

Single- and Double-Stranded Helical Polymers: Synthesis, Structures, and Functions

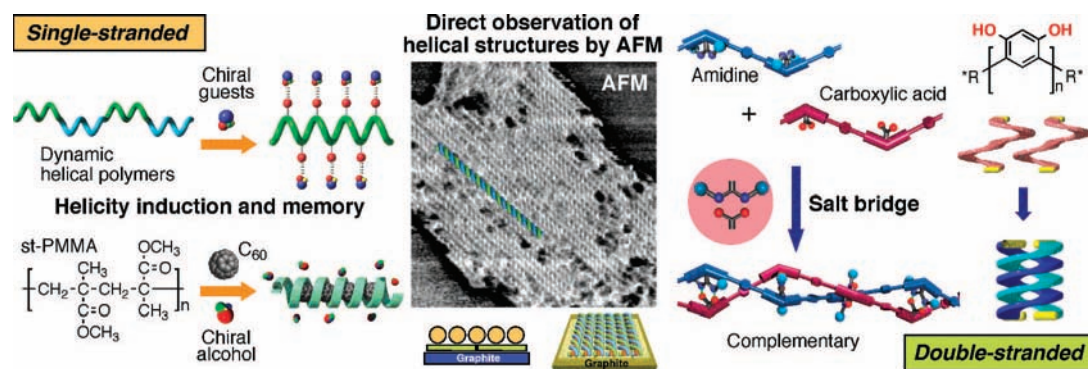
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RECEIVED ON MARCH 19, 2008

CONSPECTUS



Biological macromolecules, such as DNA and proteins, possess a unique and specific ordered structure, such as a right-handed double helix or a single α -helix. Those structures direct the sophisticated functions of these molecules in living systems. Inspired by biological helices, chemists have worked to synthesize polymers with controlled helicity, not only to mimic the biological helices but also to realize their functions. Although numerous synthetic polymers that fold into a single-handed helix have been reported, double-stranded helical polymers are almost unavailable except for a few oligomers. In addition, the exact structures of most helical polymers remain obscure. Therefore, the development of a conceptually new method for constructing double-stranded helical polymers and a reliable method for unambiguously determining the helical structures are important and urgent challenges in this area.

In this Account, we describe the recent advances in the synthesis, structures, and functions of single- and double-stranded helical polymers from our group and others and provide a brief historical overview of synthetic helical polymers. We found unique macromolecules that fold into a preferred-handed helix through noncovalent bonding interactions with specific chiral guests. During the noncovalent helicity induction process, these guest molecules significantly amplified chirality in a dynamic helical polymer. During the intensive exploration of the helicity induction mechanism, we observed an unusual macromolecular helical memory in dynamic helical polymers. Furthermore, we found that rigid-rod helical poly(phenylacetylene)s and poly(phenyl isocyanide)s showing a cholesteric or smectic liquid crystal self-assembly to form two-dimensional crystals with a controlled helical conformation on solid substrates upon exposure to solvent vapors. We visualized their helical structures including the helical pitch and handedness by atomic force microscopy (AFM).

We propose a modular strategy to construct complementary double helices by employing chiral amidinium–carboxylate salt bridges with *m*-terphenyl backbones. The double-stranded helical structures were characterized by circular dichroism in solution and X-ray diffraction of the crystals or the direct AFM observations. Serendipitously, we found that oligoresorcinols self-assemble into well-defined double helices resulting from interstrand aromatic stacking in water. These oligoresorcinols bound cyclic and linear oligosaccharides in water to form rotaxanes and hetero-double helices, respectively.

The examples presented in this Account demonstrate the notable progress in the synthesis and structural determination of helical polymers including single- and double-stranded helices. Not only do we better understand the principle underlying the generation of helical conformations, but we have also used the knowledge of these unique helical structures to develop novel helical polymers with specific functions.

Introduction

The history of synthetic helical polymers extends back to the 1950s, when Natta found highly isotactic polypropylene, which possesses a helical structure in the crystalline state.¹ Although helical polypropylene exists in a mixture of right- and left-handed helices in the solid state, this study provided one of the key discoveries in polymer chemistry demonstrating that nature's monopoly on making stereoregular macromolecules with helical conformations could be broken, and possibly representing the first example of a synthetic helical polymer. However, the helical conformation of isotactic polypropylene is not stable in solution and instantly randomizes once dissolved. Since Natta's discovery, remarkable progress in developing synthetic polymers that adopt a helical conformation even in solution has been made by the groups of Pino, Nolte, Okamoto, Green, and others. The details of their pioneering work have been thoroughly reviewed elsewhere,^{2–7} and a brief overview is described here.

In the 1960s, Pino et al. prepared a series of isotactic vinyl polymers by polymerization of α -olefins bearing optically active substituents and proposed a helical conformation with an excess helical sense in solution.⁸ Nolte et al. successfully resolved poly(*t*-butyl isocyanide) (**1**) into enantiomeric right- and left-handed helices by chiral chromatography in 1974 (Scheme 1A).⁹ In 1979, Okamoto et al. prepared the first helical vinyl polymer (**2**) by polymerization of an achiral monomer, triphenylmethyl methacrylate (TrMA), using chiral anionic initiators (Scheme 1B),¹⁰ which produced a single-handed, fully isotactic helical polymer with a large optical rotation. This process producing a preferred-handed helical polymer by the polymerization of an achiral monomer is called the helix-sense-selective polymerization. The one-handed helical **2** shows a remarkable chiral recognition for a variety of racemic compounds, giving a practically useful chiral stationary phase (CSP) for high-performance liquid chromatography (HPLC).¹¹ This was a significant milestone in the field of synthetic helical polymers, through which many optically active polymers have been prepared and applied to CSPs in HPLC.^{2,4}

Besides these helical polymers being stable in solution (static helical polymers), Green et al. discovered an alternative helical polymer, that is, a dynamic helical polymer, in the late 1980s.¹² They experimentally and theoretically revealed that stiff, rod-like polyisocyanates, such as poly(*n*-hexyl isocyanate) (**3**) and poly(2-butylhexyl isocyanate) (**4**), which are devoid of stereogenic centers, are an equal mixture of right- and left-handed helices separated by helical reversals that readily move along the polymer backbone (Scheme 1C).³

Because the helix inversion barriers of dynamic helical polyisocyanates are quite low, a small chiral bias can be cooperatively transformed into a main-chain conformational change with a large amplification. Green et al. demonstrated that the copolymerization of achiral isocyanates with a small amount of optically active ones and the copolymerization of a mixture of (*R*)- and (*S*)-enantiomeric isocyanates with a small enantiomeric excess (ee) can produce optically active polyisocyanates with an excess single-handed helical conformation. These unique features of chiral amplification in polyisocyanates were termed by Green et al. as the "sergeants and soldiers effect"¹³ and the "majority rule",¹⁴ respectively (Scheme 1C) and have been applied to other polymeric and supramolecular helical systems.^{7,15}

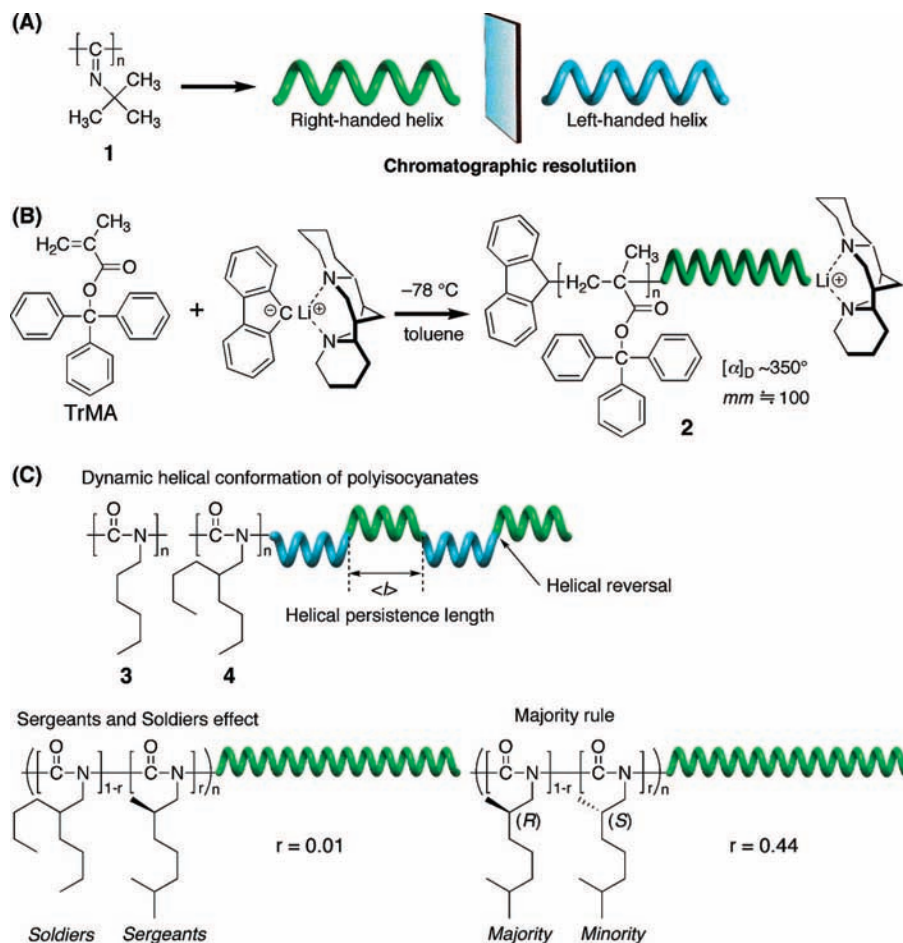
Based on these pioneering studies, the existing helical polymers exhibiting an optical activity due to the helicity can be classified into two categories, that is, static helical polymers and dynamic helical polymers, which differ through their helix inversion barriers; as a result, the former static helical conformations with a preferred-handed helix are locked during the polymerization under kinetic control due to steric repulsion of the bulky side groups. The optically active **1**,^{5,16} **2**,^{2,4} poly(2,3-quinoline)s (**5**),¹⁷ and polyguanidine (**6**),¹⁸ belonging to the former category (Scheme 2), have been prepared by the helix-sense-selective polymerization.

Besides polyisocyanates, a series of polysilanes, such as **7**,⁶ polyacetylenes (**8–13**),^{7,19–22} poly(*m*-phenylene ethynylene)s (**14**),²³ poly(*N*-alkylated *p*-benzamide) (**15**),²⁴ and poly(ureidophthalimide) (**16**)²⁵ have been prepared (Chart 1). In contrast to the static helical polymers, these dynamic helical conformations are controlled by the chiral pendant groups covalently bonded to the polymer backbones, and their helical senses are determined under thermodynamic control.

Macromolecular Helicity Induction

In 1995, we developed a facile method for constructing dynamic helical polymers with an excess helical sense through noncovalent bonding interactions with specific chiral guests after polymerization. A *cis*–*transoidal* poly((4-carboxyphenyl)acetylene) (**17**, Figure 1) prepared by the polymerization of a phenylacetylene monomer with a rhodium catalyst is optically inactive, but upon complexation with chiral primary amines, such as **31**, in dimethyl sulfoxide (DMSO), a dynamic preferred-handed helical conformation is induced in **17**, thus showing a characteristic induced circular dichroism (ICD) in the polymer backbone region (Figure 3).²⁶ The remarkable CD induction is ascribed to a change in the population of the interconvertible right- and left-handed helices of **17** assisted by noncovalent bonding interactions with nonra-

SCHEME 1. Static and Dynamic Helical Polymers



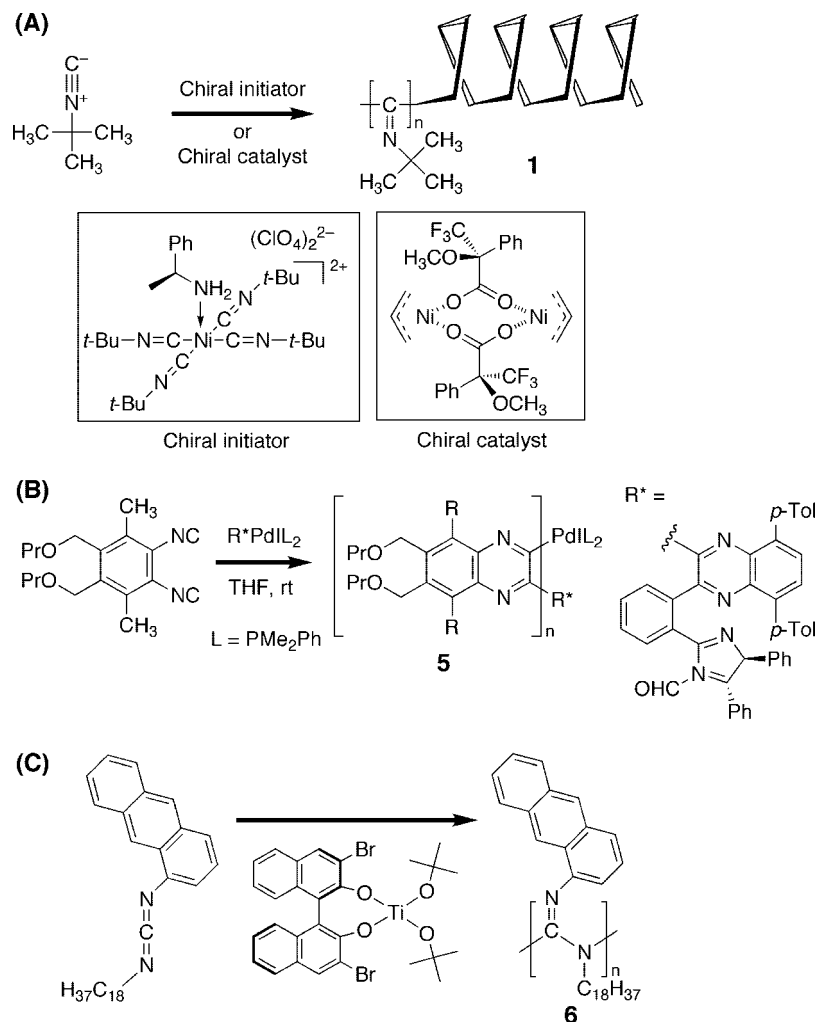
cemic amines. The Cotton effect signs corresponding to the helical sense of **17** can be used to predict the absolute configurations of chiral amines.

After the discovery of the preferred-handed helicity induction in a dynamic helical **17**, a variety of *cis*–*transoidal* polyacetylenes with functional pendant groups have been designed and synthesized (**18**–**30**, Figure 1).^{7,27} These functional polyacetylenes are also sensitive to the chirality of chiral molecules interacting with the functional groups, resulting in ICDs in organic solvents, as well as in water.²⁷ Among them, poly(phenylacetylene)s bearing the bulky diisopropylaminomethyl group (**21**)²⁸ and aza-18-crown-6-ether (**23**)²⁹ as the functional groups, were the most sensitive to the chirality of carboxylic acids and amino acids in acidic water and acetonitrile, respectively. For instance, phenyllactic acid (**32**, Figure 2)²⁸ and L-alanine²⁹ of less than 0.005% ee can be detected by **21** and **23**, respectively, showing apparent ICDs without derivatization. The main-chain stiffness of the polymers due to the bulky pendant groups may be responsible for their high sensitivity. In fact, the persistence length (q) of **21**, a useful measure to evaluate the stiffness of rod-like helical polymers, was estimated to be 26 and 28 nm in water

before and after the preferred-handed helicity induction, respectively (Figure 2).³⁰

Rod-like helical polymers with an excess one-handedness often form chiral liquid crystals (LCs) in concentrated solutions or in a melt. As expected, **21** formed a lyotropic nematic LC in concentrated water,^{30,31} which was converted into the cholesteric counterpart by doping with a small amount of nonracemic acids such as (*S*)-**32** or **32** with a very low ee (Figure 2A,C,D). Interestingly, the helical sense excess of **21** induced by the nonracemic **32** in dilute acidic water was considerably amplified in the LC state as evidenced by the decrease in the cholesteric pitch (Figure 2B).³⁰ This hierarchical amplification of the helix-sense excess of **21** during the cholesteric LC formation is likely due to the reduction of the helical reversal population in the LC state compared with that in a dilute solution, because the kinked helical polymer chain interferes with the close parallel packing of the helical polymer chains in the LC state (Figure 2A,E) as demonstrated by Green et al. in the LC polyisocyanate.³² On the basis of the X-ray analyses of the oriented films derived from the LC samples, the most plausi-

SCHEME 2. Static Helical Polymers Prepared by Helix-Sense-Selective Polymerization



ble helical structure of **21** was proposed to be a 23 unit/10 turn (23/10) helix (Figure 2F).³⁰

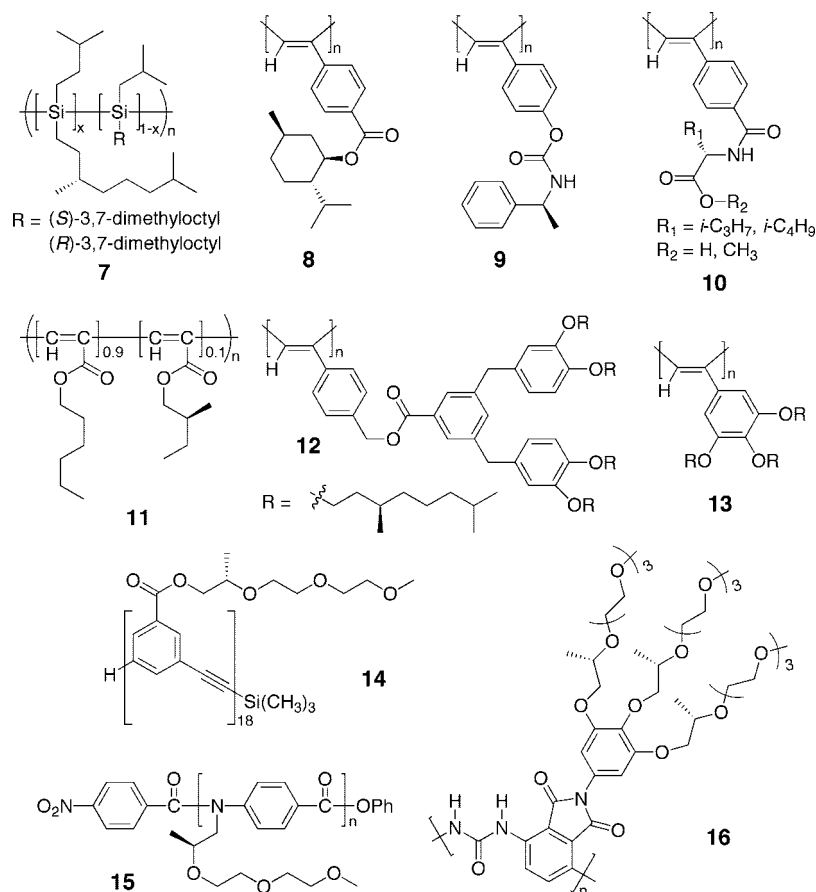
Memory of Macromolecular Helicity

The macromolecular helicity in polyacetylenes **17–30** induced by nonracemic guests is dynamic in nature, so the ICD due to the helical chirality immediately disappears when the guests are removed. However, the helicity of **17–19** and **27** induced by nonracemic amines was maintained, namely, “memorized”, after the amines were completely replaced by achiral amines, such as **33** and **34** for **17** (Figure 3)^{33,34} and **27**. This unprecedented memory effect was explained by the stabilization of the helical conformation caused by intramolecular electrostatic repulsion between the neighboring pendant groups with negative charges complexing with the oppositely charged achiral amines, leading to a strong suppression of the helix inversion of the polymers.³⁴ In addition, the memory effect clearly indicates that the helical conformations of dynamic helical polymers can also be locked, trans-

forming them into kinetically controlled, static helical polymers. In fact, an optically active poly(phenylacetylene) (**36**) stabilized by intramolecular hydrogen bonds was recently prepared by the helix-sense-selective polymerization of an achiral phenylacetylene with $[\text{Rh}(\text{nbd})\text{Cl}]_2$ in the presence of (*S*)- or (*R*)-**35** (Scheme 3).³⁵

An achiral water-soluble poly(phenyl isocyanide), the sodium salt of **37** (**37-Na**), prepared by a nickel catalyst also formed a preferred-handed helix induced by optically active amines, such as (*S*)-**38**, in water. Quite interestingly, this helicity was automatically memorized after removal of the amine (Figure 4).³⁶ In sharp contrast to the memory of the induced helical conformation of poly(phenylacetylenes), the helix formation of **37-Na** was accompanied by configurational isomerization around the C=N double bonds (*syn-anti* isomerization) into one single configuration, so this helicity memory no longer requires achiral amines to memorize the helicity in the polymer. Therefore, further modifications of the side groups with various functional groups are possible without

CHART 1



loss of the helicity memory,³⁷ and they showed cholesteric LCs. As described above, polyisocyanides belong to static helical polymers when they have a bulky side group. However, the present results reveal that poly(phenyl isocyanide)s with less bulky side groups have a dynamic helical characteristic as

well as a static one, being distinct from the other static and dynamic helical polymers.

The helicity induction and memory effect can also be applicable to a commodity plastic, syndiotactic poly(methyl methacrylate) (st-PMMA), which folded into a preferred-handed

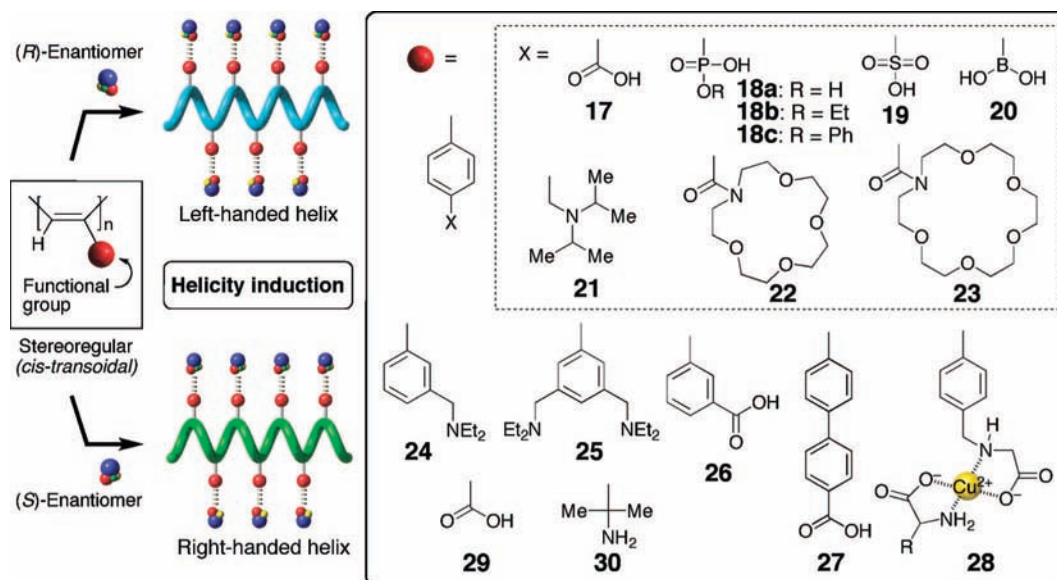


FIGURE 1. Helicity induction in polyacetylenes bearing various functional groups (17–30) upon complexation with chiral compounds.

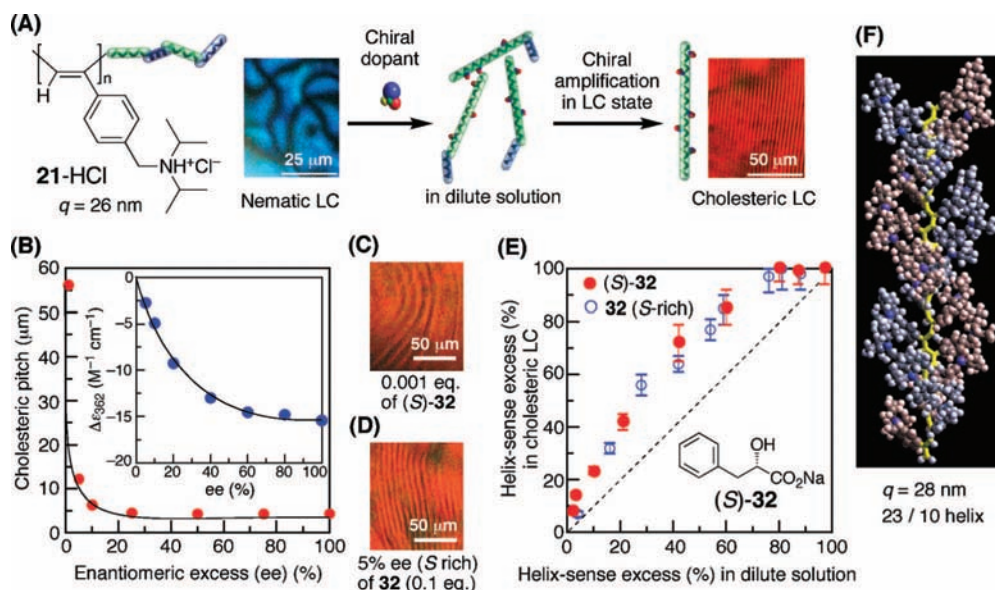


FIGURE 2. (A) Hierarchical chiral amplification in macromolecular helicity of **21** in dilute solution and LC state, (B) changes in the cholesteric pitch and ICD intensity of **21** versus the % ee of **32** (*S*-rich) in concentrated (20 wt %) and dilute (inset) water solutions, (C, D) polarized optical micrographs of cholesteric LC phases of **21** (20 wt %) in the presence of 0.001 equiv of (*S*)-**32** and 5% ee (*S*-rich) of **32** (0.1 equiv) in water, (E) plots of the calculated % ee of helical sense excess of **21** with a chiral dopant in the cholesteric LC state versus those in dilute water, and (F) a 23/10 helical structure of **21**.

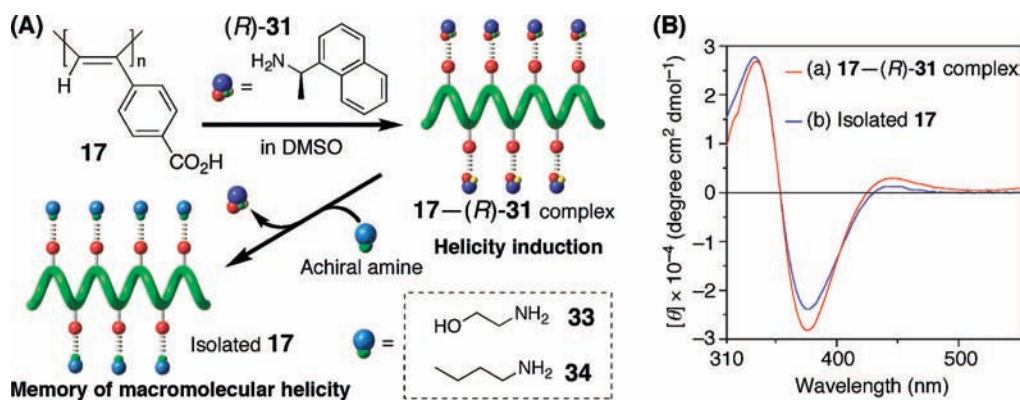
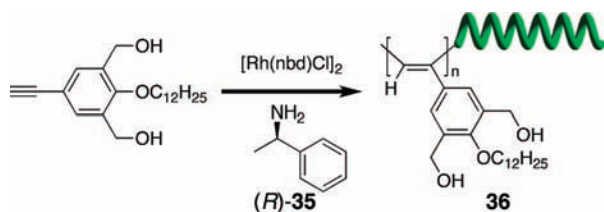


FIGURE 3. (A) Helicity induction in **17** with (*R*)-**31** and memory of the induced helicity after replacement by achiral amines and (B) CD spectra of **17**-(*R*)-**31** (a) and **17** isolated by SEC using a DMSO solution containing achiral amine **33** as the eluent (b).

SCHEME 3



helix assisted by a chiral alcohol **39** in toluene accompanied by gelation, and at the same time, fullerenes, such as C_{60} , were encapsulated within its helical cavity to form a robust, processable peapod-like crystalline complex (Figure 5).³⁸ After the removal of **39**, the st-PMMA gel exhibited a vibrational CD (VCD) and ICD in the PMMA IR regions and in the encapsu-

lated C_{60} chromophore regions, respectively, although C_{60} itself is achiral.

Direct Observations of Helical Structures by AFM

Evidence for a preferred-handed helix formation of synthetic helical polymers is usually obtained by CD or optical rotation. Based on X-ray diffraction (XRD) studies of oriented films or fibers derived from a few helical polymers, their helical structures were proposed. However, these methods are not straightforward and may not provide unambiguous helical structural information and, in particular, the helical sense.

This is the case for helical polyacetylenes except for dendronized polyacetylenes.²¹ Recently, we have successfully

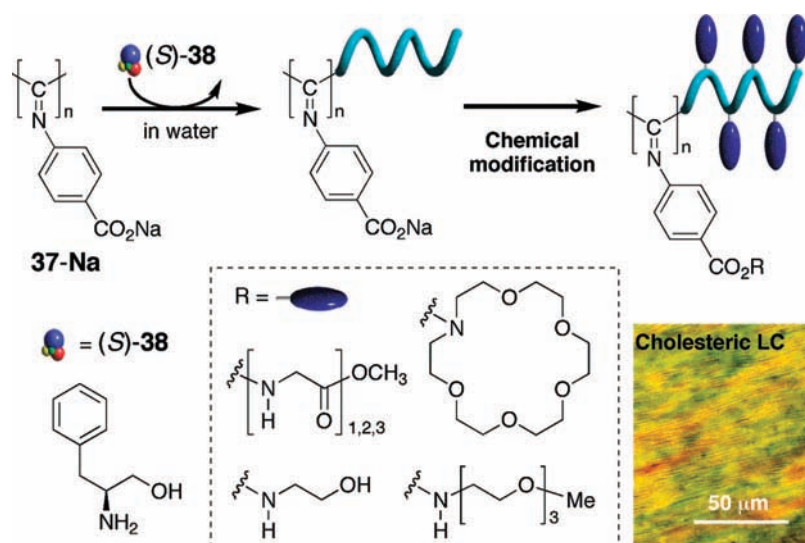


FIGURE 4. Helicity induction in **37-Na** with **(S)-38** and memory of the induced helicity after removal of **(S)-38**, modification of the pendants with helicity memory, and a typical cholesteric LC.

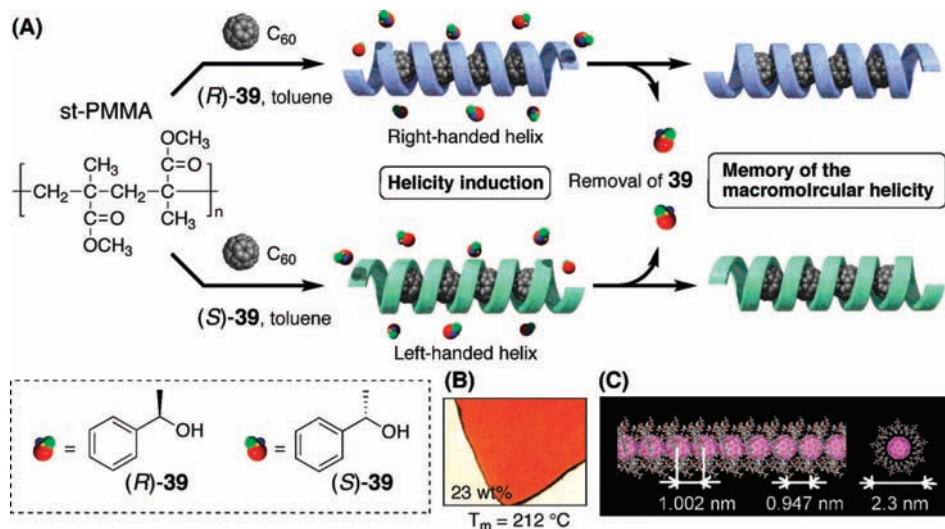


FIGURE 5. (A) Helicity induction in *st*-PMMA in the presence of C_{60} with **(S)-** or **(R)-39** and memory of the induced helicity after removal of **39**, (B) polarized optical micrograph (POM) of a *st*-PMMA- C_{60} film, and (C) a possible structure of *st*-PMMA- C_{60} complex.

determined the helical structure of a poly(phenylacetylene) bearing L- or D-alanine residues with a long *n*-decyl chain as the pendants (**40**) by direct AFM observations, together with XRD analysis and CD measurements (Figure 6).³⁹ The polyacetylene **40** showed an unprecedented change in the main-chain stiffness accompanied by inversion of the helical sense of the polymer generated by the solvent polarity (Figure 6A). The persistence length (*q*) drastically changed from 126 nm in toluene to 19 nm in THF,⁴⁰ resulting from the “on and off” fashion of the intramolecular hydrogen-bonding networks in polar and nonpolar solvents. These large *q* values are the highest among all synthetic helical polymers reported so far. The cholesteric LC **L-40** self-assembled to form a highly uniaxially oriented film in an electric field due to the large electric dipole moment along the main-chain helical axis.⁴¹

The rod-like helical **40** was found to hierarchically self-assemble on highly oriented pyrolytic graphite (HOPG) upon exposure to benzene vapors. First, flat polyacetylene monolayers epitaxially formed on the basal plane of the graphite (Figure 6B), on which helical polyacetylenes further self-assembled into chiral two-dimensional (2D) helix bundles with a controlled helicity (Figure 6C). The AFM and XRD results suggest that **40** possesses an 11/5 helix with a helical pitch of 2.3 nm, and **D-40** has a right-handed helical array with respect to the pendant arrangements, while the main chain has the opposite, left-handed helical structure. The direct evidence for the macromolecular helicity inversion of **40** in different solvents can also be observed by AFM upon exposure to each solvent vapor.⁴²

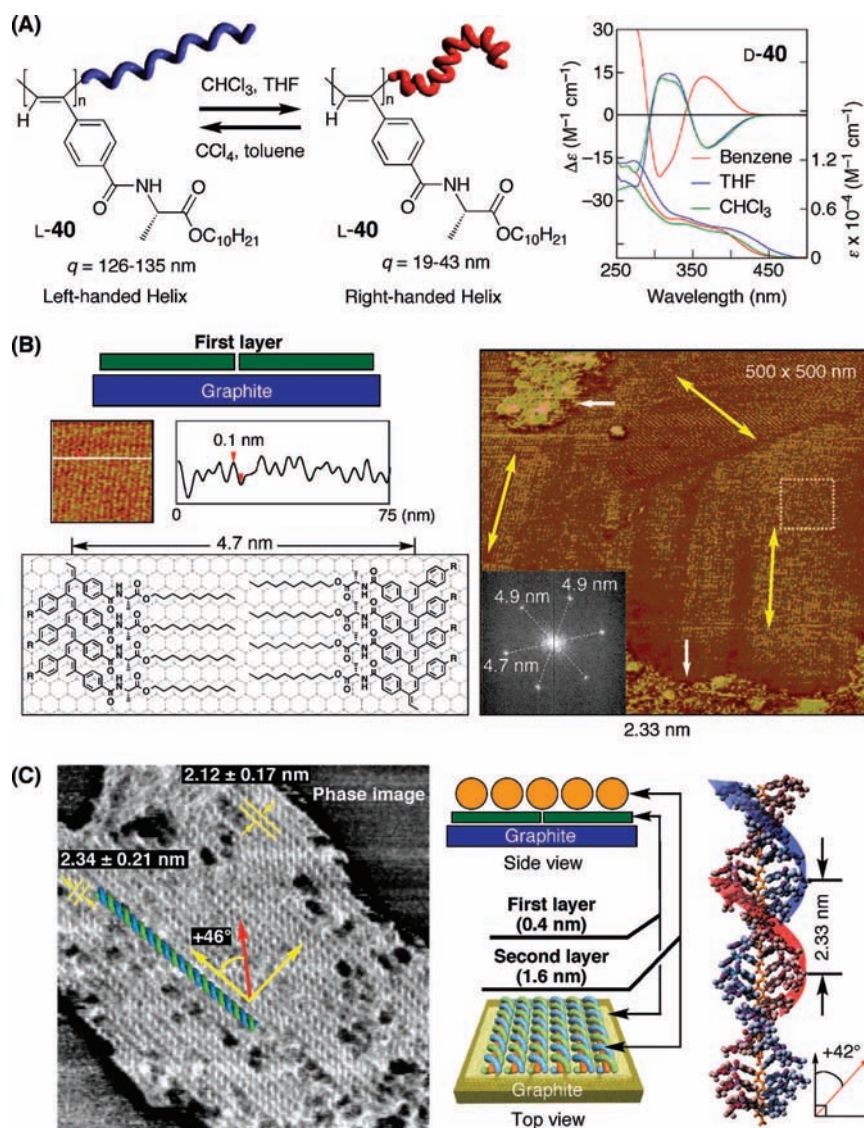


FIGURE 6. (A) Inversion of helicity of L-40 and CD and absorption spectra of D-40 in various solvents and (B, C) AFM phase images of L- or D-40 before (B) and after (C) benzene vapor exposures on HOPG, along with schematic representation of the hierarchical structure of the self-assembled 40 on HOPG and a helical structure model constructed on the basis of the X-ray structural analysis. Reproduced with permission from ref 39. Copyright 2006 Wiley-VCH.

Given the success in visualizing the helical structure of 40 by AFM, we applied this procedure to other helical polymers. Specific solvent vapor exposure to helical polymers deposited on HOPG appears to be the key process through which helical polymers may self-assemble into 2D crystals on graphite with regular helix-bundle structures. An analogous poly(phenylacetylene) bearing achiral α -aminoisobutyric acid residues with the same n -decyl chain as the pendants (41)⁴³ consists of an equal mixture of interconvertible right- and left-handed helical segments separated by helical reversals in solution. The high-resolution AFM images of 41 on HOPG clearly revealed right- and left-handed helical block segments separated by rarely occurring helical reversals in individual polymer chains (red and blue colors (right) and white arrows

in Figure 7, respectively). Careful evaluations of the height profiles indicate that there is a gap along with helical blocks of opposite sense (yellow arrows) being different from the helical reversal (white arrows); in this case, two 41 chains align with a distance of 3.4 nm. The AFM images together with the XRD analysis provide an 11/5 helix of 41 with a helical pitch of 2.3 nm. Based on statistical analysis of a series of high-resolution AFM images, helical reversals appeared only once in every ca. 300 monomer units on average in the dynamic helical 41.⁴³

An optically pure phenyl isocyanide (L-42) having the same pendant group as L-40 was also prepared and polymerized with the μ -ethynediyl Pt–Pd catalyst (43), which promoted the living polymerization of L-42 and simultaneously produced

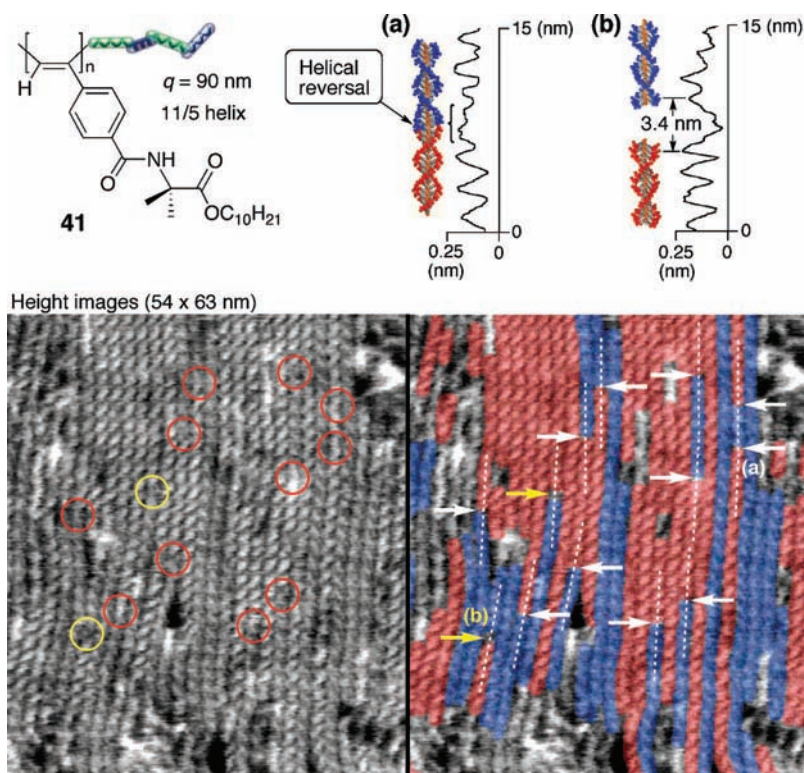


FIGURE 7. AFM height images of 2D self-assembled right- (red) and left-handed (blue) **41** on HOPG and the cross-section height profiles denoted by white dashed lines (a, b).

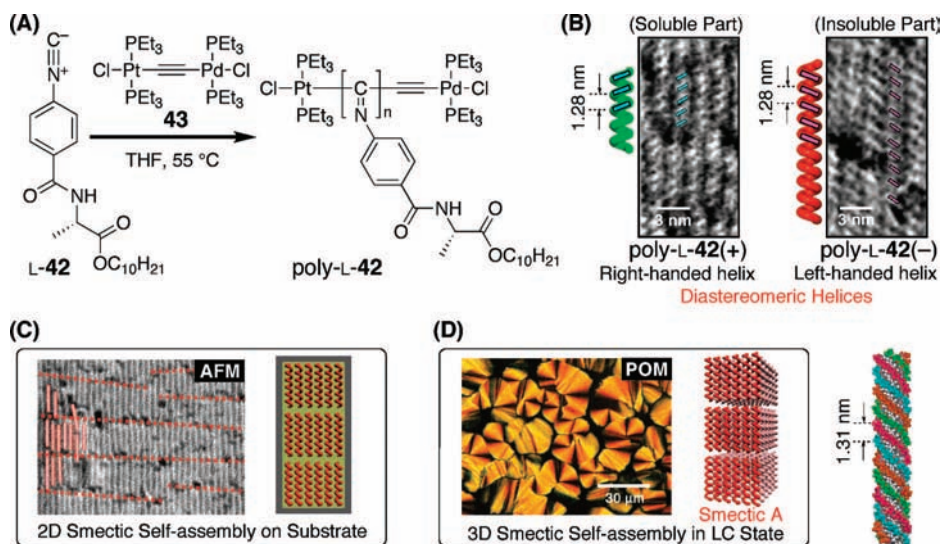
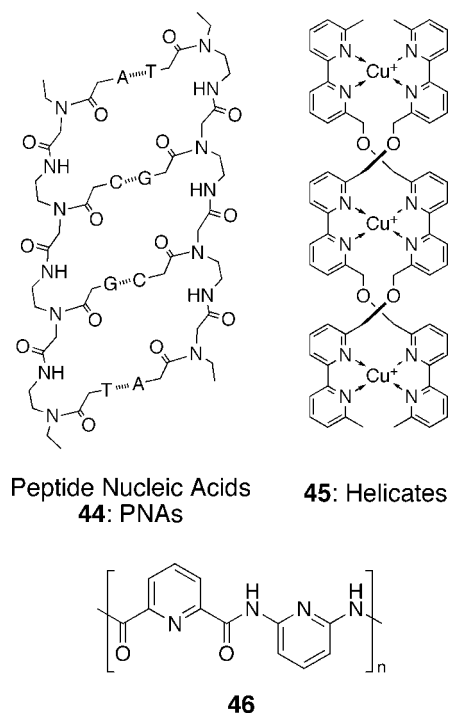


FIGURE 8. (A) Helix-sense-selective living polymerization of **L-42** with **43**, yielding a mixture of diastereomeric, right- and left-handed helical poly(**L-42**)s and 2D (B, C) and 3D (D) smectic ordering of the one-handed helical poly(**L-42**)s on HOPG (B, C) and in LC state (D).

almost completely right- and left-handed helices with different molecular weights and narrow molecular weight distributions (Figure 8A).⁴⁴ Each single-handed, rod-like helical poly-**L-42** with a controlled length and handedness can be separated by solvent fractionation with acetone and exhibits well-defined 2D and three-dimensional (3D) smectic ordering on HOPG and in an LC state, as directly observed by AFM and revealed by a polarized optical micrograph (POM) and

XRD, respectively (Figure 8B–D). Based on the high-resolution AFM (Figure 8B) combined with the XRD analysis, both right- and left-handed helical poly(**L-42**)s possess a rigid-rod 15/4 helix with a helical pitch of ca. 1.3 nm and 99% and 97% helical sense excess, respectively, assisted by four sets of intramolecular hydrogen bondings. In addition, poly(phenyl isocyanide)s showing a positive first Cotton effect sign can be assigned to a right-handed helix.⁴⁴

CHART 2



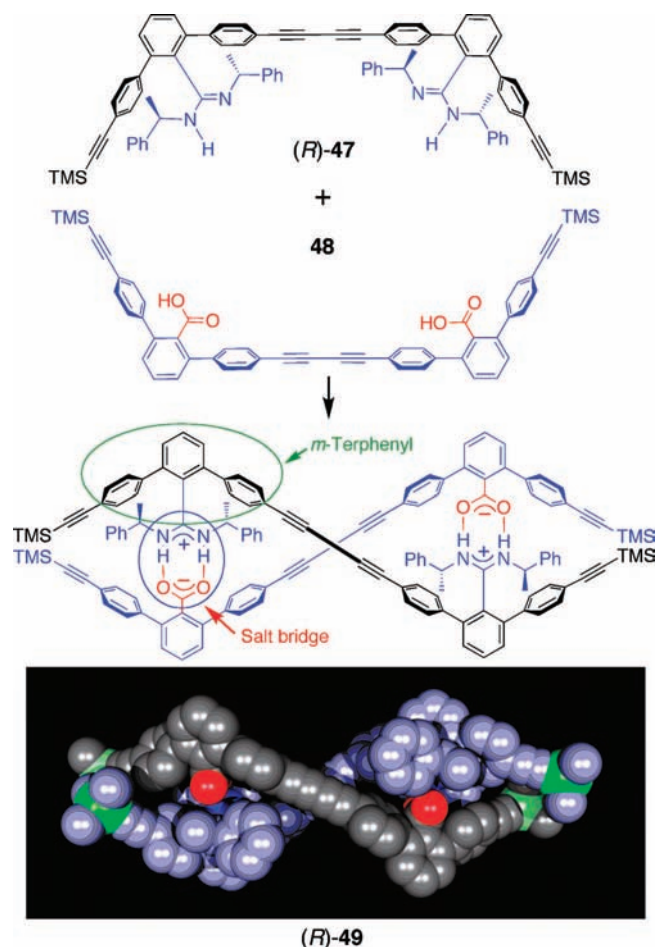
Double-Stranded Helical Polymers

In contrast to numerous synthetic polymers and oligomers with a single helical conformation, only a few structural motifs for double helical oligomers, such as peptide nucleic acids (**44**, PNA),⁴⁵ helicates (**45**),⁴⁶ and aromatic oligoamides (**46**)⁴⁷ have been reported (Chart 2).

The hydrogen-bonding interaction is a readily exploitable and versatile tool for constructing supramolecular assemblies. However, it remains difficult and challenging to design double helices of which the formation is predictable. Aiming at a rational design of artificial double helices, we designed a double-helical oligomer (**49**) that consists of two complementary molecular strands (**47** and **48**) bound together through amidinium–carboxylate salt bridges (Scheme 4).⁴⁸ The duplex, (*R*)- or (*S*)-**49**, was spontaneously formed from the (*R*)- or (*S*)-**47** and achiral **48** in chloroform through the two identical salt bridges, as supported by their ¹H NMR and mass spectra. An X-ray crystallographic study unambiguously revealed the right-handed double helical structure of the (*R*)-**49**, which was retained in solution, as evidenced by its strong CD in the absorption region of the diacetylene linkages.

Based on this model oligomer study, we then designed and synthesized a double-stranded metallosupramolecular helical polymer, (*R*)- or (*S*)-poly-**50**, in combination of the salt bridges and metal–ligand interactions (Scheme 5).⁴⁹ The supramolecular polymerization of (*R*)-**50** with 2 equiv of *cis*-diphenylbis(dimethyl sulfoxide)platinum(II) (*cis*-PtPh₂(DMSO)₂)

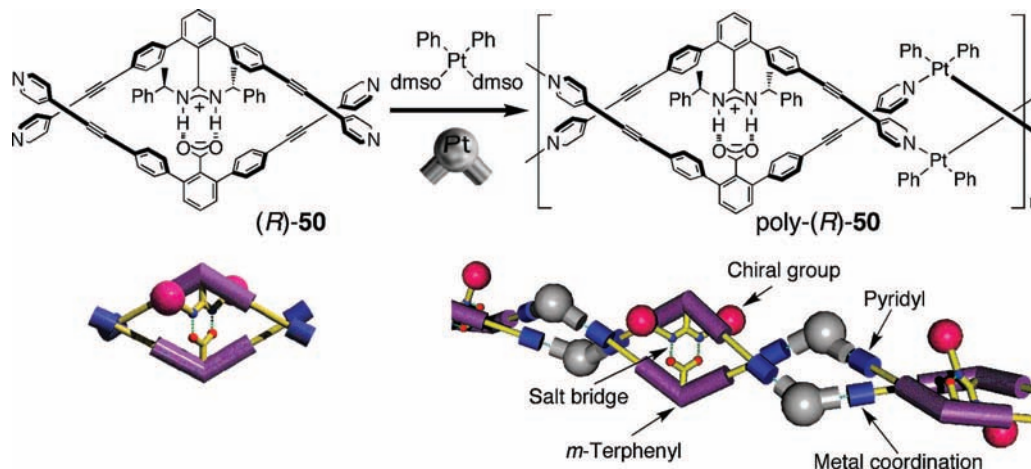
SCHEME 4. Complementary Double-Strand Helix Formation and Crystal Structure of (*R*)-**49**



readily proceeded through pyridine–Pt(II) coordination to yield (*R*)-poly-**50**, which exhibited distinct Cotton effects in the metal to ligand charge transfer band region (370–450 nm), suggesting an excess one-handed double-helical structure in solution.

Next, we synthesized a double-stranded helical polymer consisting of complementary homopolymers (Figure 9).⁵⁰ The homopolymers of chiral amidines and achiral carboxylic acids with *m*-terphenyl backbones, (*R*)-**51** and achiral **52**, were prepared by the Sonogashira polycondensation of the corresponding monomers. Upon mixing in THF, the complementary homopolymers self-assembled into the double-stranded helical polymer with a twist-sense bias through the interstrand salt bridges, as evidenced by the absorption and CD spectroscopies (Figure 9B). The double-stranded helical structure of (*R*)-**51**·**52** was determined by high-resolution AFM combined with XRD analysis, which provided the helical pitch (1.47 nm) and handedness (rich in right-handed double helix) (Figure 9C). In contrast, when mixed in less polar solvents, such as chloroform, the complementary strands kinetically formed an

SCHEME 5. Double-Stranded Metallosupramolecular Helical Polymer with Complementary Strands



interpolymer complex with an imperfect double-helical structure containing a randomly hybridized cross-linked structure. This primary complex was rearranged into the fully double-helical structure by treatment with a strong acid followed by neutralization with an amine (Figure 9D).⁵⁰

The oligoresorcinol nonamer (**53**) is a unique π -conjugated oligomer and self-assembled to form a double-stranded helix through aromatic interactions in water.⁵¹ The double helix further unraveled and entwined upon complexation with specific cyclic and linear oligosaccharides with a particular chain length or glucosidic linkage pattern, such as β - and γ -cyclodextrins (β - and γ -CyDs)⁵² and α -1,6-D-isomaltooligosaccharides,⁵³ respectively, thus forming a twisted [3]pseudorotaxane and a heteroduplex with a preferred-handed helical conformation (Figure 10) as evidenced by the appearance of the ICDs, as well as absorption and ¹H NMR spectroscopies. Since the specific recognition of oligosaccharides in water is still considered underdeveloped despite the well-established synthetic receptors for mono- and disaccharides, these results provide a new conceptual approach to saccharide recognition in water.

Applications of Helical Polymers

Potential applications of optically active helical polymers involve enantioselective catalysis and adsorbents.^{4,7,16} The one-handed helical poly(triarylmethyl methacrylate)s prepared by the helix-sense-selective polymerization, such as **2**, can resolve a wide range of racemic compounds and are commercialized.² Other helical polyacetylenes have been used as a CSP⁷ or enantioselective permeable membranes.¹⁹

Another attractive application for helical polymers is use as asymmetric catalysts, but successful examples are rare except for the one-handed helical polymethacrylates complexed with palladium, such as **54**,⁵⁴ which catalyzed the asymmetric allylic alkylation reaction. A dynamic helical polyisocyanate

complexed with rhodium (**55**) was also an effective catalyst for the asymmetric hydrogenation (Chart 3).⁵⁴

Rigid-rod helical polymers with a controlled helical sense have been employed as a novel scaffold or template to spatially organize chromophores, such as porphyrins, dyes, and various functional groups, in a one-handed helical array along the polymer backbones through covalent or noncovalent bondings.^{7,16,55,56} Static and dynamic helical polymers can be used for this purpose. For example, the homopolymerization of an achiral phenylacetylene bearing a C₆₀ pendant with long alkyl chains (**56**) and copolymerization with an optically active C₆₀ bound phenylacetylene (**57**) using a rhodium catalyst in chloroform homogeneously occurred, producing the C₆₀-containing helical poly(phenylacetylene)s soluble in chloroform (Scheme 6A).⁵⁷ The obtained copolymer exhibited an ICD both in the main-chain and in the fullerene chromophoric regions, indicating that the optically active copolymer possesses an excess of the one helical sense and that the pendant fullerene groups are arranged in helical arrays along the polymer backbones. Taking advantage of the noncovalent "helicity induction" concept, a predominantly one-handed helix can be induced in a dynamically racemic poly(phenylacetylene) (**18b**) with the negative charges by interactions with an enantiomerically pure cationic C₆₀-bisadduct (**58**), which further results in a helical array of the C₆₀-bisadducts with a predominant screw sense along the polymer chain (Scheme 6B).⁵⁸ The polymerization of achiral monomers in chiral nematic LC solvents can produce optically active π -conjugated polymers exhibiting a circular polarized luminescence, which may be a promising approach to the development of functional helical polymers.⁵⁹

A complementary double-stranded dimer of **59** composed of an achiral amidine strand and carboxylic acid strand bridged by achiral diphosphines was recently enantioselectively prepared, by

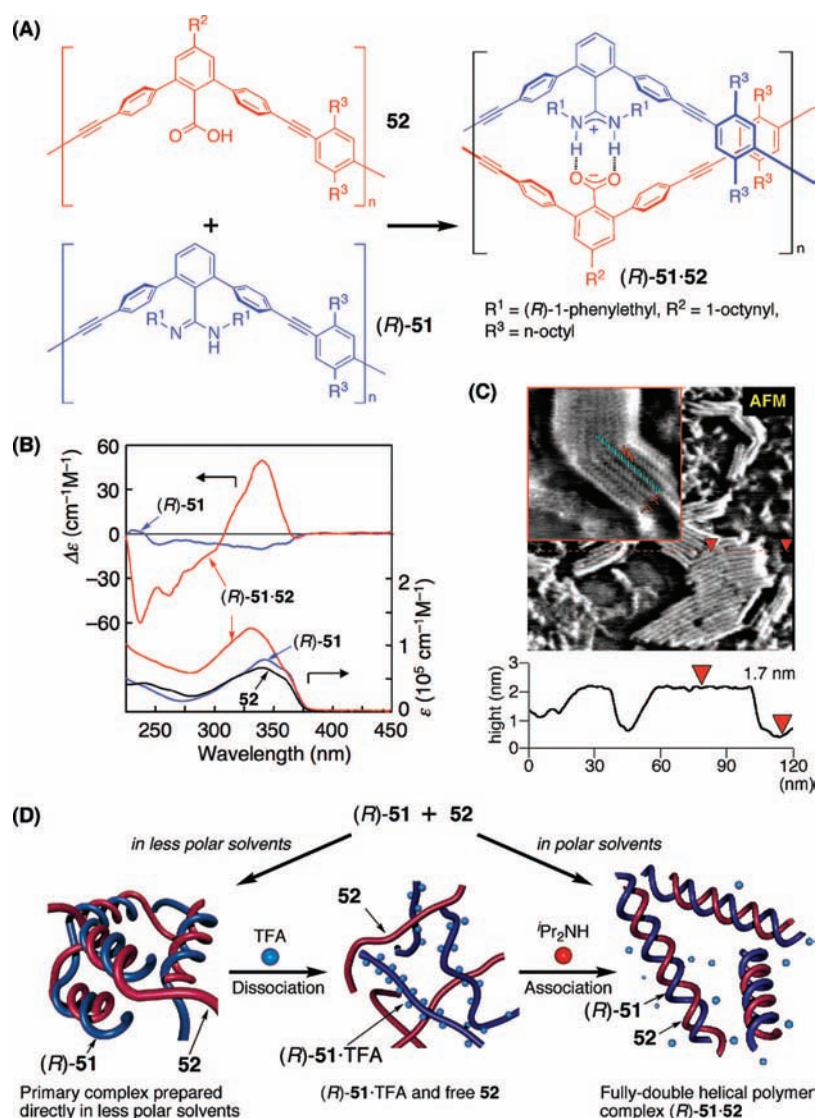


FIGURE 9. (A) Synthesis of the complementary double-helical polymer, (B) CD and absorption spectra of (R) -51, 52, and (R) -51-52 in THF, (C) AFM phase images of (R) -51-52 on HOPG with the height profile measured along the dashed line in the image and its magnified AFM image (inset), and (D) schematic illustrations of the possible mechanism for double-helix formation in CDCl_3/THF (99/1, v/v) through rearrangement of the primary complex by unraveling with trifluoroacetic acid (TFA) and neutralization with $i\text{-Pr}_2\text{NH}$.

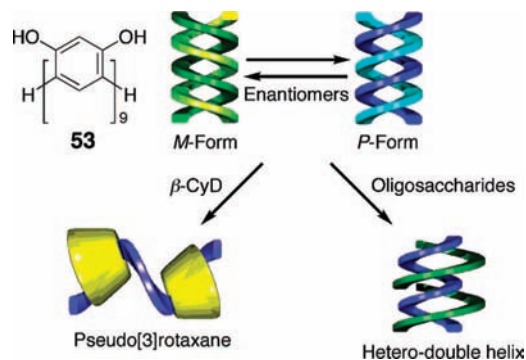
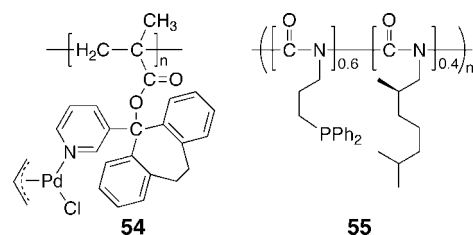


FIGURE 10. Schematic illustration of the unwinding of the double helix **53** using $\beta\text{-CyD}$ and the formation of a heterodouble helix with oligosaccharides.

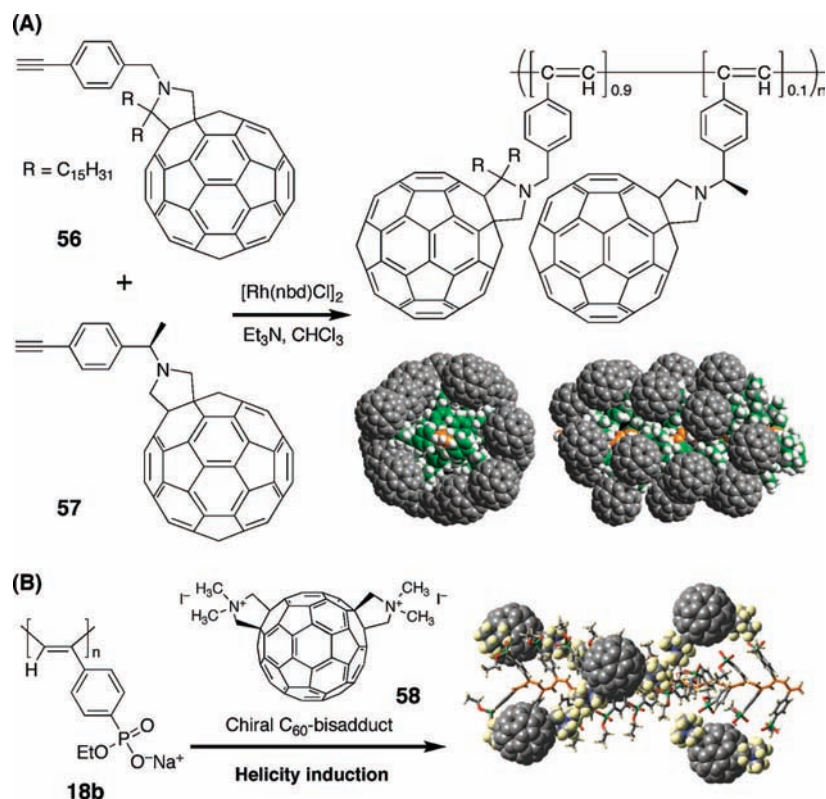
taking full advantage of the “helicity induction and memory” effect.⁶⁰ The alkynyl units on **59** can accommodate metal ions

CHART 3

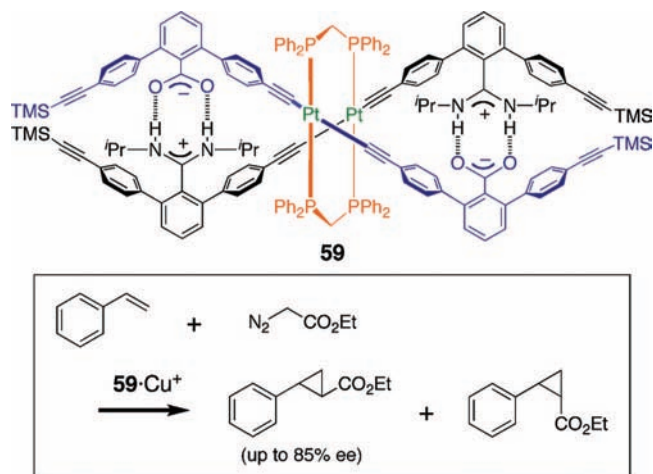


such as Cu(I) in a tweezer-like fashion (Scheme 7), and the double helical **59**—Cu(I) catalyzed the asymmetric cyclopropanation reaction of styrene with ethyl diazoacetate, thus producing an optically active product up to 85% ee. These results suggest that the chiral space generated by the double-helical structure is effective and indispensable for the high enantioselectivity, thus pro-

SCHEME 6



SCHEME 7



viding a promising and conceptually new strategy in the broad field of supramolecular catalysis with a unique double-helical structure.

Summary and Outlook

With implications for biological helices, significant progress has been made on the design and synthesis of single-stranded helical polymers over the past decade, although the control of the helical conformation of synthetic polymers during the polymerization process still remains diffi-

cult compared with those of the molecular weight and tacticity. This is because a rationale design of monomers together with that of specific chiral catalysts or initiators seems to be a prerequisite for the development of helical polymers with a controlled helical sense. The "helicity induction and memory effect" developed during the intensive studies on the dynamic helical polyacetylene derivatives has been proven to be a unique and valuable method for constructing helical polymers. This methodology has a great advantage from the practical viewpoint such that a preferred-handed helical polymer can be obtained from commodity polymers such as PMMA.³⁸

The determination of the helical structures of helical polymers including the helical pitch and handedness by microscopy, a long-standing problem in polymer chemistry, has been achieved for certain helical polymers using AFM coupled with solvent vapor exposures, which merits further progress in helical polymers with specific structures and functions.

Apart from numerous variations in single-stranded helical polymers and oligomers, the molecular design for double-stranded helical polymers is limited, despite the natural model, the double-helical DNA. The complementary double-stranded oligomers and polymers with a controlled helicity demon-

strated in this Account may be a promising approach to develop DNA-like helical systems for information storage and replication.

Future advances and challenges will likely be directed toward not only mimicking biological helices but also developing unique functions derived from helical architectures, which will provide an important step for the construction of advanced chiral materials.

We thank all of our co-workers for their great contributions reported in this Account. Financial support from Japan Science and Technology Agency and the Japan Society for the Promotion of Science is gratefully appreciated.

BIOGRAPHICAL INFORMATION

Eiji Yashima received his B.S. (1982), M.S. (1984), and Ph.D. (1988) degrees from Osaka University. In 1986, he joined Kagoshima University as an Assistant Professor. After spending one year at UMass, he moved to Nagoya University and was promoted to a full Professor in 1998. He was the project leader of the ERATO Project (JST) on "Yashima Super-structured Helix" (2002–2007). He received the Wiley Polymer Science Award from the SPSJ in 2000, the Japan IBM Science Award in 2001, Molecular Chirality Award in 2005, Thomson Scientific Research Front Award in 2007, and the Award of the Society of Polymer Science, Japan, in 2008. His current research interests are in the design and synthesis of helical molecules, supramolecules, and polymers with novel functions.

Katsuhiro Maeda received his B.S. (1993), M.S. (1995), and Ph.D. (1998) degrees from Nagoya University. In 1998, he joined Nagoya University and was promoted to an Associate Professor in 2002. After spending six months at MIT, he moved to Kanazawa University in 2008.

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FOOTNOTES

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