubstituted polyacetylenes from the monomers having chiral side chains and described that the inversion of the screw-sense of the helixes of these polymers occurs depending on the temperature (Fig. 2-16c).[42]

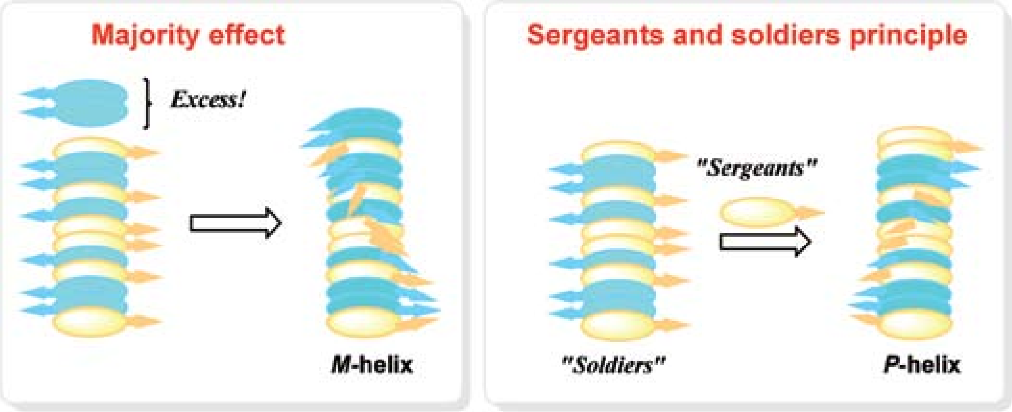
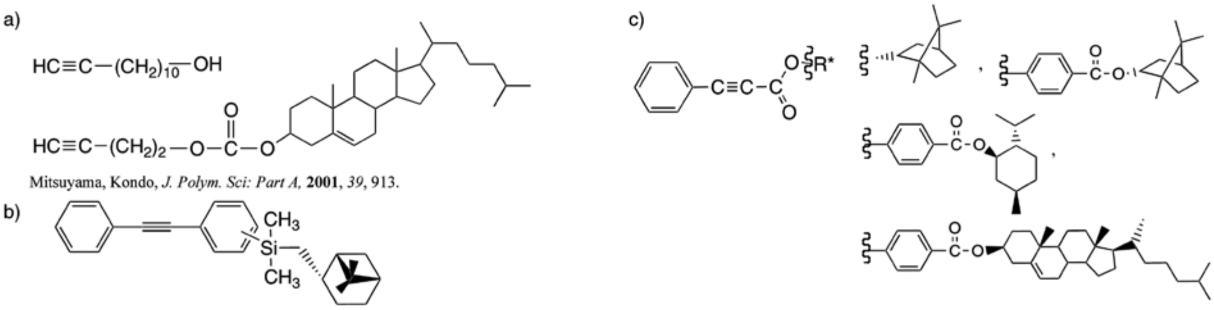


Figure 2-15. "Majority effect" and "Sergeants and soldiers principle"



Mitsuyama, Kondo, *J. Polym. Sci: Part A,* **2001**, *39*, 913.

Aoki, Kobayashi, Masuda, *Macromolecules*, **1999**, *32*, 79

Lam, Dong, Tang, *Macromolecules*, **2003**, *36*, 7927.

Figure 2-16. Monomers for preparation of disubstituted helical polyacetylenes

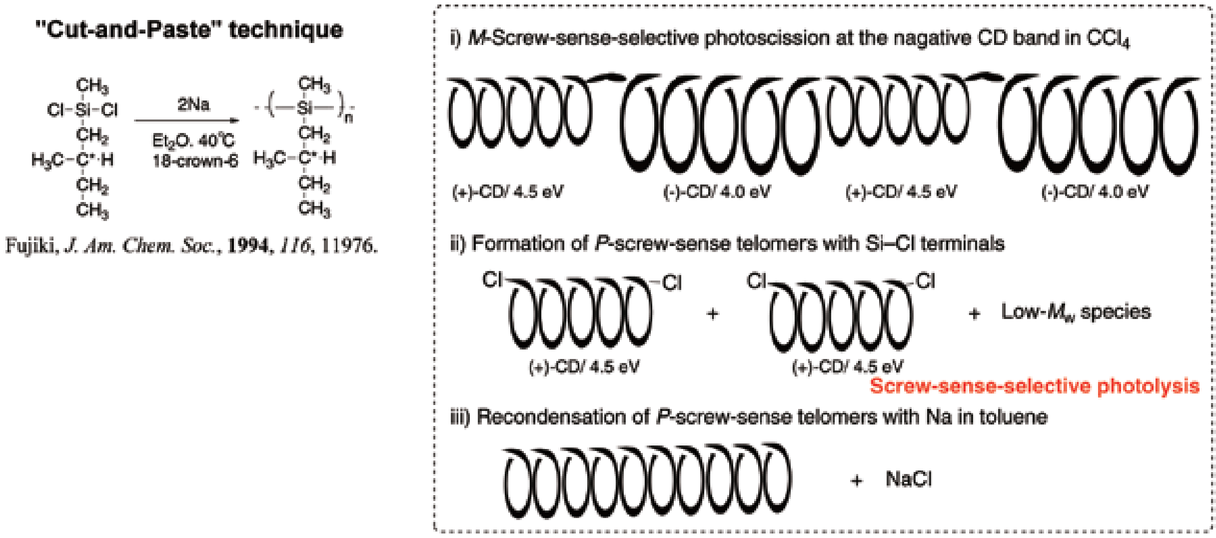
2-4. Several Topics in Synthesis of Polymers with Helical Conformation

In this section, especially unique synthetic approaches of polymers with helical conformation are described in detail and introduced their expected scope.

Topic 1. Chiroptical Transfer and Amplification of Polysilanes

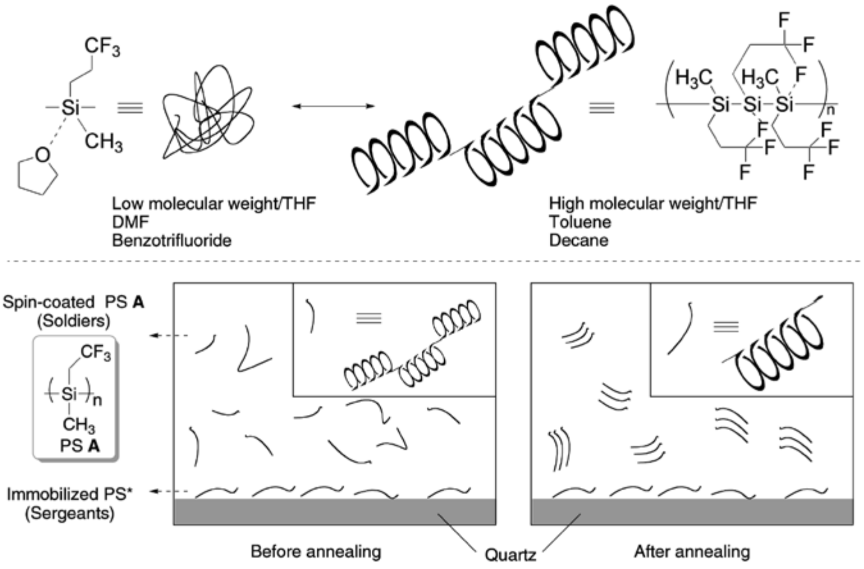
Fujiki and the co-workers successfully synthesized a variety of novel helical polysilanes via Wurtz coupling procedure. For the synthesis of one screw-sense helical polymers, the procedure employing a peculiar method called "Cut-and-Paste" technique was reported (Fig. 2-17).[43] By the aid of combination of spectroscopic measurements, poly[(*S*)-2-methylbutylsilane] has been revealed to have a helical diastereo-block type polymer main chain, where both tight *P*-helix and loose *M*-helix segments are present in the single molecular chain. In addition, each of the helical domains is proved to be composed of the repeating units of a length for nine Si atoms on the basis of the result obtained in screw-sense-selective photolysis experiments. In this course, synthesis of one screw-sense *P*-polysilane from optically inactive helical polysilane was achieved via selective photolysis of *M*-helix in CCl_4 followed by Wurtz coupling of the formed telomer.

Poly[methyl(3,3,3-trifluoropropyl)silane] is proved to achieve induction and maintenance of the helical conformation on condition that some effective intramolecular Si---F–C interaction functions.[19] For example, this polysilane takes random coil conformation when the molecular weight is rather low or when solvents composed of N, O, F atoms exhibiting coordinating property are employed. On the other hand, the polysilane of the molecular weight of higher than a certain threshold takes helical conformation without optical activity in non-coordinating solvent such as toluene or decane by reinforcement of Si---F–C interaction. The synthesis of novel



Fujiki, *J. Am. Chem. Soc.*, **1994**, *116*, 11976.

Figure 2-17. "Cut-and-Paste" technique



Saxena, Guo, Fujiki, *Macromolecules*, **2004**, *37*, 5873.

Figure 2-18. Thermodriven chiroptical transfer and amplification in "Soldier" optically inactive polysilane (PS A) from "Sergeant" optically active helical polysilane (PS*) on quartz helical polymers such as poly(*n*-decyl-3-methylbutylsilane) or poly(*n*-decylisobutylsilane) was also performed. Spin-coating of these polysilanes on the surface of quartz glass wafers pretreated with binding of chiral polysilane, heating at 80 ˚C for 1 hour, then annealing achieved helix-amplification and helix-transcription simultaneously via minute intermolecular Si–C–H---H–C–Si interaction between the chiral polysilane and the achiral polysilane (Fig. 2-18).[5,44]

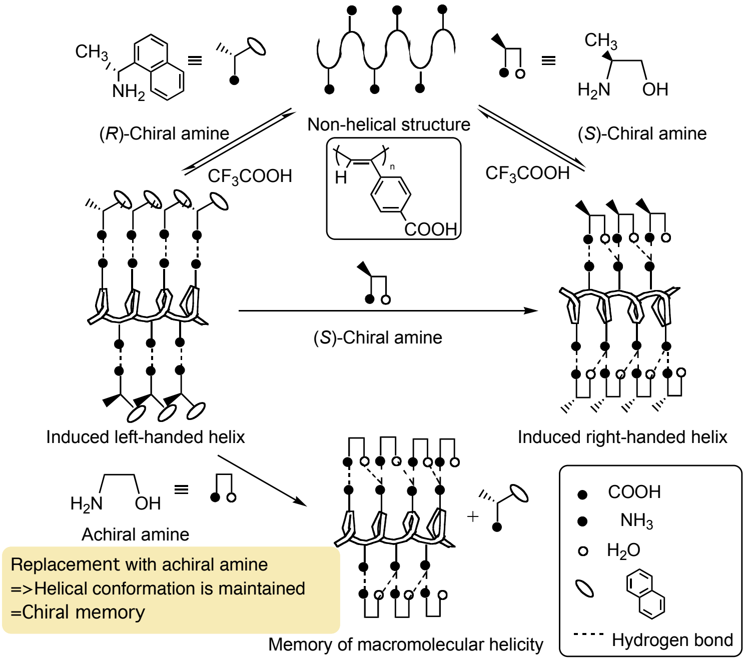
Topic 2. Chiral Memory of Polyacetylenes

Yashima and the co-workers have succeeded induction of one screw-sense helical conformation of poly(4-carboxyphenylacetylene) against initially achiral polymer with the aid of acid–base interaction with chiral amine. The induced helical conformation was retained after removal of the chiral amine by replacement with achiral one (Chiral memory; Fig. 2-19).[20] The acid–base interaction between the polymer and the chiral amine has been ascertained by measurement of the intensity of induced CD of the solution of the prescribed concentration of the polymer–chiral amine complex, which was prepared by mixing equal volumes of DMSO solutions of the polymer (0.005–10 mg/mL) and the chiral amine (0.68 M).[45] The obtained CD spectra of the chiral amine–polymer complex manifests induction of helical conformation by the addition of the chiral amine. On the basis of the experimental results employing the variety of chiral amines, both the bulkiness and the basicity prove to affect induction of helical conformation. The retention of the helical conformation after removal of the chiral source of the employed chiral amine has been proved by the following experimental result: the achiral aminoalcohol–polymer complex prepared by replacement of the chiral amine of the initial chiral amine–polymer complex with achiral aminoalcohol, which has stronger basicity than the chiral amine, shows still strong intensity of CD peak. Furthermore, the comparison of CD spectrum of the pure achiral aminoalcohol–polymer complex and that of the original complex has revealed the memorization of helical conformation. The isolation of the pure achiral complex was performed by size exclusion chromatography (SEC) using DMSO–achiral aminoalcohol as mobile phase, which completely removed the chiral amine and chiral amine–polymer complex. Yashima and the co-workers applied the concept of the chiral memory to facile probe for primary chiral amine[46] and derivation of optically inactive polyacetylene into diastereomeric helical conformations by treatment of chiral amine followed by achiral amine to a mixture of enantiomeric helical conformation resulting in retention of helical structures.[47]

3. The Factors for Induction and Maintenance of Helical Conformations of Synthetic Polymers

In the preceding parts of this review, the recent trends for investigation on the induction and maintenance of the helical conformation for artificial polymers has been described from the viewpoints including the molecular structural requirements of the monomers and the methodology for achievement the conformation. On the basis of the information introduced in this review, the characteristics of the helical artificial polymers are summarized as a diagram in Fig. 3-1.

On assumption that the formation of the helical conformations of these artificial polymers might be governed by following three factors, i.e., the stiffness of the polymer main chain structure, the properties of the helix inducing forces, and the strength of the helix fixation powers, the extraction of the governing factors from the diagram was intended. About the most fundamental feature of the linkages of the component atoms in the repeating units, the combinations are classified into $(sp^3–sp^3)_n$, $(sp^3–sp^2)_n$, $(sp^2–sp^2)_n$, and $[(sp^2)_n]$. Fig. 3-2 shows the structural relationship observed among the artificial helical polymers introduced above sections and the previously



Yashima, Maeda, Okamoto, *Nature*, **1999**, *399*, 449.

Figure 2-19. Concept of helicity induction and chiral memory known helical polymers including naturally occurring ones. Polychloral is one of the polyacetals and has the analogous structure with isotactic polypropylene. That is, the methylene unit of polypropylene main chain is replaced with oxygen atom in polychloral and the methyl side chain is substituted with trichloromethyl group similarly. Similar relationship can be observed between the molecular structures of polypropylene and poly(methyl methacrylate). Polyisocyanate is a planar polymer composed of solely amide linkage regarded as a relative polymer of polypeptide. The polyisocyanate has the main chain structure which is derived by extrusion of α-carbon unit (-CRH-) from backbone of polypeptide. That is, polyisocynate has a main chain structure composed of C–N unit with chain elongation manner of 1,2-linkage of the repeating unit. In this way, polyisonitrile has the repeating unit of single carbon that bonds two repeating units in a geminal linkage fashion. Such repeating unit is regarded as one-atom reduced structure from that of polyisocyanate, in which oxo moiety is eliminated together with conversion of vicinal linkage on C–N unit of polyisocyanate to a geminal mode of single carbon having doubly bonded nitrogen atom. On the other hand, polyacetylene has the main chain structure obtained by displacement of nitrogen atom in the enol form of polyisocyanate repeating unit with carbon atom.

Polyisocyanate has a conjugated structure bearing partial conjugation nature in the main chain and polyisonitrile has a cross-conjugated structure bearing exo double bond as the side

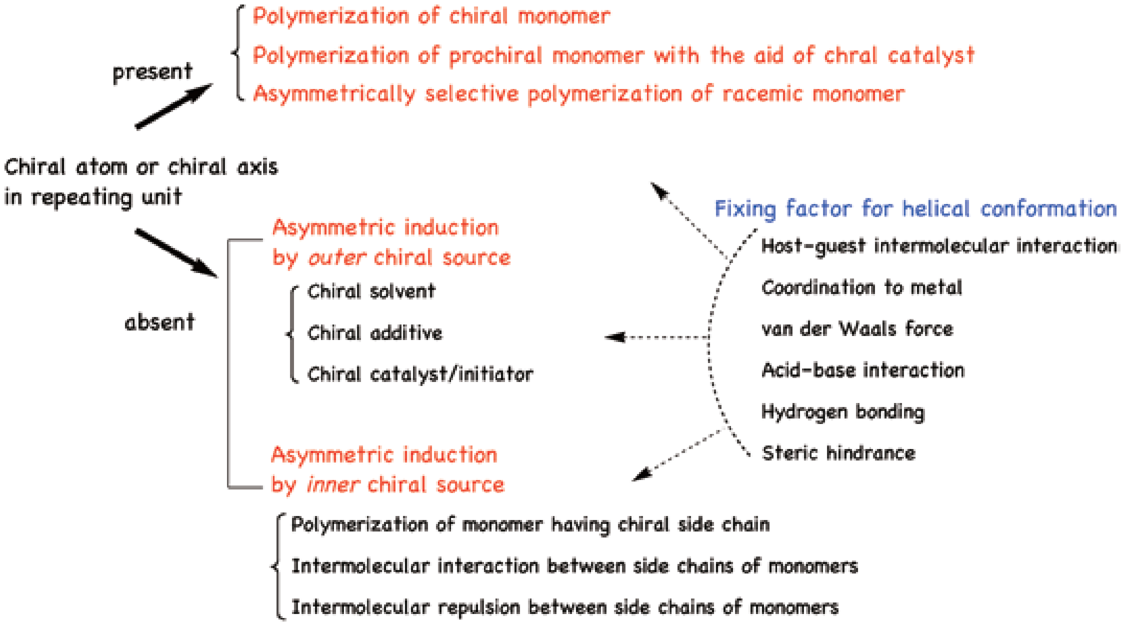


Fig. 3-1. Relationship between protocols for asymmetric induction and fixation of conformation of artificial helical polymers

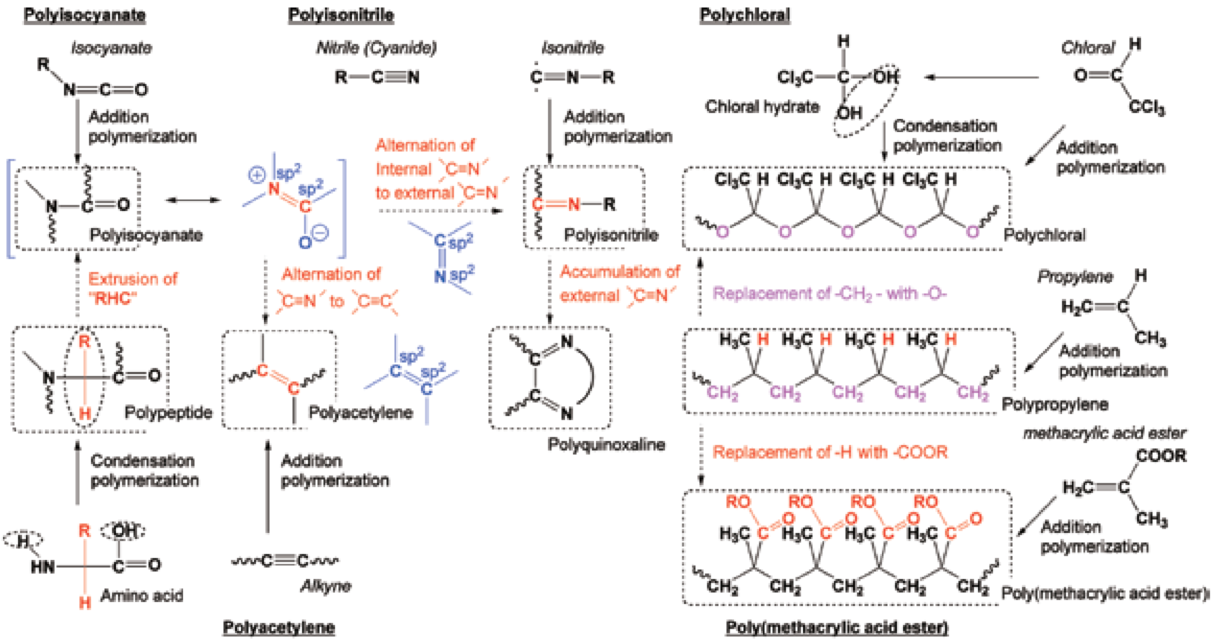


Figure 3-2. Structural relationship between helical polymers

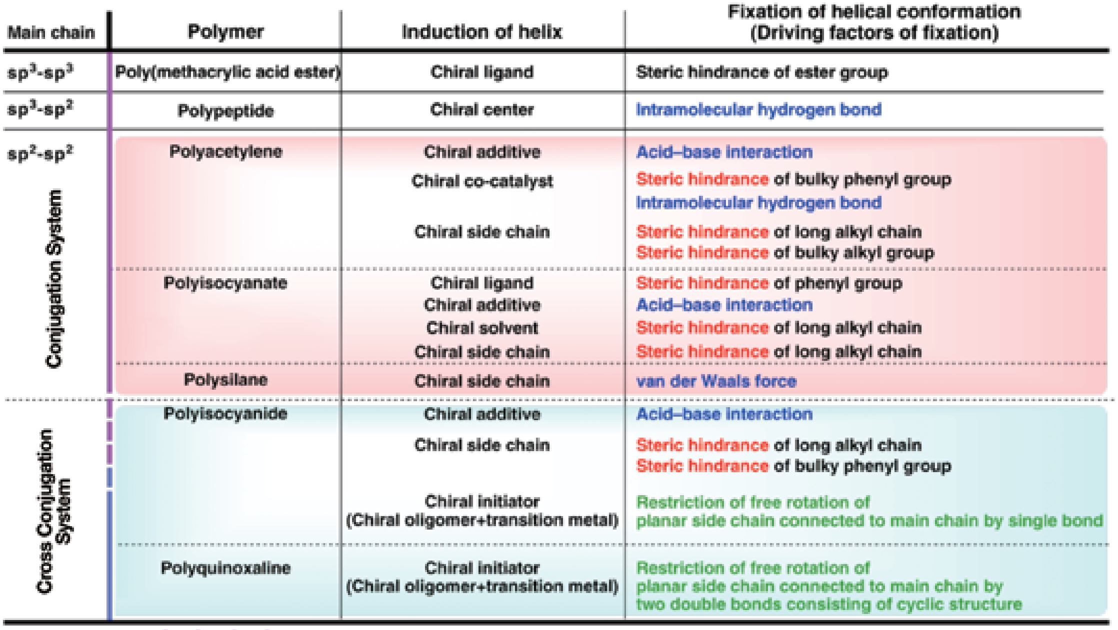
group. Conjugated and cross-conjugated structures are displayed in Fig. 1-5. Furthermore, polyquinoxaline has a repeating unit in which adjacent two exo double bonds of isonitrile are fixed in a six-membered ring.

Table 3-1 tabulates the classified fundamental polymer main chain structures together with factors for induction of helical conformation and those for fixation of yielded helical conformation. The first figure of this review (Fig. 0-1) displays the contents of Table 3-1.

As a matter of course, the relationship among the factors for induction of helical conformation of artificial polymers is summarized. Fig. 3-3 is a graphical version of the essentially same information tabulated in Table 3-1. This is an X–Y matrix of the characteristic properties of the helical artificial polymers where the intense of the chemical interaction between the specific atom group or chemical species and polymer molecules inducing helical conformation is shown on the horizontal axis, and that fixes the helical conformation is displayed on the vertical axis. In this matrix, the objected artificial helical polymers are plotted according to the fundamental polymer main chain skeleton. This plot clearly demonstrates that the polymers including both artificial and naturally occurring polymer showing helical conformation generation are present in the region located above the line in the matrix of two governing factors which runs downward from left to right. In other words, the helical conformation of artificial polymers is interpreted yielded when the two factors functions cooperatively to achieve the total effect above some threshold. Consequently, this statement is the requirement for combination of two factors on chemical structure of the artificial polymers against achievement of helical conformation. The minimum requirement for the stiffness of polymer backbone is considered as complementary for above two factors and expected to be projected at the cross point on the two axes as the minimum magnitude. On the other hand, there is rather insufficient information analyzed for requisite of rigidity on achievement of helical conformation of artificial polymers because only a few examples have been reported at the present time. However, rigidity of the polymer can be semi-empirically estimated. The large part on the information about stiffness is expected compensated by speculation such as extrapolation.

The concept for investigation on helical artificial polymers from the viewpoints of two factors of induction and fixation of helical conformation and stiffness of the polymer backbone presumably affords practical working hypothesis for molecular design of novel helical polymers at least in the initiation stage of investigation or development of some specified helical artificial polymers. Recently, there is increasing interest for induction of helical conformation of artificial polymers by the aid of non-covalent bonding type interaction. In addition, semi-rigid double stranded helix of artificial polymers by the assistance of intermolecular interaction between polymer chains has received also increasing interest aiming to develop molecular switching materials and to extend covalently bonded double stranded helix of artificial polymers. Furthermore, by applying the factors on the matrix shown in Fig. 3-3, the susceptibility of some polymers to helical conformation is possibly assessed. For example, the polymer having the factors located at the upper-right region might have rigid single stranded helical conformation and the polymer having the factors located near the crossed line might have loose helical conformation reminding of stimulus-responding properties. Conclusively, the leading idea above mentioned is expected of use to assess the helical characteristics of the designed polymers.

Table 3-1. Relationship between main chain structure and induction and fixation of helical conformation



Main chain	Polymer	Induction of helix	Fixation of helical conformation (Driving factors of fixation)
sp^3-sp^3	Poly(methacrylic acid ester)	Chiral ligand	Steric hindrance of ester group
sp^3-sp^2	Polypeptide	Chiral center	Intramolecular hydrogen bond
sp^2-sp^2 Conjugation System	Polyacetylene	Chiral additive	Acid–base interaction
		Chiral co-catalyst	Steric hindrance of bulky phenyl group Intramolecular hydrogen bond
		Chiral side chain	Steric hindrance of long alkyl chain Steric hindrance of bulky alkyl group
	Polyisocyanate	Chiral ligand	Steric hindrance of phenyl group
		Chiral additive	Acid–base interaction
		Chiral solvent	Steric hindrance of long alkyl chain
		Chiral side chain	Steric hindrance of long alkyl chain
	Polysilane	Chiral side chain	van der Waals force
Cross Conjugation System	Polyisocyanide	Chiral additive	Acid–base interaction
		Chiral side chain	Steric hindrance of long alkyl chain Steric hindrance of bulky phenyl group
		Chiral initiator (Chiral oligomer+transition metal)	Restriction of free rotation of planar side chain connected to main chain by single bond
	Polyquinoxaline	Chiral initiator (Chiral oligomer+transition metal)	Restriction of free rotation of planar side chain connected to main chain by two double bonds consisting of cyclic structure

sp^3-sp^3~sp^2-sp^{2}Conjugation system : Chiral control of semi-rigid main chain by side chain
sp^2-sp^2 Cross-conjugation system: Regulation of secondary-structure of rigid main chain

4. Conclusion

In this review, the helix forming behavior of artificial polymers having straight chain backbone is mainly discussed. The discussion is progressed under the idea that the factors affecting the properties of the polymer backbone and contributing to control the chirality by the side group should be evaluated and selected for consideration in choice of the kind of asymmetric source, i.e., monomer, initiator, additive, or side group. The chirality, the screw-sense, of the helical conformation of the polymers consisting of main chain conjugated structure, such as polyacetylenes or polyisocyanates, is considered to be controlled and governed mainly by the side chain bonding to the main chain backbone via sp^2–sp^3 type single bond. Presumably based on this consideration, the efforts have been poured into the development of asymmetric catalysts and chiral initiator capable of controlling the stereochemical feature of the polymer main chain structure itself. On the other hand, the chirality of the helical conformation of the polymers consisting of cross-conjugated main chain skeleton is considered to be controlled by the side chain linking to the cross-conjugated system on the polymer main chain via sp^2–sp^2 type double bond. Naturally, for this type of polymer, fixation of the polymer main chain conformation has been attempted by the aid of the optimization of choice of the side chain substituents or the direct controlling of helical secondary structure by the initiator itself. The combination of these concepts is displayed in the relationship matrix.

Keeping this in mind, bond formation between optically active molecules should be considered as the alternative synthetic approach for artificial helical polymers. Among these approaches, syntheses of the polymers composed of 1,1'-binaphthylylene unit have been widely investigated. 1,1'-Binaphthylyl itself is regarded as one of the molecules bearing cyclic oligoacetylene skeleton. Naturally, the accumulated forms of 1,1'-binaphthylylene units are also recognized as extended homologous molecules of the same category of the artificial polymers. When 1,1'-binaphthylylene units are linked at the 4- and 4'-positions, conjugated system are formed. Whereas the bonds are made between the 6- and 6'-positions, cross-conjugated system are yielded. Moreover, naphthalene moieties in 1,1'-binaphthylylene units are connected by carbonyl groups or ethereal oxygens, conjugated system and cross-conjugated system in the polymers bearing 4,4'- and 6,6'-connected main chain structure are inversed to the other type. The connection is made by ester or amide moiety, the conjugated/cross-conjugated manner is unchanged. The authors have been studying the synthesis of aromatic polyketones that have the molecular structure of accumulation of aromatic ring assemblies such as biphenyl, binaphthyl, terphenyl and so on,[48] the unique secondary structure observed in aromatic polyketones are to be discussed in the future.

In the researches aiming to generation of helical artificial polymers, a plenty of dynamic ideas play important roles for helical conformation construction in design and combination of monomer molecules, synthetic methodology, evaluation, and so on. About the helical artificial polymers, applications for variety of fields such as optoelectrical materials, molecular memory materials, and highly performed materials with the aid of self-reinforcement are expected. The methodology to achieve such aims is also expected applied to design and synthesis of other types of molecular materials such as supramolecular modules. It will be our great pleasure if the concepts and the understandings introduced in this review might stimulate the advancement of the related fields of chemistry of organic molecules.

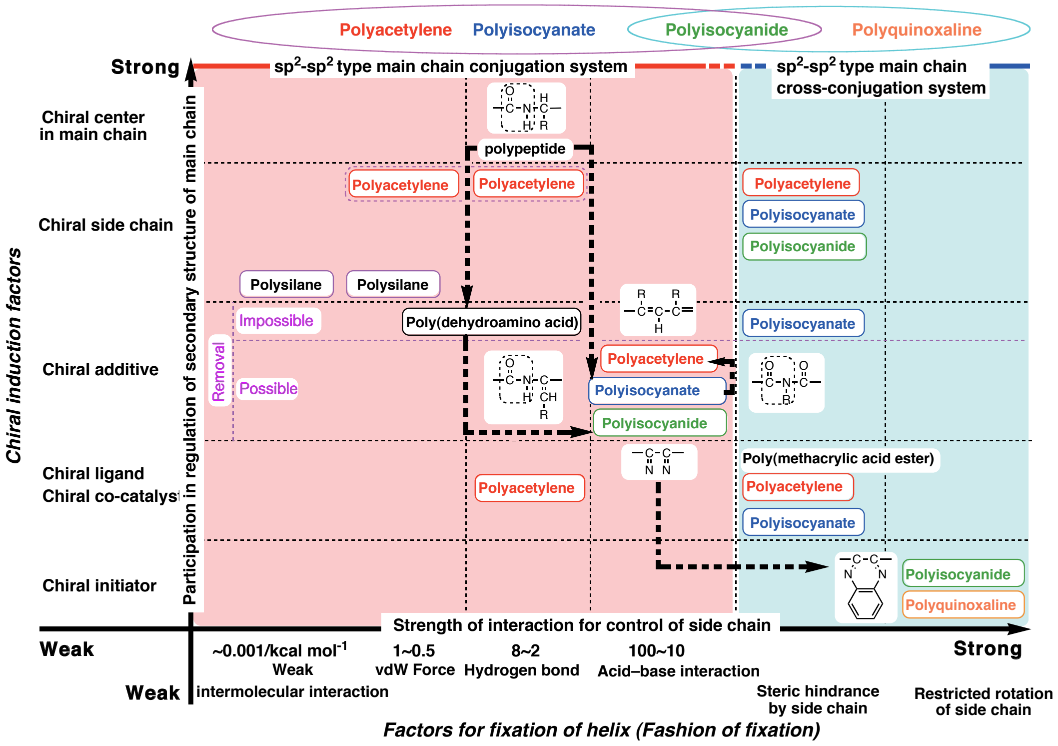


Figure 3-3. Relationship between factors for chiral induction and helical conformation fixation

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Contribution Related Compounds

T0721	*m*-Tolyl Isocyanate		25mL,	500mL
S0461	(–)-Sparteine			25g
D2395	(*R*,*R*)-(–)-2,3-Dimethoxy-1,4-bis(dimethylamino)butane		1g,	5g
D2396	(*S*,*S*)-(+)-2,3-Dimethoxy-1,4-bis(dimethylamino)butane		1g,	5g
P1241	(*S*)-(+)-1-(2-Pyrrolidinylmethyl)pyrrolidine		1g,	5g
P0767	Zinc Phthalocyanine	1g,	10g,	25g
N0453	Norbornadiene Rhodium(I) Chloride Dimer			100mg
P0794	(*R*)-(+)-1-Phenylethylamine		25mL,	500mL
P0793	(*S*)-(–)-1-Phenylethylamine		25mL,	500mL
D1949	1,2:5,6-Di-*O*-isopropylidene-α-D-glucofuranose		10g,	25g
M1169	(*R*)-2-(Methoxymethyl)pyrrolidine		1g,	5g
M1161	(*S*)-2-(Methoxymethyl)pyrrolidine		1g,	5g
M0826	(+)-Menthol		25g,	500g
M0545	(–)-Menthol	25g,	25g,	500g
B1012	(–)-Borneol		25g,	500g
P0610	Phenylpropiolic Acid		5g,	25g
M2080	Methyl Phenylpropiolate		5g,	25g
P0814	Ethyl Phenylpropiolate		5g,	25g
N0482	(*R*)-(+)-1-(1-Naphthyl)ethylamine		1g,	5g
N0481	(*S*)-(–)-1-(1-Naphthyl)ethylamine		1g,	5g
A0297	2-Aminoethanol		25g,	500g
T0367	Chloral		25g,	500g