ADVANCED HELIX-SENSE-SELECTIVE POLYMERIZATION OF ACHIRAL PHENYLACETYLENES CHONTAINING IMINO GROUPS AND APPLICATION OF THE RESULTING HELICAL POLYMER FOR MEMBRANES

YU ZANG

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YU ZANG

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PART II

General Introduction

I. Dynamic covalent imino bonds

Rowan et al. reported the general concept of dynamic covalent chemistry related to dynamic covalent bonds formed reversibly under conditions of equilibrium control. The dynamic covalent bond is a class of bonds that can break and reform under the appropriate conditions without irreversible side reactions, for example, imine bond formation and exchange reactions between imines (Figure 1). Once these bonds are exposed to appropriate external stimuli such as heating and the addition of catalysts, they become reversible and reach an equilibrium state. Reversible bonding is crucial for efficient production of thermodynamically stable product molecules.

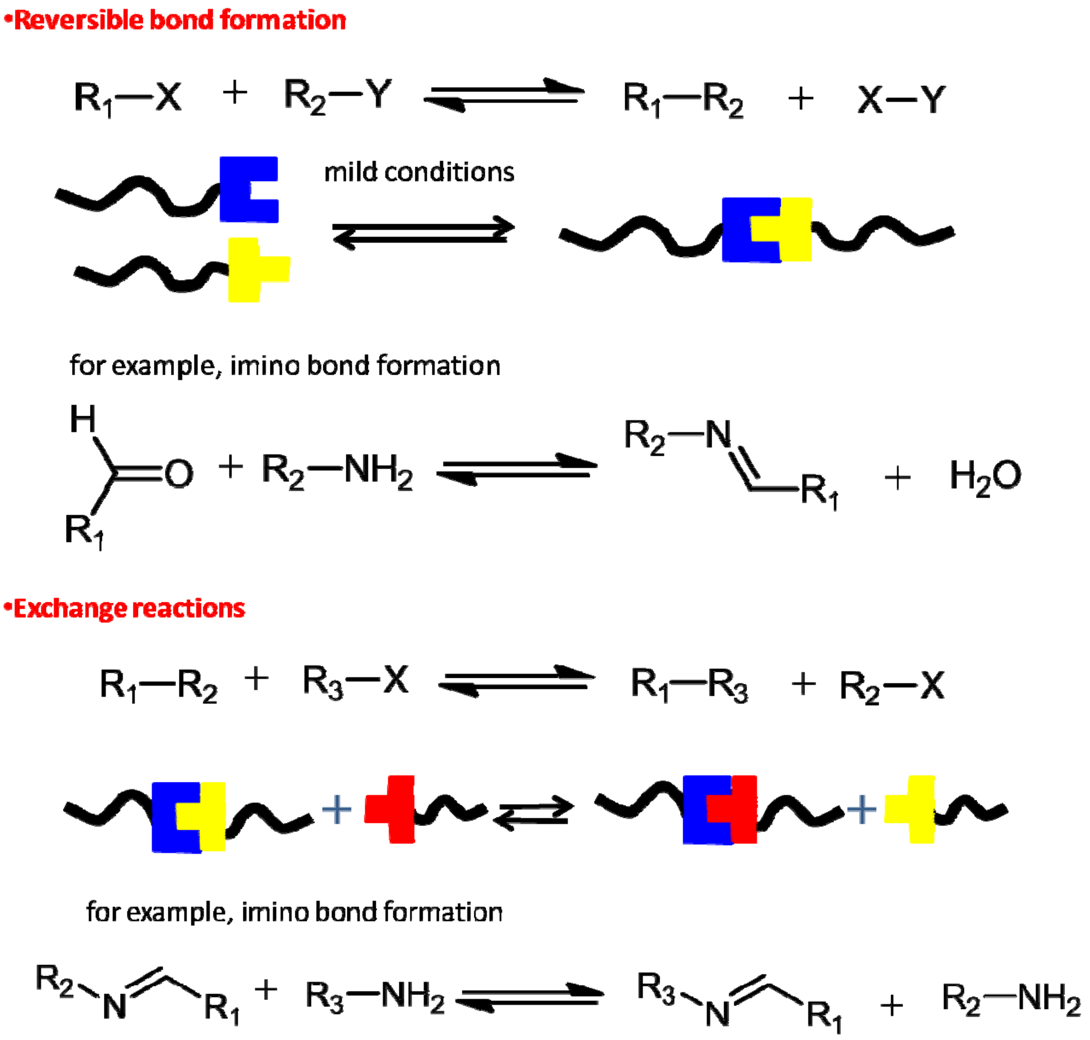


Figure 1. Dynamic covalent imino bonds.

C=N in imines and hydrazones, produced by amino/carbonyl condensations, are attractive in view of the wide range of structural variations available, the easy synthetic accessibility, and the control of yields, rates, and reversibility through conditions. Dynamic polymers having C=N bonds responding to changes in a neat/solution environment were reported by Lehn and coworkers. [3] C=N bonds in acylhydrazone groups, which are formed by the condensation of hydrazides with carbonyl groups, exhibit reversibility under mild conditions. Like polyimines, polymers with acylhydrazone functionalities exhibit dynamic aspects through the reversibility of the azomethine bond. Skene and Lehn have reported the synthesis of polyacylhydrazones and their dynamic feature. [4]

Aromatic Schiff base also showed rigdity and high planarity since the π-conjugated structures. Yamamoto and coworkers reported the dendritic polyphenylazomethines (DPAs) containing a C=N-conjugated backbone have a conformational rigidity, and their imine sites can trap metal ions (Figure 2). Particularly, the imines on DPA show a stepwise radial complexation with $SnCl_2$ from the core imines to the terminal imines based on the gradients in the basicity of the imine groups, which can be controlled by substituents on the core phenyl. [5- 7]

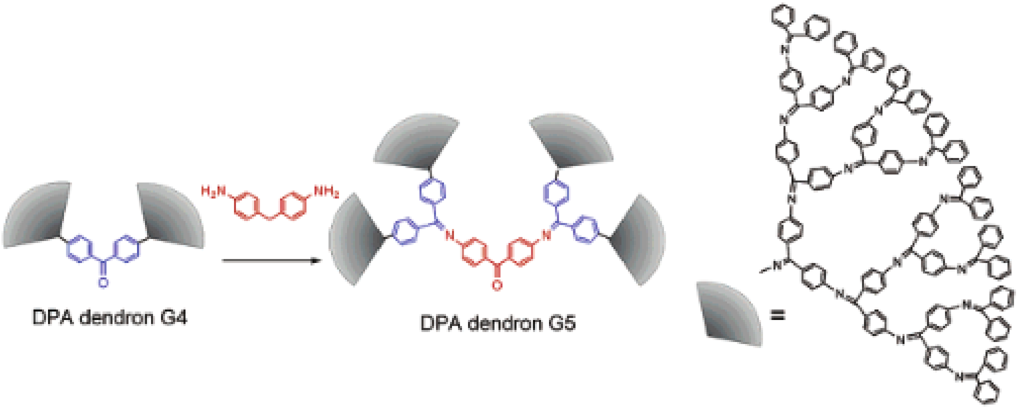


Figure 2. Dendritic polyphenylazomethines (DPAs) containing a C=N-conjugated backbone.

II. Helix-sense-selective polymerization (HSSP) and asymmetric-induced polymerization followed by polymer reaction in membrane state (AIP-RIM) of phenylacetylenes

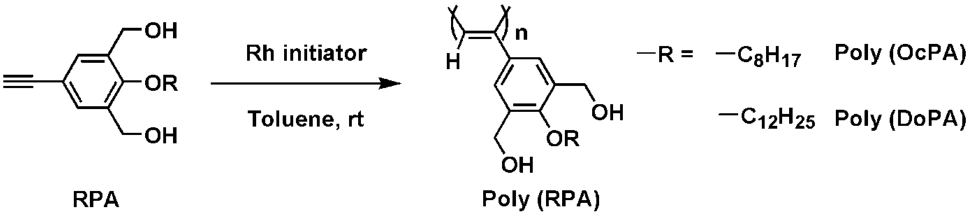
π-Conjugated polymers like polyacetylenes have aroused interest because of their noteworthy physical properties such as conductivity, organomagnetism, and optical non-linear susceptibility. Recently chiral polyacetylenes [8] have attracted much attention since the chiral structure can enhance the unique properties and add new functions.

Several kinds of asymmetric polymerizations of achiral monomers to obtain chiral polymers having their chiral structures in their main chains have been reported. Among them, a direct synthetic method of soluble chiral π-conjugated polymers whose chiral structures arise solely from the one-handed helical conformation of the conjugated main chains (therefore, they have no asymmetric carbons) and are stable alone in solution was so far only the helix-sense-selective polymerization (HSSP) of an achiral phenylacetylene monomer by using a chiral catalytic system developed in our laboratory. [9]

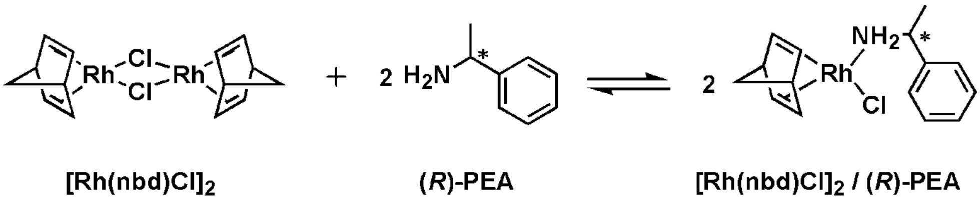
In general, there exist two methods to synthesize soluble chiral polymers whose chiral structures are present alone in the main chain as asymmetric carbons and/or as a one-handed helical conformation. One is HSSP [10] of an achiral monomer by using a chiral catalyst as a chiral source and the other is asymmetric-induced polymerization, by using achiral catalysts, of monomers having a chiral group as a chiral source, followed by removing the chiral groups by a polymer reaction in solution where the chiral groups were desubstituted from the resulting one-handed helical polymers (AIP-R). [11]

However, the examples where the two methods, HSSP and AIP-R, have been applied to π-conjugated polymers are very few. [9, 12] In fact there has been only one example by using HSSP by our group [9] and only one example by the use of AIP-R by our group [11] for obtaining soluble chiral conjugated polymers. Therefore, so far our HSSP and AIP-R were the only two methods available to obtain soluble chiral conjugated polymers whose chiral structures arise only from the one-handed helical conformation of their conjugated main chains.

The HSSP is more simple procedure than AIP-R. However, in the HSSP suitable monomers were limited and typical monomers needed two functional groups which could make hydrogen bonds like hydroxyl groups (Scheme 1, DoDHPA). [9] The one-handed helical backbone was not stable to polar solvents and heating because it was maintained by intramolecular hydrogen bonds. In addition, the efficiency of the chiral induction was not high, *i.e.*, a large ratio of the chiral cocatalyst to the monomer (Scheme 2, (*R*)- or (*S*)-PEA) was needed.



Scheme 1. Helix-sense-selective polymerization (HSSP) of RPA.



Scheme 2. Two component chiral initiator system in our previous study.

III. Highly selective photocyclic aromatization (SCAT) of cis-cisoid helical poly(phenylacetylene)s in the membrane state

A novel highly selective photocyclic aromatization (SCAT) of π-conjugated polymers from phenylacetylene having two hydroxyl groups to exclusively yield a 1,3,5-trisubstituted benzene derivative was developed by our groups and its success was confirmed by ^{1}H-NMR, GPC, and TOF-MS (Figure 3). [13] The SCAT reaction had many unique characteristics, such as unusual selectivities, as follows. 1) It is a quantitative reaction: it gave only the corresponding cyclic trimer, *i.e.*, a 1,3,5-trisubstituted benzene derivative, quantitatively(= 100%). No by-products were produced under the best condition. 2) It is an intramolecular reaction: it occurred between adjacent three monomer units in one macromolecule. 3) It is a stereospecific and topochemical or template reaction: the reactivity strongly depended on the configuration and conformation of the starting polymer substrates. 4) It is a photoreaction: high selectivity (= 100%) was observed only by the use of visible light irradiation, not by heating. 5) It is a solid state reaction: high selectivity(=100%) was observed only in the solid state, not in solution. *In addition*, 6) the resulting cyclic trimers had the ability to form a self-supporting membrane, in spite of their low molecular weights. This new approach resulted in a new class of supramolecular polymers consisting of a 1,3,5-trisubstituted benzene derivative, numbers of which were linearly linked by hydrogen bonds and stacked benzenes. Since SCAT has such high selectivities and is useful for the preparation of a self-supporting supramolecular polymer membrane, many kinds of applications can be expected.

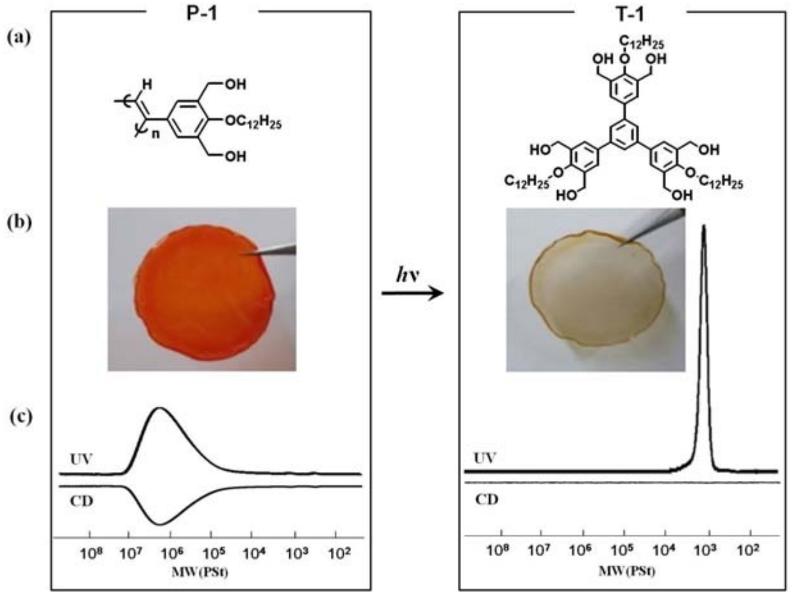
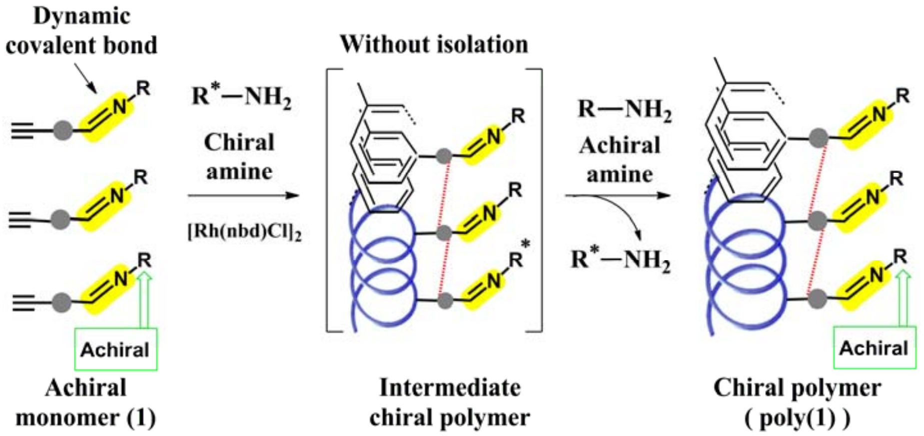


Figure 3. SCAT of P-1 to T-1 (a) chemical structures of the starting polymer(P-1) and the SCAT product(T-1). (b) Photographs of P-1(a polymer membrane) and T-1(a supramolecular polymer membrane), (c) GPC curves detected by UV and CD of P-1 and T-1.

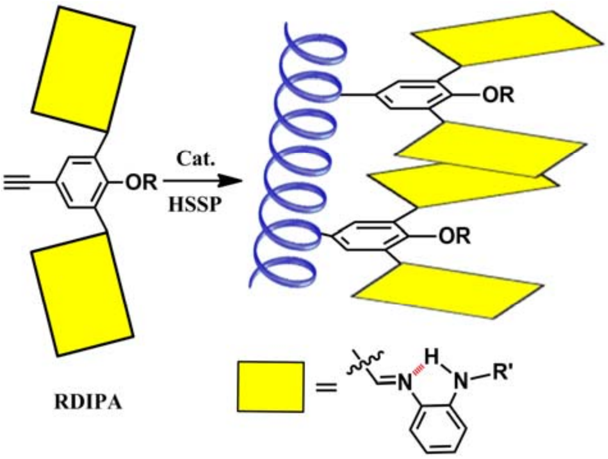
IV. Purpose of this thesis

In Chapter 1, a new conceptual approach to asymmetric polymerisation that makes one-handed helical polymers without the coexistence of any other chiral moieties from achiral monomers, pseudo helix-sense-selective polymerisation (PHSSP) was reported for the first time. Practical results from a wide range of substituted acetylenes having dynamic covalent bonds have been reported. The chiral amine in PHSSP worked not as a cocatalyst, as it does in HSSP, but rather as a reagent because it formed temporary covalent bonds with the polymer (Scheme 3). This is the origin of the name pseudo helix-sense-selective polymerisation (PHSSP). Because of the introduction of the chiral source *via* covalent bonds, the optical purity[5] and efficiency[5] in the chiral induction were much higher in PHSSP than those in HSSP. In addition, the range of chemical structures suitable for PHSSP was wider than that for HSSP. Therefore many kinds of acetylene monomers are expected to be suitable for PHSSP. Furthermore, other kinds of monomers having a different polymerisable group are also expected to be applicabgle to PHSSP. We anticipate that it will become a general method for asymmetric polymerisation.



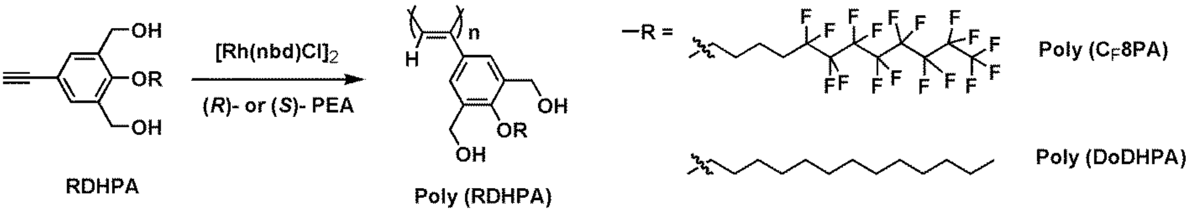
Scheme 3. PHSSP of achiral monomer by a chiral catalytic system.

In Chapter 2, the helix-sense-selective polymerization (HSSP) has been achieved of three achiral substituted acetylene monomers synthesized which contained two bulky π-conjugated planar substituents via imine groups by using the chiral catalytic system we developed before (Scheme 4). One-handed helical main chains of the resulting polymers were stabilized by intramolecular steric hindrance, not by intramolecular hydrogen bonds. Therefore the chiral main chains were very stable to polar solvent and heating. In addition, the efficiency of the chiral induction was much higher than that in the case of the previous monomers having hydoroxy groups we reported, *i.e.*, it needs only catalytic amount of chiral cocatalysts. Therefore we found more valuable and general monomers which were more suitable for the HSSP. The monomers have enhanced the value of our HSSP because the range of the molecular design has been enlarged.



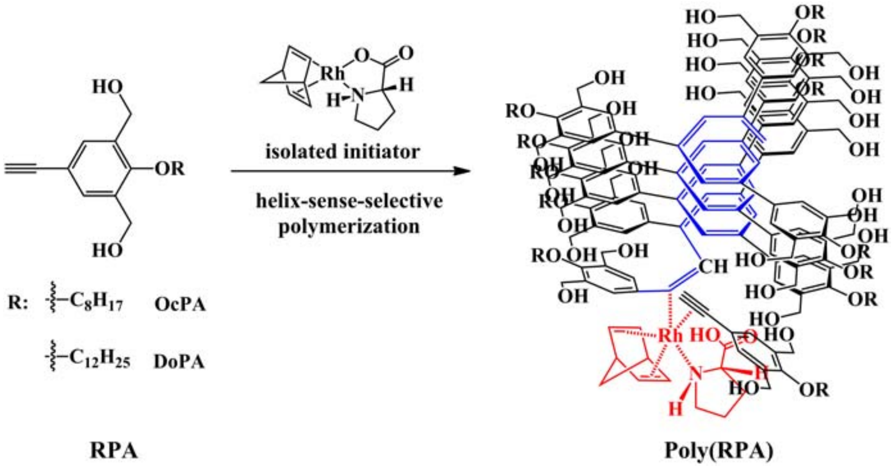
Scheme 4. HSSP of RDIPA by a chiral catalytic system.

In Chapter 3, to develop new phenylacetylene monomers suitable for HSSP we reported previously and to improve the efficiency and ability of chiral induction of HSSP, *i.e.*, it needed only catalytic amounts of the chiral source and the resulting polymer having higher relative optical purity, a novel phenylacetylene monomer having a perfluorinated alkanes as a side group (C_F8DHPA) was synthesized and polymerized by a chiral catalytic system (Scheme 5). The efficiency and ability of the chiral induction were much higher than that in the case of the previous monomers having perhydrogenated alkanes side group we reported. In addition, the fluorine containing polymers membrane showed high selectivity of SCAT and higher oxygen permselectivity than that of poly(DoDHPA) membrane.



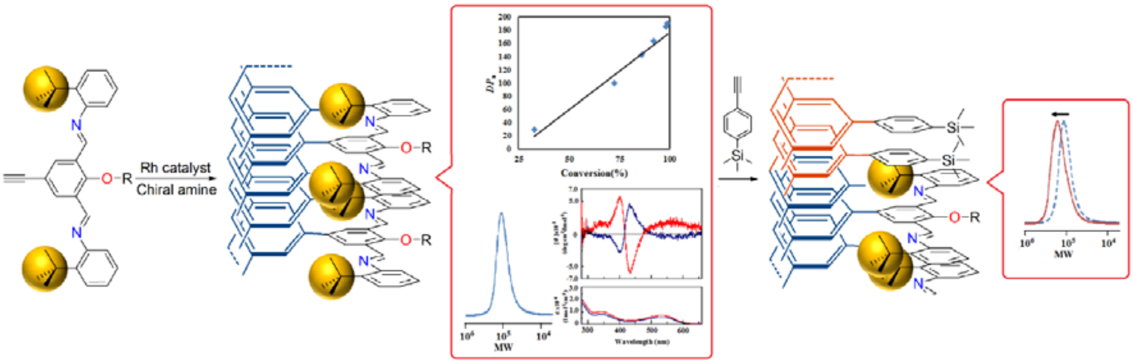
Scheme 5. HSSP of RDHPA by a chiral catalytic system.

In Chapter 4, HSSP of substituted acetylenes by using an isolated chiral Rh initiator coordinated by an amino acid ligand has been achieved (Scheme 6). The sense of the helix of the main chain of the resulting polymer was controlled by the sign of the chirality of the ligand. The HSSP by isolated initiator needed less amount of the chiral source and gave polymers having a higher [θ] value than the two component chiral initiator systems we reported previously. The resulting polymers had a higher M_w.



Scheme 6. HSSP of RPA by using an isolated chiral Rh initiator coordinated by an amino acid.

In Chapter 5, by using a new achiral phenylacetylene having bulky substituents as a monomer, living-like HSSP has been achieved. This is the first example of the HSSP of substituted acetylenes where the degree of polymerization was controlled. The resulting one-handed helical living polymer initiated polymerization of a second monomer to successfully yield a block copolymer.



Scheme 7. Living-HSSP of achiral phenylacetylenes having bulky substituents.

In Chapter 6, the monomer structures suitable to the helix-sense-selective polymerization (HSSP) and the combination of suitable chiral amines and monomers were discussed (Figure 4). For the HSSP of RDHPA the most suitable chiral amine was IIa. For TBDHPA, Ib was the best cocatalyst. For RDIPA type monomers, Ia was the best cocatalyst. The combination of monomer C_{12}DHPA and chiral amine IIa was the best to synthesize one-handed helical polymers with the highest optical purity.

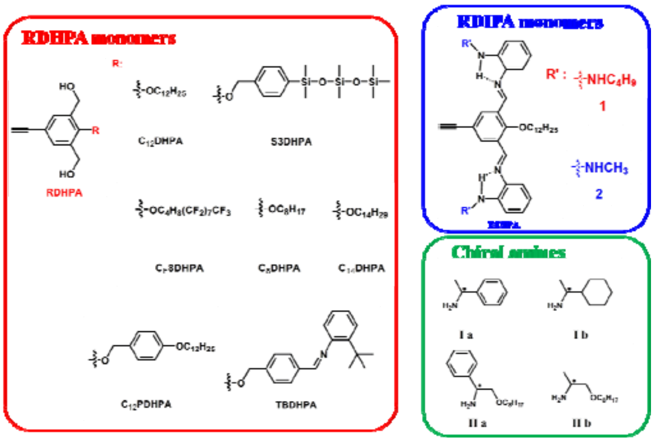


Figure 4. Suitable monomer structures and chiral amines for HSSP.

In Chapter 7, the new phenylacetylenes having two hydroxyl groups were synthesized and polymerized. The polymeric dense membranes were expected to enhance gas permselectivity because of the high regularity of the polymer structure (Figure 5). Gas permselectivities of the resulting membranes were determined and the membrane forming ability was optimized by selecting a better casting solvent. The effects of the two hydroxyl groups and the conformation of the main chain on the gas permselectivity were discussed.

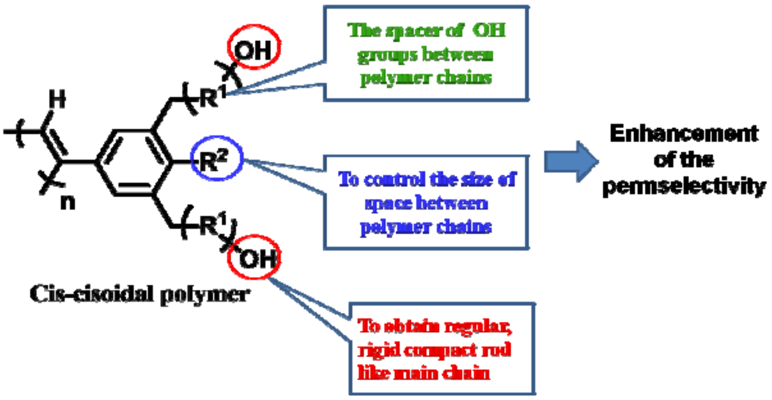


Figure 5. The structure of new polyphenylacetylenes having two hydroxyl groups.

In Chapter 8, to obtain membranes having much higher oxygen permselectvity with high permeabilities for mixture of molecules, membranes having regular molecular-size pores with thinner thickness are desired. As such membranes, we selected a composite membrane consisting of a supramolecular membrane from amphiphilic SCAT products supported on polymeric membranes such as poly(vinyl alcohol) and poly(vinyl acetate) (Figure 6). We selected surface modification technology by solvent casting of mixture of a small amount of a low surface energy compound and base polymers. By the surface modification, the oxygen permselectivity increased largely with almost no drop in permeability.

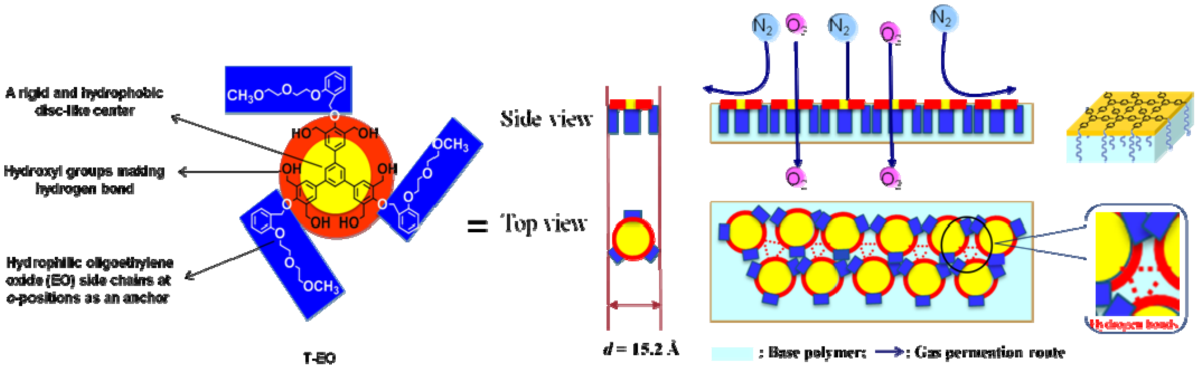


Figure 6. Imaginative figure of 2D distribution state of T-EO on surface of the blend membrane.

In Chapter 9, there are many kinds of polymers in the world, almost all the polymers were one-dimensional (linear or branched) or three-dimensional (cross-linking) structures. No report can be found for the organic, soluble, and self-supporting two dimensional organic polymer ("2D polymer") having high molecular weight which structure can be characterized clearly. Since there is no report on the "2D polymer" described above, to review the reported of "2D polymer" is impossible. Therefore, in this review, a traditional "2D polymer" or a part of that will be reported.

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PART I

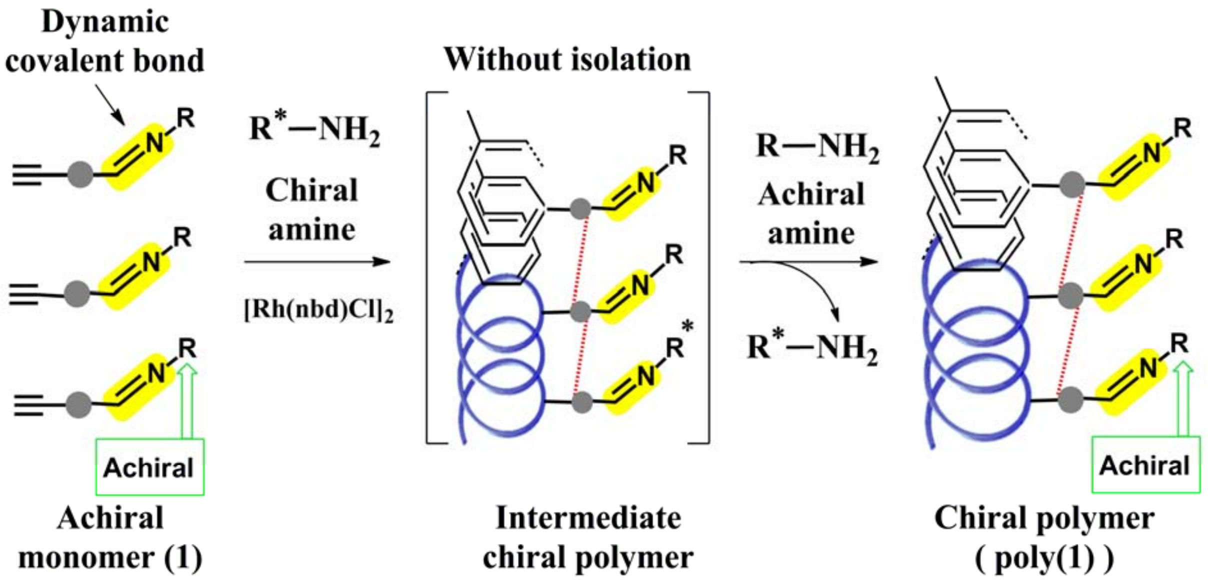
Advanced Helix-Sense-Selective Polymerization of Achiral Phenylacetylenes Containing Imino Groups

Chapter 1

Pseudo Helix-Sense-Selective Polymerization of Achiral Phenylacetylenes Containing Imino Groups

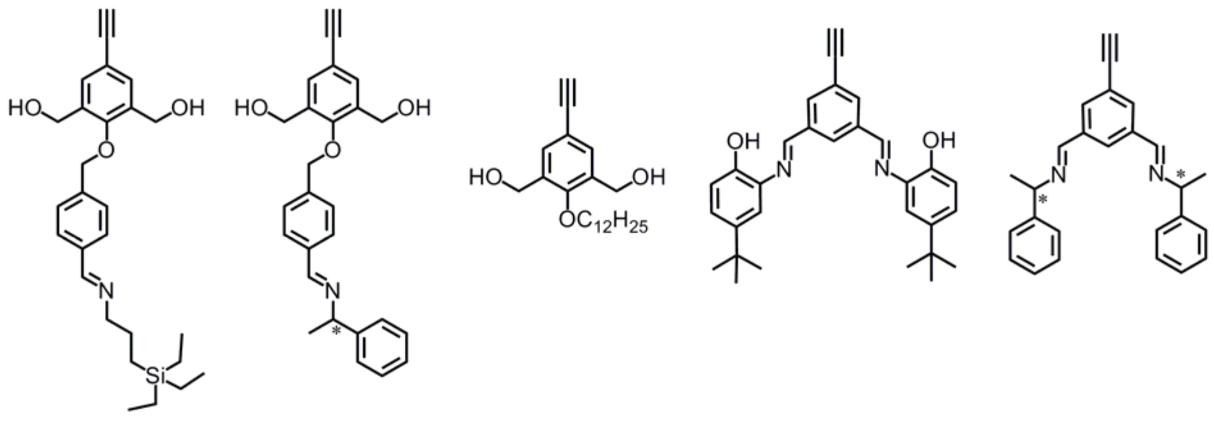
1.1 Abstract

A new conceptual approach to asymmetric polymerisation that makes one-handed helical polymers without the coexistence of any other chiral moieties from achiral monomers, pseudo helix-sense-selective polymerisation (**PHSSP**) was reported for the first time. Practical results from a wide range of substituted acetylenes having dynamic covalent bonds have been reported. The chiral amine in **PHSSP** worked not as a cocatalyst, as it does in **HSSP**, but rather as a reagent because it formed temporary covalent bonds with the polymer. This is the origin of the name pseudo helix-sense-selective polymerisation (**PHSSP**). Because of the introduction of the chiral source *via* covalent bonds, the optical purity [5] and efficiency [5] in the chiral induction were much higher in **PHSSP** than those in **HSSP**. In addition, the range of chemical structures suitable for **PHSSP** was wider than that for **HSSP**. Therefore many kinds of acetylene monomers are expected to be suitable for **PHSSP**. Furthermore, other kinds of monomers having a different polymerisable group are also expected to be applicabgle to **PHSSP**. We anticipate that it will become a general method for asymmetric polymerisation.



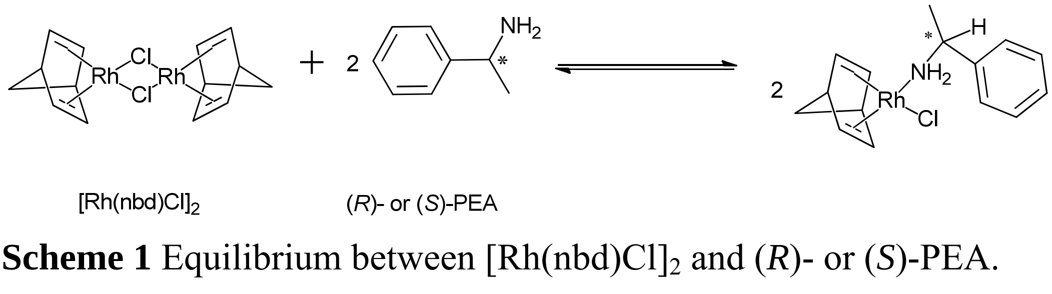
1.2 Introduction

As an example of a novel asymmetric polymerisation, [1] we previously reported helix-sense-selective polymerisation (**HSSP**) [1e,2] producing *static* one-handed helical conjugated polymers from an *achiral* monomer (**DoDHPA**, Chart 1) with two hydroxyl groups, using a chiral catalytic system consisting of a rhodium complex and a chiral amine. [2] To the best of our knowledge, it has so far been possible to synthesise *soluble* chiral *conjugated* polymers whose chiral structures arise solely from the one-handed helical conformation of the conjugated main chains and are *static* and stable *alone* in solution *only* by the **HSSP** method developed in our laboratory. In the **HSSP**, the chiral amine coordinates to the dimeric rhodium complex to yield a chiral monomeric complex which acts as a chiral initiator (Scheme 1).



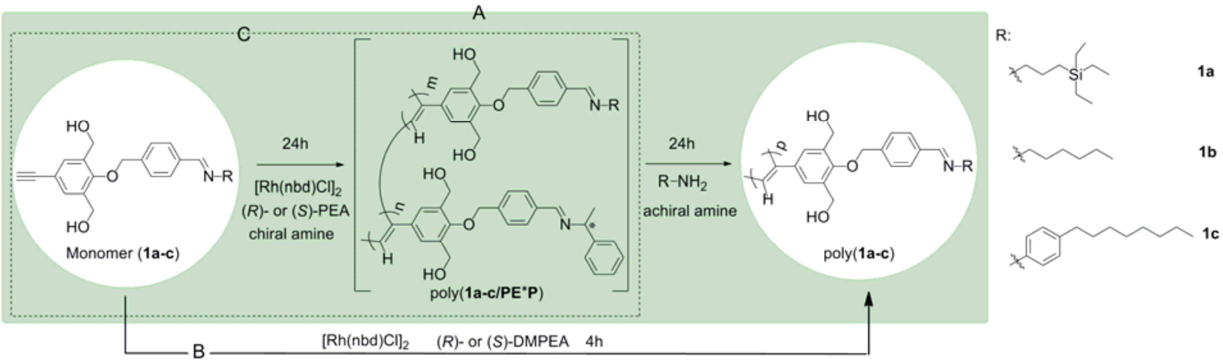
1a PE*P DoDHPA **2a** PP*P

Chart 1 Chemical structures of the monomers used in this study.



Scheme 1 Equilibrium between [Rh(nbd)Cl]$_2$ and (*R*)- or (*S*)-PEA.

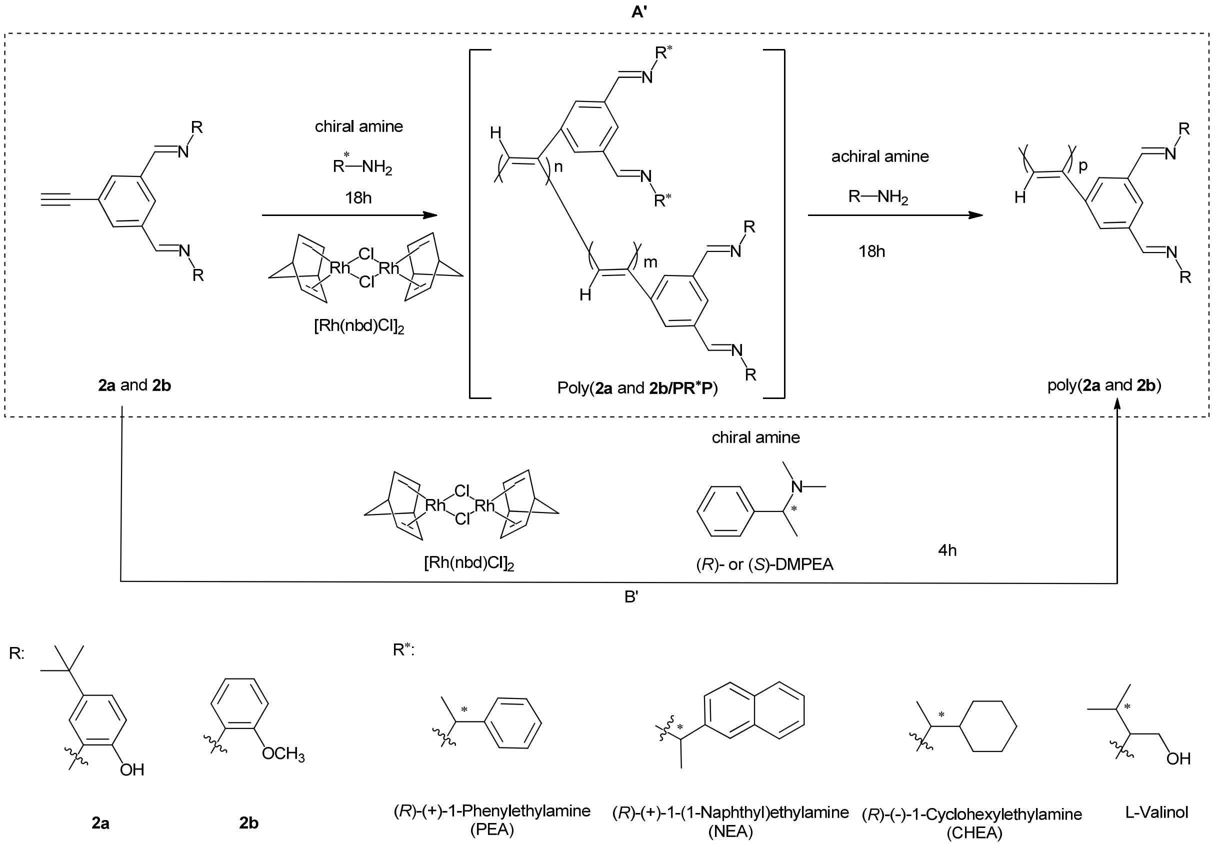
However, suitable monomers were limited, [3] and the efficiency of the chiral induction was not high. [4] It may be possible to achieve a higher optical purity [5] and efficiency [5] in the chiral induction to the main chain, while employing the same experimental procedure as the **HSSP** in the following manner. The asymmetric polymerisation could use a chiral source that is introduced *via* a strong bond into a monomer. Then, if the chiral pendant groups in the resulting polymer can be removed *in situ* easily, while maintaining the one-handed helicity, an improvement over the **HSSP** is likely. As examples of such an easily breakable strong bond, dynamic covalent bonds are promising. Dynamic covalent bonds are strong and they can easily and reversibly form and cleave. [6]



Scheme 2 A: Pseudo helix-sense-selective polymerisation (**PHSSP**) using (*R*)- or (*S*)-phenylethylamine (PEA) as a chiral source without isolation of poly(**1a-c/PE*P**), **B**: Helix-sense-selective polymerisation (**HSSP**) using (*R*)- or (*S*)-*N*, *N*-dimethylphenylethylamine (DMPEA) as a cocatalyst and **C**: *In-situ* asymmetric-induced polymerisation (***in-situ*** **AIP**) using (*R*)- or (*S*)-phenylethylamine (PEA) as a chiral source of monomers (**1a-c**) in THF at room temperature.

Here, we propose a new concept of asymmetric polymerisation where the practical procedure and chemical structures of the final polymers obtained are the same as in the **HSSP**, but the chiral source is not a catalyst but a reagent, because it has temporarily formed covalent bonds with the polymer (Scheme 2

A and Scheme 3 A). Therefore, we named it *pseudo* helix-sense-selective polymerisation (**PHSSP**) (Scheme 2A and Scheme 3 A). In this communication, the new **PHSSP** concept and its practical results for a wider range of substituted acetylenes having *dynamic covalent bonds* are reported for the first time. It provides a new asymmetric polymerisation method to obtain one-handed helical polymers from *achiral* monomers, without the coexistence of any other chiral moieties with a higher optical purity[5] and efficiency[5] of the chiral induction than the **HSSP**.



Scheme 3 **A'**: Pseudo helix-sense-selective polymerisation (**PHSSP**) by using various chiral amines as chiral sources, **B'**: Helix-sense-selective polymerisation (**HSSP**) by using (*R*)- or (*S*)-DMPEA as a cocatalyst of monomers **2a** and **2b** in this study.

1.3 Experimental

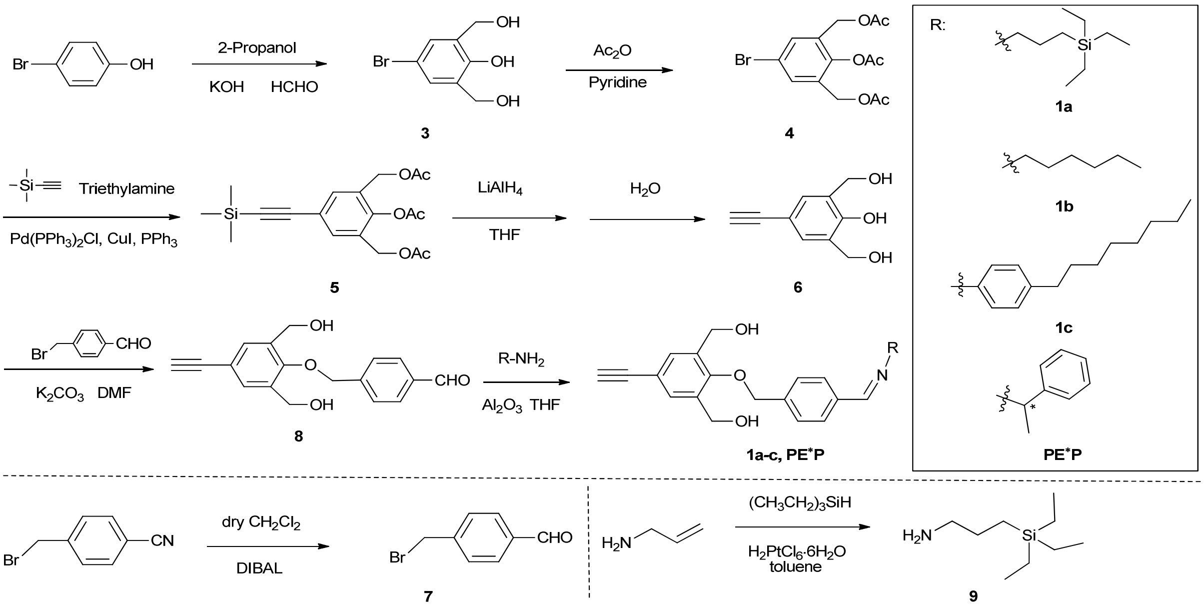
1.3.1 Materials

All the solvents used for monomer synthesis and polymerisation were distilled as usual. The polymerisation initiator, $[Rh(nbd)Cl]_2$ (nbd=2,5 norbornadiene), purchased from Aldrich Chemical Co., Inc., was used as received. The silicon-containing reagent, trimethylsilylacetylene was purchased from Shinetsu Chemical Co., Ltd., and used as received.

1.3.2 Measurements

Average molecular weight (*Mw*) was estimated by gel permeation chromatography (tetrahydrofuran as an eluent, polystyrene calibration) using JASCO Liquid Chromatography instruments with PU 2080, DG 2080 53, CO 2060, UV 2070, CD 2095, and two polystyrene gel columns (Shodex KF 807L). NMR spectra were recorded on a JEOL GSX 270 at 400 MHz for ^1H. IR spectra were recorded on a JASCO FTIR 4200 spectrometer. CD spectra were measured with a JASCO J 720 spectropolarimeter.

1.3.3 Synthetic procedures of the monomers 1a-c and PE*P (Scheme 4)



Scheme 4. Synthetic route to the monomers **1a-c** and **PE*P**.

1.3.3.1 Synthesis of 4-bromo-2, 6-bis(hydroxymethyl)-1-phenol (**3**)

According to the literature procedure, **3** was prepared as a white solid. Yield: 80.9% (136g). ^{1}H NMR (DMSO-d_6): $\delta = 8.76$ (s, 1H, PhO*H*), 7.29 (s, 2H, Ph*H*), 5.31 (t, 2H, $J = 5$Hz, CH_2OH), 4.51 (d, 4H, $J = 5$Hz, CH_2OH).

1.3.3.2 Synthesis of 2,6-bis(acetoxymethyl)-4-bromo-1-phenyl acetate (**4**)

To a pyridine solution (100mL) of **3** (20g, 85.8mmol), acetic anhydride (48.6mL, 515mmol) was added dropwise at 0°C. The solution was stirred for 1.5h at room temperature and then ethyl acetate (200mL) was added to the mixture. Then the mixture was washed with saturated aqueous solution of $CuSO_4 \cdot 5H_2O$ to remove pyridine. The organic layer was dried over anhydrous $MgSO_4$. After concentration, the crude product was purified by silica-gel column chromatography to give **4** as a white solid. Yield: 70% (21.5g). Rf = 0.36 (ethyl acetate/hexane = 1/2). ^{1}H NMR (DMSO-d_6): $\delta = 7.68$ (s, 2H, Ph*H*), 4.97 (s, 4H, $Ph(CH_2O)_2$, 2.31 (s, 3H, $PhOCOCH_3$), 2.03 (s, 6H, $Ph(CH_2OCOCH_3)_2$).

1.3.3.3 Synthesis of 2, 6-Bis(acetoxymethyl)-4-(trimethylsilylethynyl)-1-phenyl acetate (**5**)

A mixture of **4** (10.76g, 30mmol), triphenylphosphine (550mg, 2.1mmol), copper (I) iodide (690mg, 3.6mmol), bis(triphenylphosphine)palladium(II)dichloride (420mg, 0.6mmol) and trimethylsilylacetylene (6.2mL, 45mmol) in triethylamine (120mL) was refluxed for 24h. After the mixture was filtered, the solvent was removed by evaporation. The crude product was purified by silica-gel column chromatography to give **5** as a brown liquid. Yield: 87.7% (9.9g). Rf = 0.32 (ethyl acetate/hexane = 1/3). ^{1}H NMR ($CDCl_3$, TMS): $\delta = 7.50$ (s, 2H, Ph*H*), 4.98 (s, 4H, $Ph(CH_2OAc)_2$), 2.32 (s, 3H, $PhOCOCH_3$), 2.06 (s, 6H, $Ph(CH_2OCOCH_3)_2$), 0.22 (s, 9H, $Si(CH_3)_3$).

1.3.3.4 Synthesis of 2, 6-bis(hydroxymethyl)-4-ethynylphenol (**6**) [S2]

To a mixture of lithium aluminum hydride (2.0g, 52.4mmol) and tetrahydrofuran (87.0mL), a tetrahydrofuran solution (15.0mL) of **5** (9.87g, 26.2mmol) was added dropwise at 0°C. After the mixture was stirred for 2h at room temperature, deionized water (72.0mL) was added dropwise to the reaction mixture at 0°C. The mixture was stirred for 12h at room temperature. The reaction mixture was treated with 2N HCl aq. to precipitate aluminum salts. After the mixture was filtered, tetrahydrofuran was removed by evaporation. The product was dissolved in ethyl acetate and the solution was washed with water. The organic layer was dried over anhydrous $MgSO_4$ and concentrated. The crude product was purified by silica-gel column chromatography to give **6** as a white solid. Yield: 81.4% (3.8g). Rf = 0.27 (ethyl acetate/hexane = 1/1). ^{1}H NMR (DMSO-d_6): δ= 8.98 (s, 1H, PhO*H*), 7.27 (s, 2H, Ph*H*), 5.29 (s, 2H, Ph(CH_2OH)$_2$), 4.52 (s, 4H, Ph(CH_2OH)$_2$), 3.91 (s, 1H, *H*C≡C).

1.3.3.5 Synthesis of 4-bromomethylbenzaldehyde (**7**) [S3]

4-Cyanobenzyl bromide (14g, 71.4mmol) was dissolved in dry CH_2Cl_2 (260mL) and the solution was stirred at 0℃. 1.0M diisobutylaluminium hydride hexane solution (DIBAL, 70mL, 70mmol) was added dropwise to the solution at 0℃. The solution was stirred for 15min and then DIBAL solution (35mL) was added dropwise again. The mixture was stirred for 15min at 0℃ and then 30min at room temperature. The reaction mixture was treated with 50% H_2SO_4 (150mL) aq. to precipitate the aluminium salt. After the mixture was filtered, the solution was washed with water and extracted with CH_2Cl_2. The organic layer was dried over $MgSO_4$ and concentrated to give aim product **7** as a white solid. Yield: 56.3% (8.0g). ^{1}H NMR ($CDCl_3$, TMS): δ= 10.0 (s, 1H, PhC*H*O), 7.85 (d, 2H, J=8Hz, BrCH$_2$Ph*H*), 7.54 (d, 2H, J=8Hz, *H*PhCHO), 4.50 (s, 2H, BrC*H*$_2$Ph).

1.3.3.6 Synthesis of 4-(4'-formylbenzyloxy)-3,5-bis(hydroxymethyl)phenylacetylene (**8**)

A mixture of **6** (3.79g, 21.3mmol), **7** (4.23g, 21.3mmol) and K_2CO_3 (8.8g, 63.9mmol) in DMF (107mL) was stirred for 50h at 70℃. After the mixture was filtered, the solvent was removed. The residue was washed with water and extracted with ethyl acetate. The organic layer was dried over $MgSO_4$ and concentrated. The crude product was purified by silica-gel column chromatography to give aim product **8**. Rf = 0.7 (chloroform/methanol = 95/5). ^1H NMR ($CDCl_3$, TMS): δ= 10.0 (s, 1H, PhC*H*O), 7.94 (d , 2H, J=8Hz, *H*PhCHO), 7.63 (d , 2H, J=8Hz, OCH_2PhH), 7.54 (s, 2H, HC≡CPh*H*), 5.08 (s, 2H, $PhOCH_2Ph$), 4.69 (d, 4H, J=6Hz, $Ph(CH_2OH)_2$), 3.07 (s, 1H, *H*C≡C), 1.74 (t, 2H, J=6Hz, $Ph(CH_2OH)_2$).

1.3.3.7 Synthesis of 3-(triethylsilyl)propylamine (**9**)

$H_2PtCl_6·6H_2O$ (26mg, 0.05mmol), toluene (15mL) was added to the flask and stirred at 80℃ until $H_2PtCl_6·6H_2O$ was dissolved completely. Triethylsilane (8mL, 50.2mmol) and allylamine (4.2mL, 55.2mmol) was added dropwise to the solution at 40℃ separately and stirred at 85℃ for 120h. The crude product was purified by vacuum distillation at 54℃ (250Pa) to give aim product **9** as a colorless liquid. Yield: 67.7% (5.89g). ^1H NMR ($CDCl_3$, TMS): δ= 2.65 (t, 2H, J=7Hz, NH_2CH_2), 1.42 (m, 2H, $NH_2CH_2CH_2CH_2$), 1.27(s, 2H, NH_2), 0.92 (t, 9H, J=8Hz, $Si(CH_2CH_3)_3$), 0.59 (t, 2H, J=8Hz, $NCH_2CH_2CH_2Si$), 0.49 (q, 6H, J=8Hz, $Si(CH_2CH_3)_3$).

1.3.3.8 Synthesis of 4-[4’-{(3-triethylsilyl)propyliminomethyl}benzyloxy]-3,5-bis(hydroxymethyl)phenylacetylene **(1a)**

A mixture of **8** (500mg, 1.68mmol), **9** (586mg, 3.36mmol) and Al_2O_3 (10g) in dry THF (16mL) was stirred for 3 days at room temperature. After the mixture was filtered, the solvent was removed to yield a white solid. The crude product was purified by recrystallization in $CHCl_3$/hexane to give monomer **1a** as a white solid. Yield: 56.5% (428mg). ^1H NMR ($CDCl_3$, TMS): δ= 8.21 (s, 1H, PhC*H*=N), 7.76 (d, 2H, J=8Hz, NCHPh*H*), 7.50 (s, 2H, C≡CPh*H*), 7.45 (d, 2H, J=8Hz, PhOCH$_2$Ph*H*), 4.99 (s, 2H, PhOC*H*$_2$Ph), 4.65 (d, 4H, J=6Hz, Ph(C*H*$_2$OH)$_2$), 3.59 (t, 2H, J=7Hz, NC*H*$_2$CH$_2$), 3.04 (s, 1H, *H*C≡C), 1.90 (t, 2H, J=6Hz, Ph(CH$_2$O*H*)$_2$), 1.68 (m, 2H, NCH$_2$C*H*$_2$CH$_2$), 0.91 (t, 9H, J=8Hz, Si(CH$_2$C*H*$_3$)$_3$), 0.53 (t, 2H, J=8Hz, NCH$_2$CH$_2$C*H*$_2$Si), 0.49 (q, 6H, J=8Hz, Si(C*H*$_2$CH$_3$)$_3$). IR (cm^{-1}, KBr): 3322 (OH), 3233 (HC≡C), 1643 (C=N). Anal. Cacld for $C_{27}H_{37}O_3NSi$: C, 71.80; H, 8.26; N, 3.10. Found: C, 71.74; H, 8.17; N, 3.10.

1.3.3.9 Synthesis of 4-[4'-(hexyliminomethyl)benzyloxy]-3,5-bis(hydroxymethyl)phenylacetylene (**1b**)

A mixture of **8** (200g, 0.67mmol), hexylamine (177μL, 1.35mmol) and Al_2O_3 (5.0g) in dry THF (7mL) was stirred for 3 days at room temperature. After the mixture was filtered, the solvent was removed to yield a white solid. The crude product was purified by recrystallization in $CHCl_3$/hexane to give monomer **1b** as a white solid. Yield: 58% (148mg). ^{1}H NMR (CDCl$_3$, TMS): δ= 8.28 (s, 1H, PhC*H*=N), 7.74 (d, 2H, J=8Hz, NCHPh*H*CH$_2$), 7.52 (s, 2H, HC≡CPh*H*), 7.44 (d, 2H, J=8Hz, OCH$_2$Ph*H*), 5.00 (s, 2H, PhOC*H*$_2$Ph), 4.66 (br, 4H, Ph(C*H*$_2$OH)$_2$), 3.59 (t, 2H, J=7Hz, NH$_2$C*H*$_2$CH$_2$), 3.05 (s, 1H, *H*C≡CPh), 2.00 (br, 2H, Ph(CH$_2$O*H*)$_2$), 1.70 (m, 2H, NCH$_2$C*H*$_2$CH$_2$), 1.33 (m, 6H, CH$_2$(C*H*$_2$)$_3$CH$_3$), 0.89 (t, 3H, J=7Hz, CH$_2$C*H*$_3$). IR (cm^{-1}, KBr): 3332 (OH), 3243 (HC≡C), 1637 (C=N).

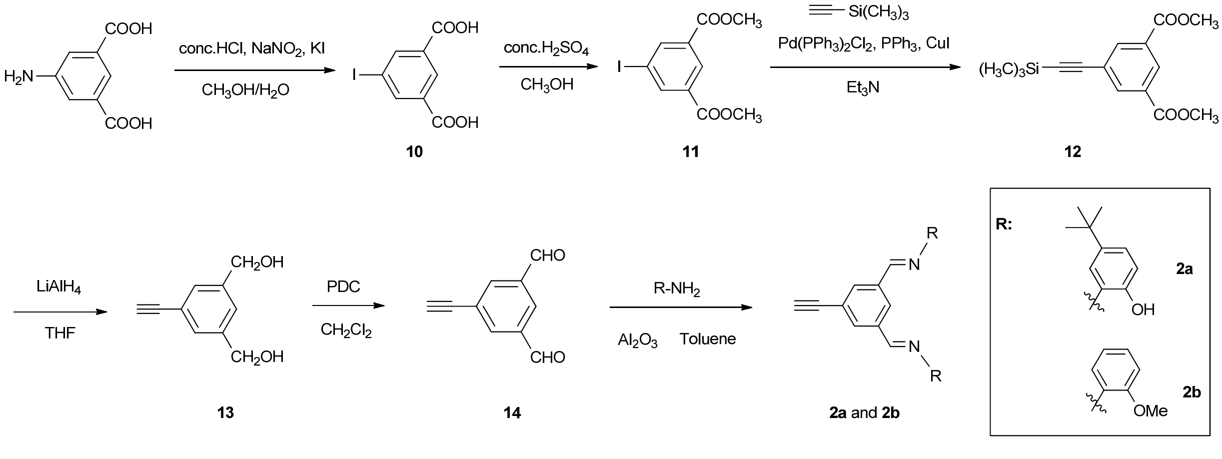
1.3.3.10 Synthesis of 4-[4'-(4''-n-octylphenyliminomethyl)benzyloxy]-3,5-bis(hydroxymethyl)phenylacetylene (**1c**)

A mixture of **8** (500mg, 1.69mmol), 4-n-octylaniline (520mg, 2.53mmol) and Al_2O_3 (10g) in dry THF (17mL) was stirred for 3 days at room temperature. After the mixture was filtered, the solvent was removed to yield a white solid. The crude product was purified by recrystallization in $CHCl_3$/hexane to give monomer **1c** as a white solid. Yield: 47% (383mg). ^{1}H NMR (CDCl$_3$, TMS): δ= 8.50 (s, 1H, PhC*H*=N), 7.92 (d, 2H, J=8Hz, N=CHPh*H*), 7.53 (s, 2H, HC≡CPh*H*), 7.51 (d, 2H, J=8Hz, OCH$_2$Ph*H*), 7.20 (d, 2H, N-Ph*H*CH$_2$ CH$_2$), 7.16 (d, 2H, CHN-Ph*H*CH$_2$), 5.05 (s, 2H, PhOC*H*$_2$Ph), 4.69 (d, 4H, J=6Hz, Ph(C*H*$_2$OH)$_2$), 3.06 (s, 1H, *H*C≡CPh), 2.63 (t, 2H, J=8Hz, PhC*H*$_2$CH$_2$), 1.90 (t, 2H, J=6Hz, Ph(CH$_2$O*H*)$_2$), 1.63 (m, 2H, PhCH$_2$C*H*$_2$CH$_2$), 1.27 (br, 10H, CH$_2$(C*H*$_2$)$_5$CH$_3$), 0.88 (t, 3H, J=7Hz, CH$_2$C*H*$_3$). IR (cm^{-1}, KBr): 3355 (OH), 3282 (HC≡C), 1625 (C=N). Anal. Cacld for $C_{32}H_{37}O_3N$: C, 79.47; H, 7.71; N, 2.90. Found: C, 79.36; H, 7.68; N, 2.94.

1.3.3.11 Synthesis of 4-[4'-(phenylethyliminomethyl)benzyloxy]-3,5-bis(hydroxymethyl)phenylacetylene (**PE*P**)

A mixture of **8** (500g, 1.68mmol), (*R*)-phenylethylamine (432.7μl, 3.37mmol) and Al_2O_3 (10g) in dry THF (16mL) was stirred for 3 days at room temperature. After the mixture was filtered, the solvent was removed to yield a white solid. The crude product was purified by recrystallization in CHCl$_3$/Hexane to give monomer **PEP** as a white solid. Yield: 53% (210mg). ^{1}H NMR (CDCl$_3$, TMS): δ= 8.36 (s, 1H, PhC*H*=N), 7.77 (d, 2H, J=8Hz, Ph*H*CH=N), 7.48 (s, 2H, HC≡CPh*H*), 7.42 (d, 2H, J=8Hz, OCH$_2$Ph*H*), 7.40 (d, 2H, J=7Hz, N-CHPh*H*), 7.32 (t, 2H, J=7Hz, N-CHPh*H*), 7.22 (t, 1H, J=7Hz, N-CHPh*H*), 4.96 (s, 2H, PhOC*H*$_2$Ph), 4.62 (br, 4H, Ph(C*H*$_2$OH)$_2$), 4.53 (q, 1H, J=7Hz, NC*H*Ph), 3.03 (s, 1H, *H*C≡CPh), 2.13 (br, 2H, Ph(CH$_2$O*H*)$_2$), 1.57 (d, 3H, J=7Hz, CHC*H*$_3$).

1.3.4 Synthetic procedures of the monomers 2a and 2b (Scheme 5)



Scheme 5. Synthetic route to the monomers **2a** and **2b**.

1.3.4.1 Synthesis of 5-iodoisophthalic acid (**10**)

5-Aminoisophthalic acid (30.0g, 161.5mmol) and the cold $NaNO_2$ aqueous solution (28.0g/43.0mL, 168.6mmol) were added to a mixture of ice (50g), methanol (200mL), concentrated hydrochloric acid (40mL, 1.35mol) with stirring. Then the mixture was added to a solution of KI aqueous solution. After stirring for 20min at room temperature, the Na_2SO_3 was added to the mixture and stirred for another 20min. The mixture was filtered, the solvent was removed and the crude product was purified by *vacuo* drying to give aim product **10** as a yellow solid. Yield: 67% (31.6g). ^{13}C NMR (DMSO-d_6, TMS): δ= 165.0 (*C*OOH), 141.3 (Ph*C*), 133.0 (Ph*C*), 129.0 (Ph*C*), 94.7 (*C*-I). IR (cm^{-1}, KBr): 3300~2500 (OH), 1716 (C=O).

1.3.4.2 Synthesis of methyl 5-iodoisophthalate (**11**) [S4]

A mixture of **10** (31.6cg, 108mmol), methanol (900mL, 37.3mol) and concentrated sulfuric acid (31.6mL, 592mmol) was stirred for 24h at 65℃. After the mixture was filtered, the solvent was removed. The residue was washed with water and extracted with ethyl acetate. The organic layer was dried over $MgSO_4$ and concentrated. The crude product was purified by silica-gel column chromatography to give aim product **11** as a white solid. Yield: 83.8% (29.0g). Rf = 0.58 (ethyl acetate/hexane = 1/4). ^1H NMR ($CDCl_3$, TMS): δ= 8.63 (t, 1H, J=2Hz, Ph*H*), 8.55 (d, 2H, J=2Hz, Ph*H*), 3.95 (s, 6H, OCH_3).

1.3.4.3 Synthesis of methyl 5-(trimethylsilylethynyl)isophthalate (**12**) [S5]

A mixture of **11** (7.88g, 24.6mmol), triphenylphosphine (41.9mg, 159μmol), copper (I) iodide (31mg, 163μmol), bis(triphenylphosphine)palladium(II)dichloride (43.3mg, 61.7μmol) and trimethylsilylacetylene (6.09mL, 42.3mmol) in triethylamine (300mL) was refluxed for 24 h. After the mixture was filtered, the solvent was removed by evaporation. The crude product was purified by silica-gel column chromatography to give **12** as a white solid. Yield: 99.6% (6.75g). Rf = 0.4

(ethyl acetate/hexane = 1/10). ^{1}H NMR ($\mathrm{CDCl_3}$, TMS): δ= 8.60 (t, 1H, J=2Hz, Ph*H*), 8.29 (d, 2H, J=2Hz, Ph*H*), 3.95 (s, 6H, $\mathrm{OC}H_3$), 0.26 (s, 9H, $\mathrm{Si(C}H_3)_3$).

1.3.4.4 Synthesis of 3,5-bis(hydroxylmethyl)phenylacetylene (**13**)

To a mixture of lithium aluminum hydride (0.711 g, 18.7mmol) and tetrahydrofuran (40mL), a tetrahydrofuran solution (8mL) of **12** (3.84 g, 13.9mmol) was added dropwise at 0°C. After the mixture was stirred for 7h at room temperature, deionized water (1mL) was added dropwise to the reaction mixture at 0°C. The mixture was stirred for 8h at room temperature. The reaction mixture was treated with 2N HCl aq. to precipitate aluminum salts. After the mixture was filtered, tetrahydrofuran was removed by evaporation. The product was dissolved in ethyl acetate and the solution was washed with water. The organic layer was dried over anhydrous $\mathrm{MgSO_4}$ and concentrated. The crude product was purified by silica-gel column chromatography to give **13** as a white solid. Yield: 80.5% (1.82g). Rf = 0.13 (ethyl acetate/hexane = 1/1). ^{1}H NMR ($\mathrm{CDCl_3}$, TMS): δ= 7.42 (s, 2H, Ph*H*), 7.37 (s, 1H, Ph*H*), 4.69 (d, 4H, J=6Hz, $\mathrm{Ph(C}H_2\mathrm{OH)_2}$), 3.08 (s, 1H, *H*C≡C), 1.73 (t, 2H, J=6Hz, $\mathrm{Ph(CH_2O}H)_2$).

1.3.4.5 Synthesis of 3,5-bis(formyl)phenylacetylene (**14**)

To a mixture of pyridinium dichromate (PDC) (8.7g, 23.1mmol) and $\mathrm{CH_2Cl_2}$ (100mL), a $\mathrm{CH_2Cl_2}$ solution (100mL) of **13** (0.75 g, 4.62mmol) was added dropwise at 0°C. After the mixture was stirred for 48h at room temperature, the mixture was filtered, $\mathrm{CH_2Cl_2}$ was removed by evaporation. The crude product was purified by silica-gel column chromatography to give **14** as a yellow solid. Yield: 45.2% (0.33g). Rf = 0.33 (ethyl acetate/hexane = 1/4). ^{1}H NMR ($\mathrm{CDCl_3}$, TMS): δ= 10.0 (s, 2H, C*HO*), 8.34 (t, 1H, J=2Hz, Ph*H*), 8.23 (d, 2H, J=2Hz, Ph*H*), 3.27 (s, 1H, *H*C≡C).

1.3.4.6 Synthesis of 3,5-bis(*N*-2-hydroxyl-5’-*tert*-butylphenyliminomethyl)phenylacetylene (**2a**)

A mixture of **14** (201mg, 1.27mmol), 2-amino-4-*tert*-butylphenol (467mg, 2.83mmol) and $\mathrm{Al_2O_3}$ (1g) in dry toluene (20mL) was stirred for 18h at room temperature. After the mixture was filtered, the solvent was removed to yield a yellow solid. The crude product was purified by Al_2O_3 column chromatography to give **2a** as a yellow solid. Yield: 53.8% (310mg). Rf = 0.52 (ethyl acetate/hexane = 1/6).^{1}H NMR ($CDCl_3$, TMS): δ= 8.76 (s, 2H, N=C*H*), 8.40 (br, 1H, HC≡CPh*H*), 8.17 (d, 2H, J=2Hz, HC≡CPh*H*), 7.34 (d, 2H, J=2Hz, C=NPh*H*), 7.30-7.28 (d, d, 2H, J=8Hz, J=2Hz, C=NPh*H*), 7.03 (s, 2H, PhO*H*), 6.97 (d, 2H, J=8Hz, C=NPh*H*), 3.33 (s, 1H, C≡C*H*), 1.35 (s, 18H, ($PhC(CH_3)_3)_2$). IR (cm^{-1}, KBr): 3450 (OH), 3304 (H≡C), 2965 (C-H), 2398 (C≡C), 2000-1800 (Ar-H), 1625 (C=N). Anal. Cacld for $C_{30}H_{32}O_2N_2$: C, 79.61; H, 7.13; N, 6.19. Found: C, 79.36; H, 7.01; N, 6.11.

1.3.4.7 Synthesis of 3,5-bis(*N*-*o*-methoxylphenyliminomethyl)phenylacetylene (**2b**)

A mixture of **14** (123mg, 0.778mmol), *o*-anisidine (200μl, 1.77mmol)) and Al_2O_3 (0.6g) in dry toluene (15mL) was stirred for 18h at room temperature. After the mixture was filtered, the solvent was removed to yield a yellow solid. The crude product was purified by Al_2O_3 column chromatography to give **2b** as a yellow solid. Yield: 45.5% (130mg). Rf = 0.36 (ethyl acetate/hexane = 1/10).^{1}H NMR ($CDCl_3$, TMS): δ= 8.54 (s, 2H, N=C*H*), 8.39 (br, 1H, HC≡CPh*H*), 8.18 (d, 2H, J=2Hz, HC≡CPh*H*), 6.96-7.04 (m, 6H, C=NPh*H*), 3.90 (s, 6H, ($PhOCH_3)_2$), 3.15 (s, 1H, C≡C*H*. IR (cm^{-1}, KBr): 3450 (OH), 3228 (H≡C), 2935 (C-H), 2357 (C≡C), 1624 (C=N), 1246 (C-O-C).

1.3.5 Polymerisation of all the monomers

1.3.5.1 Pseudo helix-sense-selective polymerisation (**PHSSP**) (Schemes 2 and 3, routes **A** and **A'**).

A typical procedure for **1a** was as follows: A solution of $[Rh(nbd)Cl]_2$ (0.8mg, 1.76μmol) and (*S*)- or (*R*)-phenylethylamine (PEA) (28.21μl, 0.22mmol) in dry THF (0.44mL) was added to a dry THF (0.44mL) solution of **1a** (40mg, 88μmol). The reaction solution was stirred at room temperature for 24h. Then the achiral amine **9** (136μl, 0.88mmol) was added to the solution, and continued to stir for 24h. The crude polymer was purified by reprecipitation of the THF solution into a large amount of methanol and the formed solid was dried *in vacuo* to give a red solid.

Other pseudo helix-sense-selective polymerisation (**PHSSP**) of the monomers **1a-c**, **2a** and **2b** were carried out similarly (Schemes 2 and 3, routes **A** and **A'**).

Poly(**1a**) 100%: ^{1}H NMR (DMSO-d_6/CCl$_4$=1/5): δ= 8.11 (br, 1H, PhCH=N), 3.50 (br, 2H, NCH_2CH$_2$), 1.60 (br, 2H, NCH$_2$CH_2CH$_2$), 0.84 (br, 9H, Si(CH$_2$CH_3)$_3$), 0.44 (br, 2H, NCH$_2$CH$_2$CH_2Si), 0.44 (br, 6H, Si(CH_2CH$_3$)$_3$) (Fig. S5, c)). IR (cm^{-1}, KBr): 3375 (OH), 1645 (C=N).

Poly(**1a**) 96%: ^{1}H NMR (DMSO-d_6/CCl$_4$=1/5): δ= 8.11 (br, 1H, PhCH=N), 7.54-6.88 (br, 6H, PhH), 5.89 (br, cis proton in the main chain), 4.73 (br, 2H, PhOCH_2Ph), 4.31 (br, 4H, Ph(CH_2OH)$_2$), 3.49 (br, 2H, NCH_2CH$_2$), 1.61 (br, 2H, NCH$_2$CH_2CH$_2$), 1.47 (br, 0.12H, CHCH_3 in poly(PEP)), 0.88 (t, 9H, J=8Hz, Si(CH$_2$CH_3)$_3$), 0.50 (br, 2H, NCH$_2$CH$_2$CH_2Si), 0.46 (q, 6H, J=8Hz, Si(CH_2CH$_3$)$_3$) (Fig. S5, d)). IR (cm^{-1}, KBr): 3336 (OH), 1645 (C=N).

1.3.5.2 Helix-sense-selective polymerisation (**HSSP**) (Schemes 2 and 3, routes **B** and **B'**).

A typical procedure for monomer (**1a**) was as follows: A solution of [Rh(nbd)Cl]$_2$ (0.8mg, 1.76μmol) and (*S*)- or (*R*)-*N*,*N*-dimethylphenylethylamine (DMPEA) (36.3μl, 0.22mmol) in dry THF (0.44mL) was added to a dry THF (0.44mL) solution of **1a** (40mg, 88μmol). The reaction solution was stirred at room temperature for 24h. The crude polymer was purified by reprecipitation of the THF solution into a large amount of methanol and the formed solid was dried *in vacuo* to give a red solid.

Other helix-sense-selective polymerisation (**HSSP**) of the monomers **1a-c**, **2a** and **2b** were carried out similarly (Schemes 2 and 3, routes **B** and **B'**).

Poly(**1a**) 100%: ^{1}H NMR (DMSO-d_6/CCl$_4$=1/5): δ= 8.15 (br, 1H, PhC*H*=N), 7.58-6.92 (br, 6H, Ph*H*), 5.91 (br, cis proton in the main chain), 4.75 (br, 2H, PhOC*H*$_2$Ph), 4.35 (br, 4H, Ph(C*H*$_2$OH)$_2$), 3.53 (br, 2H, NC*H*$_2$CH$_2$), 1.65 (br, 2H, NCH$_2$C*H*$_2$CH$_2$), 0.88 (br, 9H, Si(CH$_2$C*H*$_3$)$_3$), 0.51 (br, 2H, NCH$_2$CH$_2$C*H*$_2$Si), 0.51 (br, 6H, Si(C*H*$_2$CH$_3$)$_3$) (Fig. S5, b)). IR (cm^{-1}, KBr): 3375 (OH), 1645 (C=N).

1.3.5.3 *In-situ* asymmetric induced polymerisation (***in-situ* AIP**) (Scheme 2, route **C**).

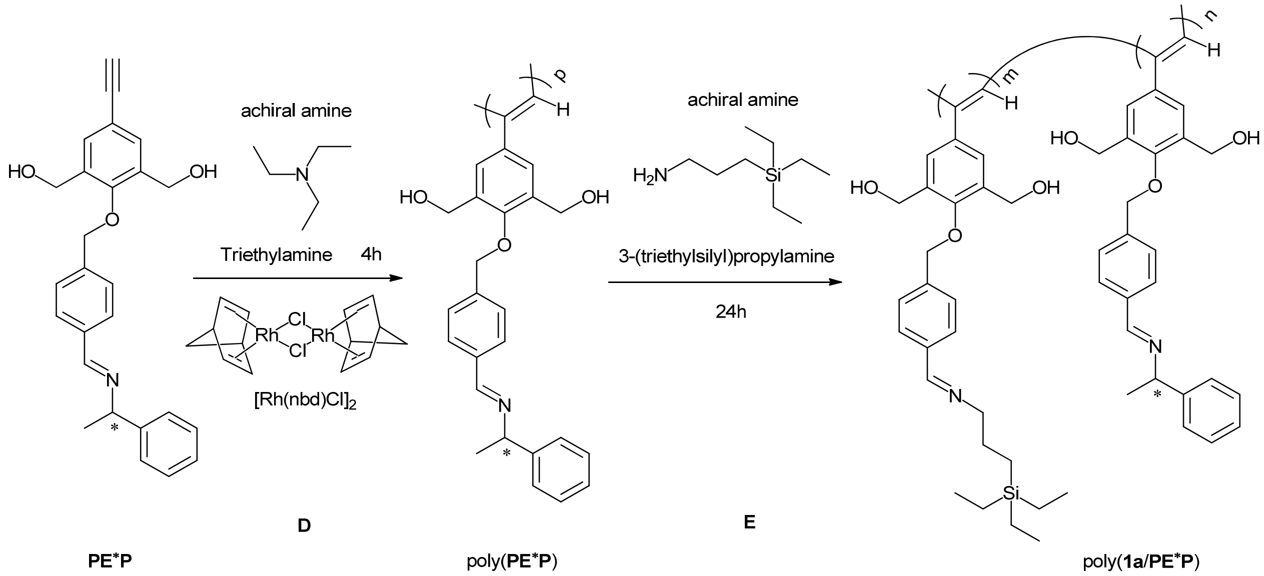
A typical procedure for monomer (**1a**) was as follows: A solution of [Rh(nbd)Cl]$_2$ (0.8mg, 1.76μmol) and (*S*)- or (*R*)-phenylethylamine (PEA) (28.21μl, 0.22mmol) in dry THF (0.44mL) was added to a dry THF (0.44mL) solution of **1a** (40mg, 88μmol). The reaction solution was stirred at room temperature for 24h. The crude polymer was purified by reprecipitation of the THF solution into a large amount of methanol and the formed solid was dried *in vacuo* to give a red solid.

Other *in-situ* asymmetric induced polymerisation (***in-situ* AIP**) of the monomers **1a-c** were carried out similarly (Scheme 2, route **C**).

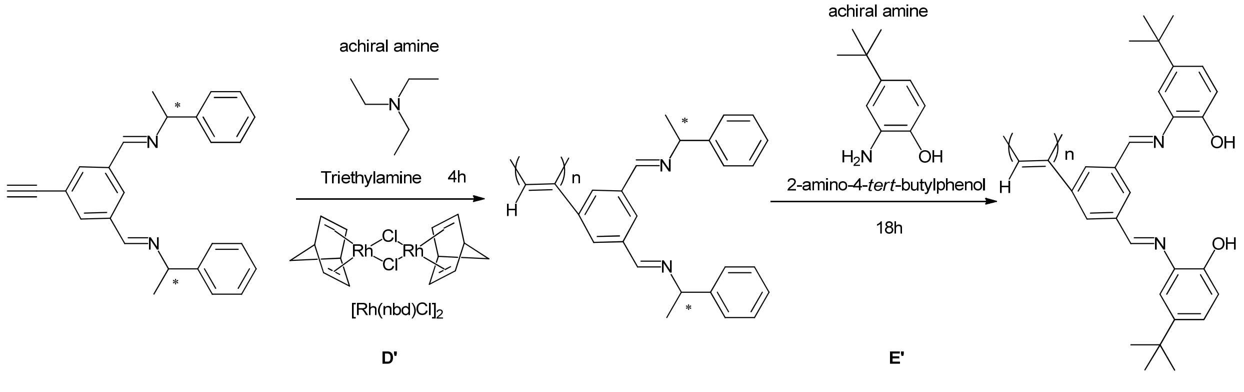
1.3.5.4 Asymmetric-induced polymerisation (**AIP**) (Schemes 6 and 7, routes **D** and **D'**).

A typical procedure for monomer (**PE*P**) was as follows: A solution of [Rh(nbd)Cl]$_2$ (1.15mg, 2.5μmol) and triethylamine (TEA) (43.3μl, 0.31mmol) in dry THF (0.625mL) was added to a dry THF (0.625mL) solution of **PE*P** (50mg, 125μmol). The reaction solution was stirred at room temperature for 4h. The crude polymer was purified by reprecipitation of the THF solution into a large amount of methanol and the formed solid was dried *in vacuo* to give a red solid.

The asymmetric-induced polymerisation (**AIP**) of **PP*P** was carried out similarly (Scheme S5, route **D'**).



Scheme 6 D: Asymmetric-induced polymerisation (**AIP**) of **PE*P**, **E**: Exchange reaction (**ER**) of PEA residues in poly(**PE*P**) with 3-(triethylsilyl)propylamine (For comparison of **PHSSP** of **1a**).



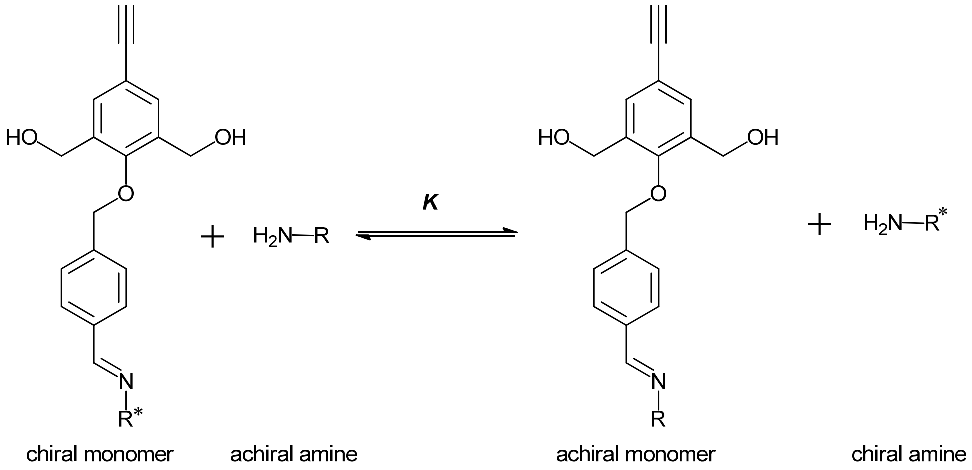
Scheme 7 D': Asymmetric-induced polymerisation (**AIP**) of **PP*P**, **E'**: Exchange reaction (**ER**) of PEA residues in poly(**PP*P**) with 2-amino-*tert*-butylphenol (For comparison of **PHSSP** of **2a**).

1.3.5.5 Exchange reaction (**ER**) (Schemes 6 and 7, routes **E** and **E'**).

A typical procedure for monomer (**PE*P**) was as follows: 3-(Triethylsilyl)propylamine (**9**) (0.1mL) was added to a dry THF (1mL) solution of poly(**PE*P**) (22mg) prepared by AIP. The reaction solution was stirred at room temperature for 24h. The crude polymer was purified by reprecipitation of the THF solution into a large amount of methanol and the formed solid was dried *in vacuo* to give a red solid.

The exchange reaction (**ER**) of **PP*P** was carried out similarly (Scheme 7, route **E'**).

1.3.6 Exchange reaction of a chiral amine residue in a monomer with an achiral amine (Scheme 8)



Scheme 8 Equilibrium constant (*K*) for a model exchange reaction of a chiral amine residue (R*-N=) in a monomer with an achiral amine(R-NH_2) for **PHSSP** of **1**.

A typical procedure for achiral amine 3-(triethylsilyl)propylamine (**9**) was as follows: Achiral amine **9** (43.3mg, 0.25mmol) was added to a $CDCl_3$ (0.25ml) solution of **PE*P** (10mg, 25μmol). The reaction solution was stirred at room temperature for 24h. The result solution was loaded into a Teflon screw-capped NMR tube. The equilibrium constant was then determined from the ration of the integrated ^{1}H NMR signals.Other exchange reactions of a chiral amine residue in a monomer with an achiral amine were carried out similarly (Scheme 8).

1.4 Results and discussion

1.4.1 Monomer design

Two kinds of achiral monomers having one or two achiral amine residues *via* dynamic covalent imine bonds (**1a-c** in Scheme 2 and **2a** and **2b** in and Scheme 3) were designed and synthesized for **PHSSP**. The former (**1a-c**) was expected to be suitable for not only **PHSSP** but also **HSSP** because **1a-c** contain two hydroxyl groups which can make intramolecular hydrogen bonds to maintain one-handed helicity of the resulting polymers, while suitability of the latter (**2a** and **2b**) for **PHSSP** and **HSSP** was not clear although they contain two planer bulky substituents which can maintain one-handed helicity.

1.4.2 Selection of the best chiral amine by preliminary experiments (Table 1)

The chiral amines should have a low basicity to keep low conversion in the exchange reaction at the first step of **PHSSP** (Scheme S3), because they should be removed completely at the second step. We attempted to carry out **PHSSP** (for the detail procedure, see the experimental part)) of **2a** using four chiral amines, PEA, NEA, CHEA, and L-valinol (Scheme 3). As the results, when PEA was used, the content of the chiral units was lowest (Table 1, nos.4, 6-8). It was reasonable because PEA had the lowest basicity (the highest Ka^* value) among them. About chiral induction ability of the chiral amines, since the final polymers in the **PHSSP** procedure showed the biggest ***g*** value assigned to the main chain (Table 1, nos.4, 6-8) in spite of the lowest content of the chiral amine units, we decided to select PEA as the best chiral amine for **PHSSP**.

Table 1 Attempt of pseudo helix-sense-selective polymerisation (**PHSSP**) of various monomers **1a-c** [a], **2a** [b] and **2b** [b] by using (*R*)-(+)-1-phenylethylamine (PEA), (*R*)-(+)-1-(1-naphthyl)ethylamine (NEA), (*R*)-(-)-1-cyclohexylethylamine (CHEA) and L-valinol as a chiral source to select monomers for **PHSSP**

No.	Monomer [c]	Chiral amine [d]	Yield (%)	M_w [e] ($\times10^5$)	Achiral [f] amine unit (mol %)	**g** 310nm [g] ($\times10^{-5}$)	**g** 430nm [g] ($\times10^{-5}$)	Ka^* [h] ($\times10^{-10}$)	Ka [h] ($\times10^{-10}$)	K [i]
1	1a	(R)-PEA	72.2	4.60	100 [j]	-2.70	2.07	9.12	0.15	4.69
2	1b	(R)-PEA	30.6	1.50	96.0	(-0.09) [k]	(0.06) [k]	9.12	0.20	5.01
3	**1c**	(R)-PEA	65.8	0.47	45.0	(-0.34) [k]	(0.20) [k]	9.12	1.10×10^5	0.14
4	**2a**	(R)-PEA	20.8	3.60	97.3	—	(-0.02) [k, l]	9.12	1.44×10^5	—
5	**2b**	(R)-PEA	45.8	4.70	47.9	—	(0.20) [k, l]	9.12	0.43×10^5	—
6	**2a**	(R)-NEA	10.3	0.36	67.7	—	(-7.3×10^{-3}) [k, l]	4.37	1.44×10^5	—
7	**2a**	(R)-CHEA	2.3	0.27	63.9	—	(5×10^{-4}) [k, l]	0.13	1.44×10^5	—
8	**2a**	L-valinol	trace	—	—	—	—	1.50×10^{-3}	1.44×10^5	—

[a] In THF for 48 h, [monomer]=0.1mol/L, [monomer]/$[Rh(nbd)Cl]_2$=50, [chiral amine]/[monomer]=2.5, [achiral amine]/[monomer]=10. [b] In toluene for 36 h, [monomer]=0.1mol/L, [monomer]/$[Rh(nbd)Cl]_2$=100, [chiral amine]/[monomer]=2.5, [achiral amine]/[monomer]=10. [c] For the codes, see Schemes 1 and S3. [d] For the codes, see Scheme S3. [e] By GPC (polystyrene, THF). [f] Determined by ^{1}H-NMR in the final polymers. [g] $\mathbf{g}=([\theta]/3300/\varepsilon)\times0.001$ in $CHCl_3$. [h] See Equations 1, Ka^* for the chiral amines, Ka for the corresponding achiral amines calculated using Advanced Chemistry Development Software V11.02 from SciFinder. [i] See Equations 2 and Scheme S6, equilibrium constant of exchange reaction determined by ^{1}H-NMR. [j] By elemental analysis. [k] The polymers contain the chiral monomer units. [l] Calculated from the peak at 440nm.

1.4.3 Selection of the best achiral amine by preliminary experiments (Table 1)

The achiral amines should have a higher basicity and higher conversion to attain complete removal of the chiral amine units from the intermediate chiral polymers in the re-exchange reaction at the second step of **PHSSP** (Schemes 2 and 3). We attempted to carry out **PHSSP** (for the detail procedure, see the experimental part)) of **1a-c** using PEA (Scheme 2, Table 1, nos.1-3). As results, when **1a** and **1b** were used, the contents of the chiral units were almost zero (Table 1, nos.1 and 2). In particular in the case of **1a**, it had no chiral units, *ie*, an ideal result was achieved (Table 1, no.1). It was reasonable because the corresponding amine of **1a** had the highest basicity (the lowest *Ka* value) among them. Since poly(**1a**) from **1a** showed the biggest ***g*** value assigned to the main chain (Table 1, no.1) in spite of the no content of the chiral amine units, we decided to select the corresponding achiral amine of **1a** (= 3-triethylsilylpropylamine) as the best achiral amine for **PHSSP**. Similarly to the case of **1a**, the corresponding amine of **2a** was selected as the better achiral amine between **2a** and **2b** (Table 1, nos.4 and 5).

1.4.4 Determination of the amount of achiral amines by preliminary experiments (Table 2 and Fig. 1)

To optimise the ratio of the amount of achiral amines to the amine residues in the polymer for **PHSSP**, an exchange reaction (Scheme 7 E') between the corresponding achiral amine to **2a** (= 2-amino-4-*tert*-butylphenol) and the chiral amine(PEA) residues in poly(**PP*P**) as a model reaction of the 2nd step in **PHSSP**. As a result (Table 2 and Fig.1), when the ratio of 2-amino-4-*tert*-butylphenol to the PEA residues in poly(**PP*P**) exceeded 10, the content of the chiral unit in the final polymer became almost constant. Therefore we decided to use 10 for the ratio in **PHSSP**.

Table 2 Exchange reaction of poly(**PP*****P**) using achiral amine 2-Amino-4-*tert*-butylphenol [a]

Run	[2-Amino-4-*tert*-butylphenol] / [poly(**PP*****P**)]	Yield (%)	M_w [b] (x10^5)	Achiral [c] amine unit (mol %)
1	100	42.4	6.19	87.9
2	50	50.0	15.7	87.6
3	10	19.7	7.61	85.9
4	2	45.0	10.0	47.3
5	1	63.6	8.33	7.16
6	0	79.3	5.88	0

[a] In toluene for 18h, [poly(**PP*****P**)]=0.1mol/L. [b] By GPC (polystyrene, THF). [c] In final polymers, by ^{1}H-NMR spectra.

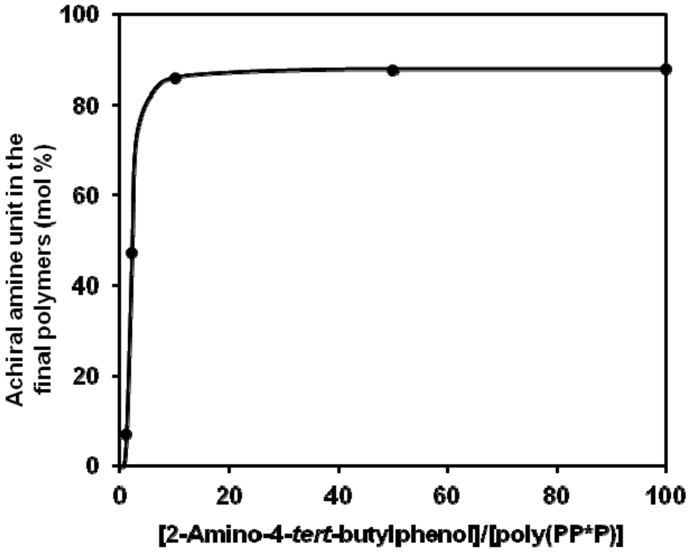


Fig. 1 Plots of the achiral amine units in the final polymers *vs* [2-amino-4-*tert*-butylphenol]/[PEA units in poly(**PP*P**)] in **ER** to optimise the condition in **PHSSP** of **2a** (Scheme 7 E' and Table 2).

1.4.5 Higher optical purity [5] and efficiency [5] in the chiral induction

In **PHSSP** (Scheme 2A) the first step involves a simultaneous exchange reaction and asymmetric-induced *co*polymerisation (**AIP**) of the original achiral monomer with the resulting chiral monomer (***in-situ*** **AIP**, Scheme 2C). The second step is the re-exchange reaction of the chiral amine residues of the intermediate polymer with the corresponding achiral amine to give the final polymer, purely derived from the starting monomers. The requirements for the compounds in **PHSSP** are i) a small amount of the chiral source (chiral amine) is able to induce main-chain chirality in high optical purity [5] and efficiency [5] in the first step and ii) a small amount of the achiral amine can re-exchange completely, while maintaining the one-handed helicity in the second step.

To realise **PHSSP**, we selected compounds, *i.e.,* achiral amines, chiral amines, and achiral monomers which satisfy the above requirements. We designed and synthesised two types of new achiral monomers having an achiral amine residue *via* imine groups of dynamic covalent bonds (**1a-c** in Scheme 2 and **2a** and **2b** in Chart 1 and Scheme 3). After optimizing the compounds and conditions for **PHSSP**, we carried out a practical **PHSSP** of **1a** in the presence of a catalytic amount of (*S*)- or (*R*)-phenylethylamine (**PEA**) using $[Rh(NBD)Cl]_2$ (NBD = norbornadiene) as an initiator (Scheme 2A). After *in-situ* treatment of the intermediate poly (**1a**/**PE*P**) with the corresponding achiral amine, 3-(triethylsilyl)propylamine, we successfully obtained one-handed helical polymers which had *no* chiral monomer units, as confirmed by NMR or EA (See Fig.S5), and showed CD peaks that could be assigned to the main chains (Fig.2 (a), Table 3, nos.1-3 and Table 4, nos. 1 and 2). The formation of the intermediate, poly (**1a**/**PE*P**) was confirmed by its isolation in ***in-situ*** **AIP** (Scheme 2C) separately carried out (Table 3, no.6). Therefore, **PHSSP** has been achieved for the first time and its mechanism was confirmed. Compound **2a** was also thought to be suitable for **PHSSP** (Table 3, no.7). [7] Therefore, a wide range of monomer structures was found to be suitable for **PHSSP**.

The **PHSSP** of **1a** produced a one-handed helical polymer without any other chiral moieties under conditions where such a chiral polymer was not obtained in **HSSP** (Table 3, nos.2 and 5). Furthermore, the CD intensity values (*g* values) of the polymers prepared by **PHSSP** were more than 21 times higher than those made by **HSSP** under the same conditions (Fig.2 (a), Table 3, nos.1 and 4 and

Fig. 3).[8] In addition, **PHSSP** has been achieved while using only a small amount of the chiral source (5 mol % of the monomer) (Table 3, no.3). To obtain polymers having the same *g* value in **PHSSP** (Table 3, no.3), 50 times amounts of the chiral source was necessary in **HSSP** (Table 3, no.4).[9] Under conditions where a one-handed helical polymer was not produced in **HSSP** of **2a**, **PHSSP** of **2a** gave a one-handed helical polymer (Fig.2(b), Table 3, nos.7 and 9). In summary, chiral polymers showing a stronger CD signal were obtained using a smaller amount of the chiral source in **PHSSP** than in **HSSP**. In other words, the same chiral source in **PHSSP** was found to function more effectively than in **HSSP** under the same conditions. Since their practical procedures were almost the same, **PHSSP** is the best asymmetric polymerisation method to obtain one-handed helical poly(substituted acetylene)s.[11] We found that different types of monomers, **1a** having two hydroxyl groups and **2a** having two planar bulky substituents were suitable for **PHSSP**. In addition, many kinds of substituents can be introduced by exchange reactions at the imino groups in the monomers and polymers. Therefore, we can expect to obtain many kinds of such chiral polymers. Although this report focused on **PHSSP** of substituted acetylenes, other monomers having a different polymerisable group can be applied to **PHSSP**. As a result, we expect an extensive and rapid development of the method.

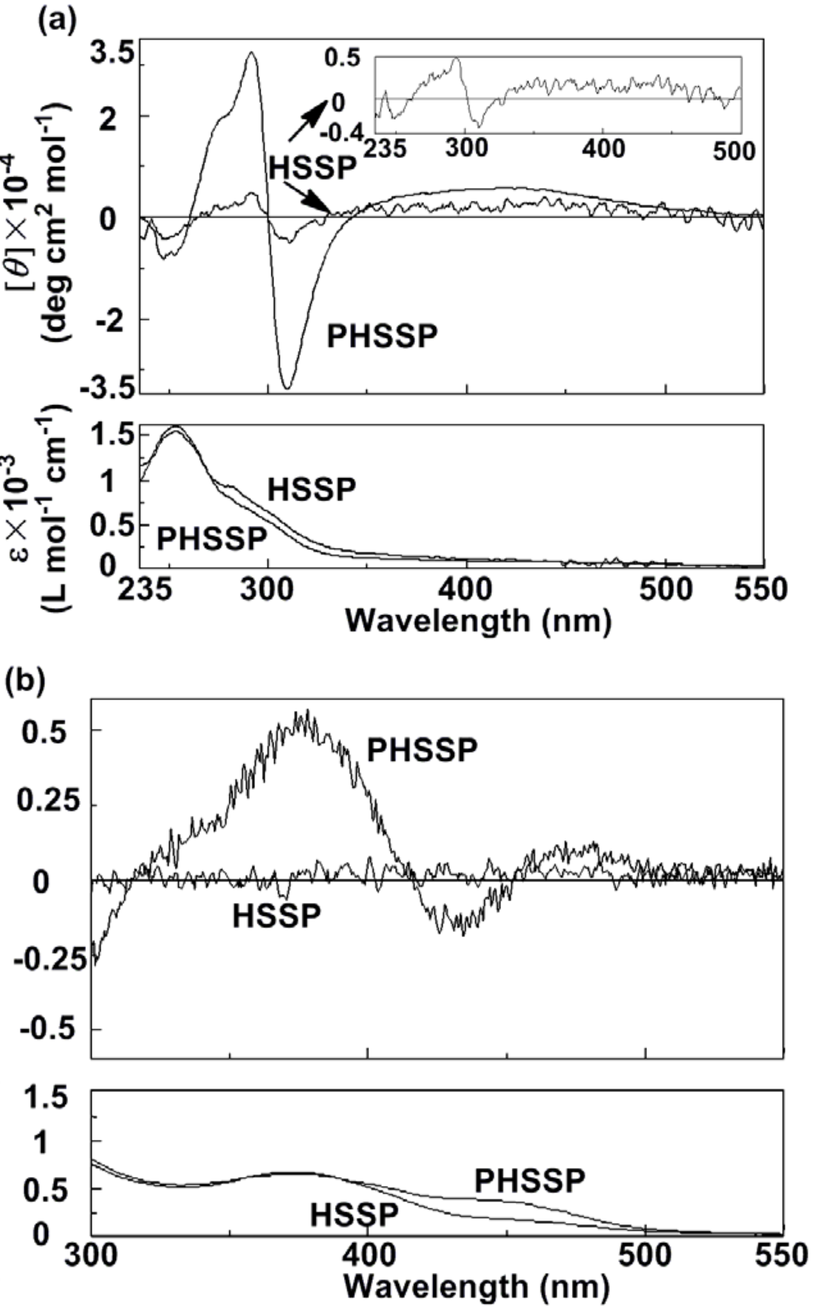


Fig. 2 CD and UV-vis spectra in $CHCl_3$ of the polymers prepared by pseudo helix-sense-selective polymerisation (**PHSSP**) and helix-sense-selective polymerisation (**HSSP**) of (a) **1a**; (b) **2a** (Polymerisation condition: [chiral amine] / [monomer] = 2.5).

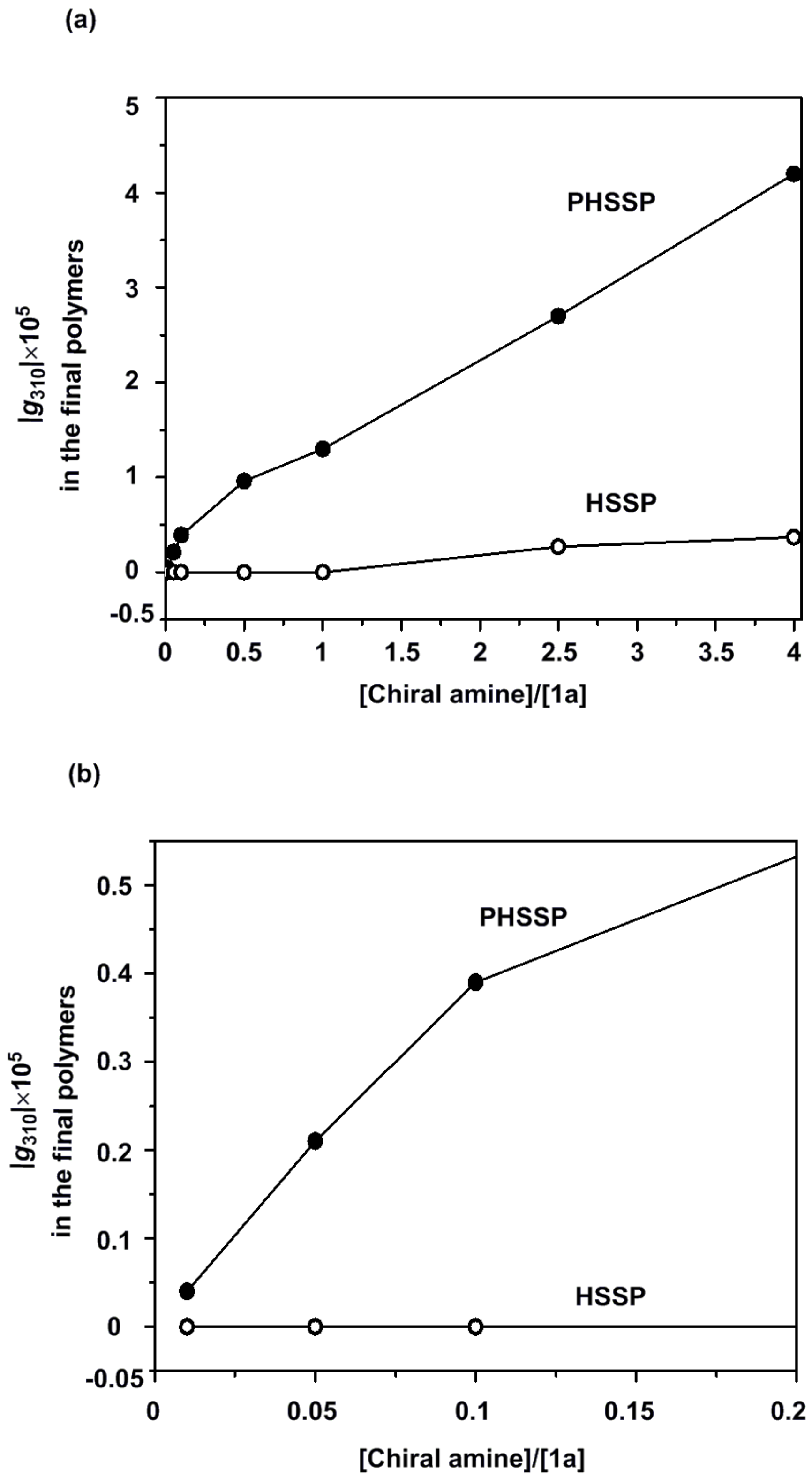


Fig. 3 Plots of **g** values *vs* [chiral amine]/[**1a**] in the feed of poly(**1a**)s prepared by pseudo helix-sense-selective polymerisation (**PHSSP**) and helix-sense-selective polymerisation (**HSSP**) (a), and its enlarged one (b).

Table 3 Pseudo helix-sense-selective polymerisation (**PHSSP**) by using (*R*)- or (*S*)-PEA as a chiral source and helix-sense-selective polymerisation (**HSSP**) by using (*R*)- or (*S*)-DMPEA as a cocatalyst of monomers **1a** [a] and **2a** [b] with other related asymmetric polymerisation

No.	Monomer	Code [c]	Method [c]	[chiral amine]/[monomer]	Yield (%)	M_w [d] ($\times 10^5$)	Achiral [e] amine unit (mol %)	Final polymer	g_{310nm} [f] ($\times 10^{-5}$)	g_{430nm} [f] ($\times 10^{-5}$)	Reative O. P. [g] (%)
1 [a]	**1a**	A	PHSSP	2.5	72.2	4.6	100 [h]	poly(**1a**)	-2.7	2.1	100
2 [a]	**1a**	A	PHSSP	1.0	38.5	1.7	100	poly(**1a**)	-1.3	0.90	43
3 [a]	**1a**	A	PHSSP	0.050	34.0	9.0	100	poly(**1a**)	-0.21	0.10	4.8
4 [a]	**1a**	B	HSSP	2.5	67.3	1.8 [i]	100	poly(**1a**)	-0.27	0.10	4.8
5 [a]	**1a**	B	HSSP	1.0	37.5	1.2 [i]	100	poly(**1a**)	0	0	0
6 [a]	**1a**	C	*in-situ* AIP	2.5	48.0	2.7	46	poly(**1a/PE*P**)	(-5.2) [j]	(3.8) [j]	—
7 [b]	**2a**	A'	PHSSP	2.5	20.8	3.6	97.3 [h]	poly(**2a/PP*P**)	—	-0.020 [k]	—
8 [l]	**2a/PP*P**	D'	AIP	— [m]	12.9	0.20	93.4	poly(**2a/PP*P**)	—	0	—
9 [b]	**2a**	B'	HSSP	2.5	11.0	0.20	100	poly(**2a**)	—	0	—

[a] In THF, [**1a**]=0.1mol/L, [**1a**]/[Rh(nbd)Cl]$_2$=50, [achiral amine]/[**1a**]=10, for the abbreviations, see the Notes and Scheme 2. [b] In toluene, [monomer]=0.1mol/L, [monomer]/[Rh(nbd)Cl]$_2$=100, [achiral amine]/[monomer]=10, see Scheme S3. [c] For the codes and abbreviations, see Schemes 2-7. [d] By GPC (polystyrene, THF). [e] Determined by ^{1}H-NMR spectra in the final polymers. [f] $\boldsymbol{g}$=([θ]/3300/ε)$\times$0.001 in CHCl$_3$. [g] Relative optical purity of poly(**1a**) based on the $\boldsymbol{g}_{430nm}$ value of No. 1. [h] By elemental analysis. [i] Partly soluble, soluble part was 60% in THF. [j] The polymers contain the chiral monomer units. [k] Calculated from the peak at 440nm. [l] See Scheme S5 in toluene [**PP*P**]=0.1mol/L, [**PP*P**]/[Rh(nbd)Cl]$_2$=100, [triethylamine]/[**PP*P**]=1.0, [achiral amine]/[poly(**PP*P**)]=10. [m] Triethylamine was used as a cocatalyst.

Table 4 Pseudo helix-sense-selective polymerisation (**PHSSP**) by using (*R*)- or (*S*)-PEA as a chiral source and helix-sense-selective polymerisation (**HSSP**) by using (*R*)- or (*S*)-DMPEA as a cocatalyst of monomers **1a** [a] and **2a** [b] with other related asymmetric polymerisation

No.	Monomer	Code [c]	Method [c]	[chiral amine] / [monomer]	Yield (%)	M_w [d] ($\times 10^5$)	Achiral [e] amine unit (mol %)	$\boldsymbol{g}_{310nm}$ [f] ($\times 10^{-5}$)	$\boldsymbol{g}_{430nm}$ [f] ($\times 10^{-5}$)	Final polymer	Relative O. P. [g] (%)
1 [a]	**1a**	A	PHSSP	0.50	27.0	1.0	100	-0.96	0.80	poly(**1a**)	38
2 [a]	**1a**	A	PHSSP	0.10	24.5	1.3	100	-0.39	0.40	poly(**1a**)	19
3 [h]	**PE*P**	D	AIP	— [i]	96.3	4.9	0	(-6.1) [j]	(3.6) [j]	poly(**PE*P**)	—
4 [h]	**PE*P**	D+E	AIP+ER	— [i]	62.1	3.8	89	(-4.6) [j]	(2.5) [j]	poly(**1a/PE*P**)	—
5 [k]	**PP*P**	D'+E'	AIP+ER	— [i]	78.4	1.6	100	—	-0.020 [l]	poly(**2a/PP*P**)	1.0
6 [m]	**DoDHPA**	F	HSSP	0.50	67.3	11	100	0.40	0.30	poly(**DoDHPA**)	14
7 [m]	**DoDHPA**	F [n]	HSSP	0.50	85.3	0.30	100	0.40	0.30	poly(**DoDHPA**)	14
8 [m]	**DoDHPA**	F	HSSP	0.25	69.8	33	100	0.060	0.060	poly(**DoDHPA**)	2.9

[a] In THF, [**1a**]=0.1mol/L, [**1a**]/[Rh(nbd)Cl]$_2$=50, [achiral amine]/[**1a**]=10, for the abbreviations, see the notes and scheme 2. [b] In toluene, [monomer]=0.1mol/L, [monomer]/[Rh(nbd)Cl]$_2$=100, [achiral amine]/[monomer]=10, see scheme 3. [c] For the codes and abbreviations, see Chart 1. [d] By GPC (polystyrene, THF). [e] Determined by ^{1}H-NMR in the final polymers. [f] $\boldsymbol{g}$=([θ]/3300/ε)×0.001 in CHCl$_3$. [g] Relative optical purity based on the $\boldsymbol{g}_{430nm}$ value of No. 1 in Table 3. [h] See Scheme 6, in THF, [**PE*P**]=0.1mol/L, [**PE*P**]/[Rh(nbd)Cl]$_2$=50, [triethylamine]/[**PE*P**]=2.5, [achiral amine]/[poly(**PE*P**)]=10. [i] Triethylamine was used as a cocatalyst. [j] The polymers contain the chiral monomer units. [k] See Scheme 7 in toluene, [**PP*P**]=0.1mol/L, [**PP*P**]/[Rh(nbd)Cl]$_2$=100, [triethylamine]/[**PP*P**]=1.0, [achiral amine]/[poly(**PP*P**)]=10. [l] Calculated from the peak at 440nm. [m] In toluene [**DoDHPA**]=0.1mol/L, [**DoDHPA**]/[Rh(nbd)Cl]$_2$=200. [n] (*R*)-DMPEA was used as a cocatalyst.

1.5 Conclusions

In conclusion, we have reported for the first time a new conceptual approach to asymmetric polymerisation that makes one-handed helical polymers without the coexistence of any other chiral moieties from achiral monomers, pseudo helix-sense-selective polymerisation (**PHSSP**). We have reported practical results from a wide range of substituted acetylenes having dynamic covalent bonds. The chiral amine in **PHSSP** worked not as a cocatalyst, as it does in **HSSP**, but rather as a reagent because it formed temporary covalent bonds with the polymer. This is the origin of the name pseudo helix-sense-selective polymerisation (**PHSSP**). Because of the introduction of the chiral source *via* covalent bonds, the optical purity [5] and efficiency [5] in the chiral induction were much higher in **PHSSP** than those in **HSSP**. In addition, the range of chemical structures suitable for **PHSSP** was wider than that for **HSSP**. Therefore many kinds of acetylene monomers are expected to be suitable for **PHSSP**. Furthermore, other kinds of monomers having a different polymerisable group are also expected to be applicabgle to **PHSSP**. We anticipate that it will become a general method for asymmetric polymerisation.

References and Notes

[1] For reviews on asymmetric polymerisation: (*a*) Y. Okamoto and E. Yashima, *Prog. Polym. Sci.*, 1990, **15**, 263; (*b*) Y. Okamoto and T. Nakano, *Chem. Rev.*, 1994, **94**, 349; (*c*) E. Yashima, K. Maeda, H. Iida, Y. Furusho, and Y. Nagai, *Chem. Rev.*, 2009, **109**, 6102; (*d*) S. Ito and K. Nozaki, Asymmetric Polymerisation, In *Catalytic Asymmetric Synthesis*, ed. I. Ojima, Wiley, Hoboken, 3rd edn. 2010, pp. 931-985; (*e*) T. Aoki, T. Kaneko and M. Teraguchi, *Polymer*, 2006, **47**, 4867.

[2] For **HSSP** of substituted acetylenes: (*a*) T. Aoki, T. Kaneko, N. Maruyama, A. Sumi, M. Takahashi, T. Sato and M. Teraguchi, *J. Am. Chem. Soc.*, 2003,

125, 6346; (*b*) S. Hadano, T. Kishimoto, T. Hattori, D. Tanioka, M. Teraguchi, T. Aoki, T. Kaneko, T. Namikoshi and E. Marwanta, *Macromol. Chem. Phys.*, 2009, **210**, 717; (*c*) H. Jia, S. Hadano, M. Teraguchi, T. Aoki, Y. Abe, T. Kaneko, T. Namikoshi and E. Marwanta, *Macromolecules*, 2009, **42**, 17. (*d*) L. Liu, Y. Zang, S. Hadano, T. Aoki, M. Teraguchi, T. Kaneko and T, Namikoshi, *Macromolecules*, 2010, **43**, 9268. (*e*) T. Nishimura, Y. Ichikawa, T. Hayashi, N. Onishi, M. Shiotsuki and T. Masuda, *Organometallics*, 2009, **28**, 4890.

[3] For example, most monomers suitable for **HSSP** should contain two hydroxyl groups which make intramolecular hydrogen bonds maintaining the one-handed helicity in the resulting polymer and one hydrophobic group, like **DoDHPA**.[1e, 2]

[4] For example, in the **HSSP** of **DoDHPA**, [chiral amine (chiral source)] / [monomer] = 2.5 was necessary.[1e, 2]

[5] The optical purity was relatively estimated by comparing the intensity of CD peaks (*g* values) for the obtained polymers having the same chemical structures and we defined a relative optical purity (Table 3), because the CD intensity of poly(**1a**) having 100% optical purify was unknown. The efficiency of the chiral induction was estimated by the values of [chiral amine (chiral source)] / [monomer].

[6] For reviews on dynamic covalent bonds: (*a*) S. J. Rowan, S. J. Cantrill, G. R. L. Cousins, J. K. M. Sanders and J. F. Stoddart, *Angew. Chem. Int. Ed.*, 2002, **41**, 898; (*b*) T. Maeda, H. Otsuka and A. Takahara, *Prog. Polym. Sci.*, 2009, **34**, 581.

[7] The final polymer by **PHSSP**, poly(**2a**/**PP*P**) showing CD signals contained small amounts of chiral units (Table 3, no.7). However, since poly(**2a**/**PP*P**) having almost the same composition separately prepared by copolymerisation of **2a** and **PP*P** showed no CD(Table 3, no. 8), **PHSSP** for **2a** was thought to be realised.

[8] For **PHSSP**, (*R*)- or (*S*)-phenylethylamine (PEA) was used, but in **HSSP** in this study (*R*)- or (*S*)-*N*,*N*-dimethylphenylethylamine (DMPEA) was used to avoid the exchange reaction. For **HSSP** of **DoDHPA**, the two chiral amines, PEA and DMPEA gave similar degrees of relative optical purity in the chiral induction (Table 4, nos.6 and 7).

[9] The intermediate polymers poly(**1a**/**PE*P**) having different compositions were separately synthesised and isolated by ***in-situ*** **AIP** (Table 3, no.6). A nonlinear relationship between *g* values and the contents of the chiral monomer units of the obtained polymers was observed (Fig.S1). This was thought to be the reason why catalytic amounts of chiral amine caused **PHSSP**. In the case of dynamic helical polymers, the "sergeants and soldiers effect" has been reported.[10] However, in this study, the one-handed helical structure was produced mainly during polymerisation, not after polymerisation. This was apparent because the CD of poly(**1a**) in a non-polar solvent disappeared due to the scission of the intramolecular hydrogen bonds when polar solvent was added to the original CD-active solution, and then no recovery in CD was observed when a non-polar solvent was added to the CD-inactive solution (Figs. S2-4). It was exactly the same phenomena observed for poly (**DoDHPA**) prepared by **HSSP** of the achiral monomer.[2] Therefore, even if poly(**1a**) contained a very small amount of chiral monomer units which could not be detected by NMR and EA, the sergeants and soldiers effect was excluded after polymerisation. In the case of poly(**2a**), the one handed helical structure was also produced mainly during polymerisation and not after polymerisation because the corresponding copolymer (see notes and references 7) separately prepared from the corresponding chiral monomer(**PP*P**) showed no CD. Therefore, these one-handed helical polymers are not dynamic, but are static, and the sergeants and soldiers effect did not occur after polymerisation.

[10] For the sergeants and soldiers effect: (*a*) M. M. Green, C. Andreola, B. Muońz and M. P. Reidy, *J. Am. Chem. Soc.*, 1988, **110**, 4063; (*b*) M. M. Green and M. P. Reidy, *J. Am. Chem. Soc.*, 1989, **111**, 6452; (*c*) S. Lifson, C. Andreola, N. C. Peterson and M. M. Green, *J. Am. Chem. Soc.*, 1989, **111**, 8850; (*d*) R. Nomura, Y. Fukushima, H. Nakako and T. Masuda, *J. Am. Chem. Soc.*, 2000, **122**, 8830; (*e*) R. B. Prince, J. S. Moore, L. Brunsveld and E.W. Meijer, *Chem. Eur. J.*, 2001, **7**, 4150; (*f*) M. M. J. Smulders, I. A.W. Filot, J. M. A. Leenders, P. V. D. Schoot, A. R. A. Palmans, A. P. H. J. Schenning and E. W. Meijer, *J. Am. Chem. Soc.*, 2010, **132**, 611.

[11] On the other hand, the final polymer separately obtained by **AIP** of **PE*P** followed by exchange reaction**(ER)** (Scheme 6) contained the chiral units (Table 4, no.4). Since poly (**PE*P**) had low solubility after isolation, the conversion of **ER** was lower than that in **PHSSP**. Therefore, it showed the advantage of the *in-situ* procedure in **PHSSP.**

Supporting Information (SI)

(1) Non-linear relationship

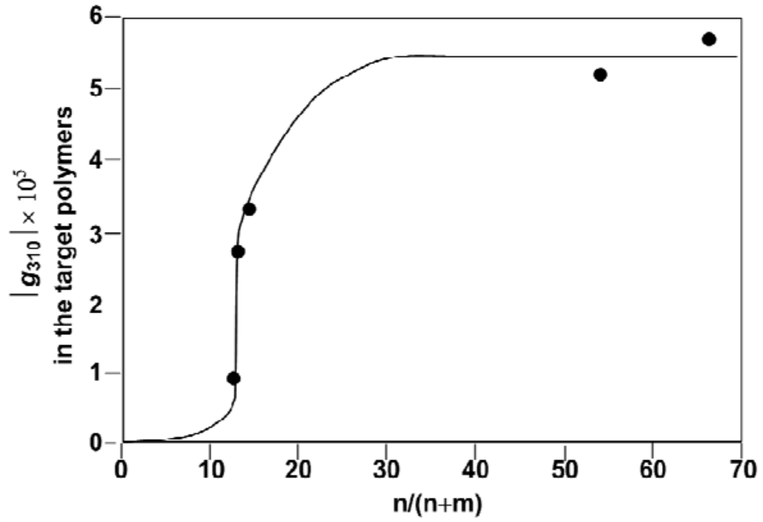


Fig. S1 Plots of ***g*** values vs **n**/(**n+m**) of poly(**1a**/**PE*P**) prepared by *in-situ* asymmetric-induced polymerisation (***in-situ* AIP**) by using different amount of (*R*)- or (*S*)-PEA as a chiral source.

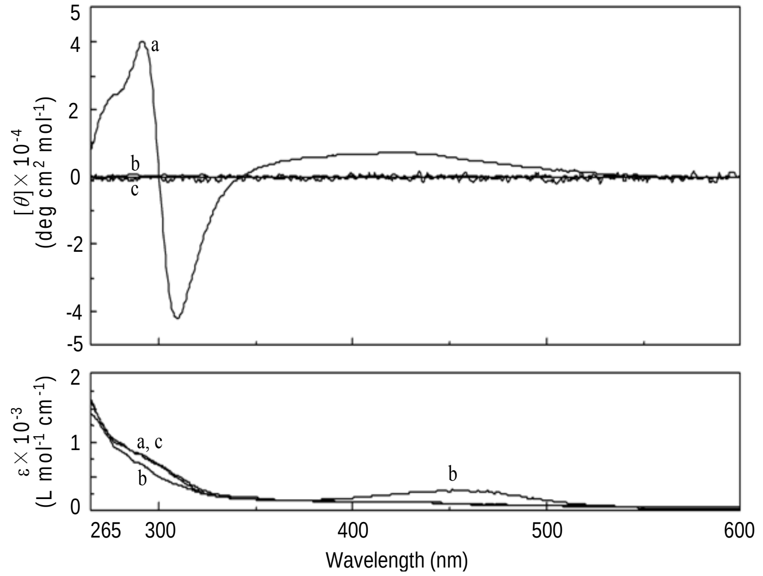


Fig. S2 CD and UV-vis spectra of poly(**1a**) prepared by pseudo helix-sense-selective polymerisation (**PHSSP**) of monomer (**1a**) ([chiral amine]/[**1a**]=2.5) in (a) $CHCl_3$, (b) $CHCl_3$/DMSO=55/45 (v/v), (c) $CHCl_3$/DMSO=95/5 (v/v) ((c) was the solution prepared by addition of $CHCl_3$ to the solution of (b)).

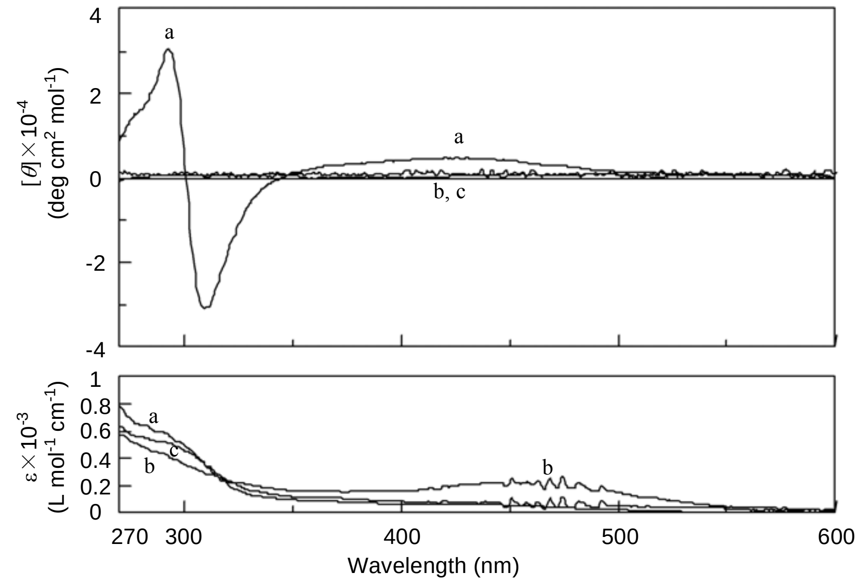


Fig. S3 CD and UV-vis spectra of poly(**1a**) prepared by ***in-situ*** **AIP** of monomer (**1a**) ([chiral amine]/[**1a**]=0.1) in (a) $CHCl_3$, (b) $CHCl_3$/DMSO=55/45 (v/v), (c) $CHCl_3$/DMSO=95/5 (v/v) ((c) was the solution prepared by addition of $CHCl_3$ to the solution of (b)).

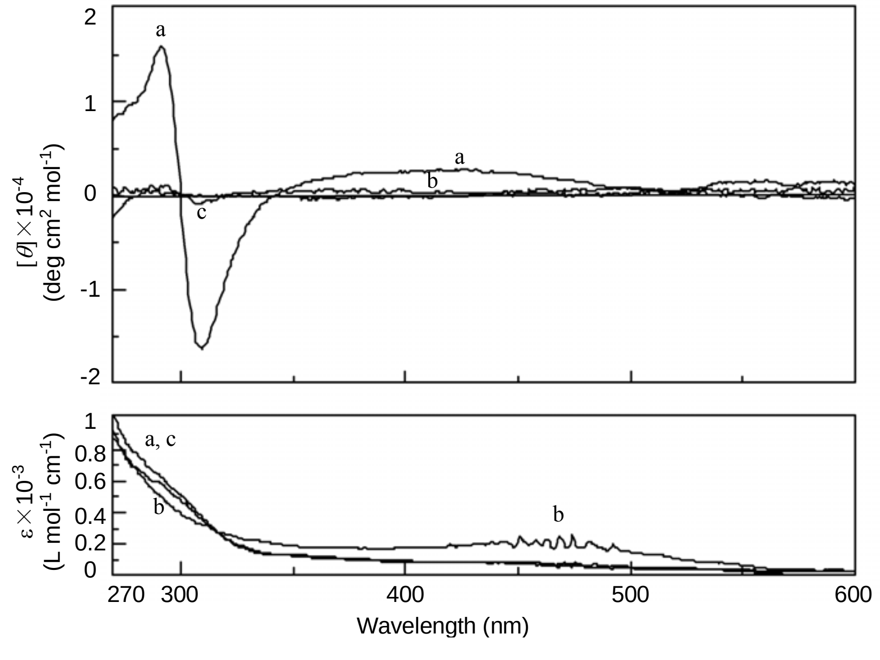


Fig. S4 CD and UV-vis spectra of poly(**1a**) prepared by ***in-situ*** **AIP** of monomer (**1a**) ([chiral amine]/[**1a**]=1.0) in (a) $CHCl_3$, (b) $CHCl_3$/DMSO=55/45 (v/v), (c) $CHCl_3$/DMSO=95/5 (v/v) ((c) was the solution prepared by addition of $CHCl_3$ to the solution of (b)).

(3) NMR of the final polymer prepared by **PHSSP** of **1a**

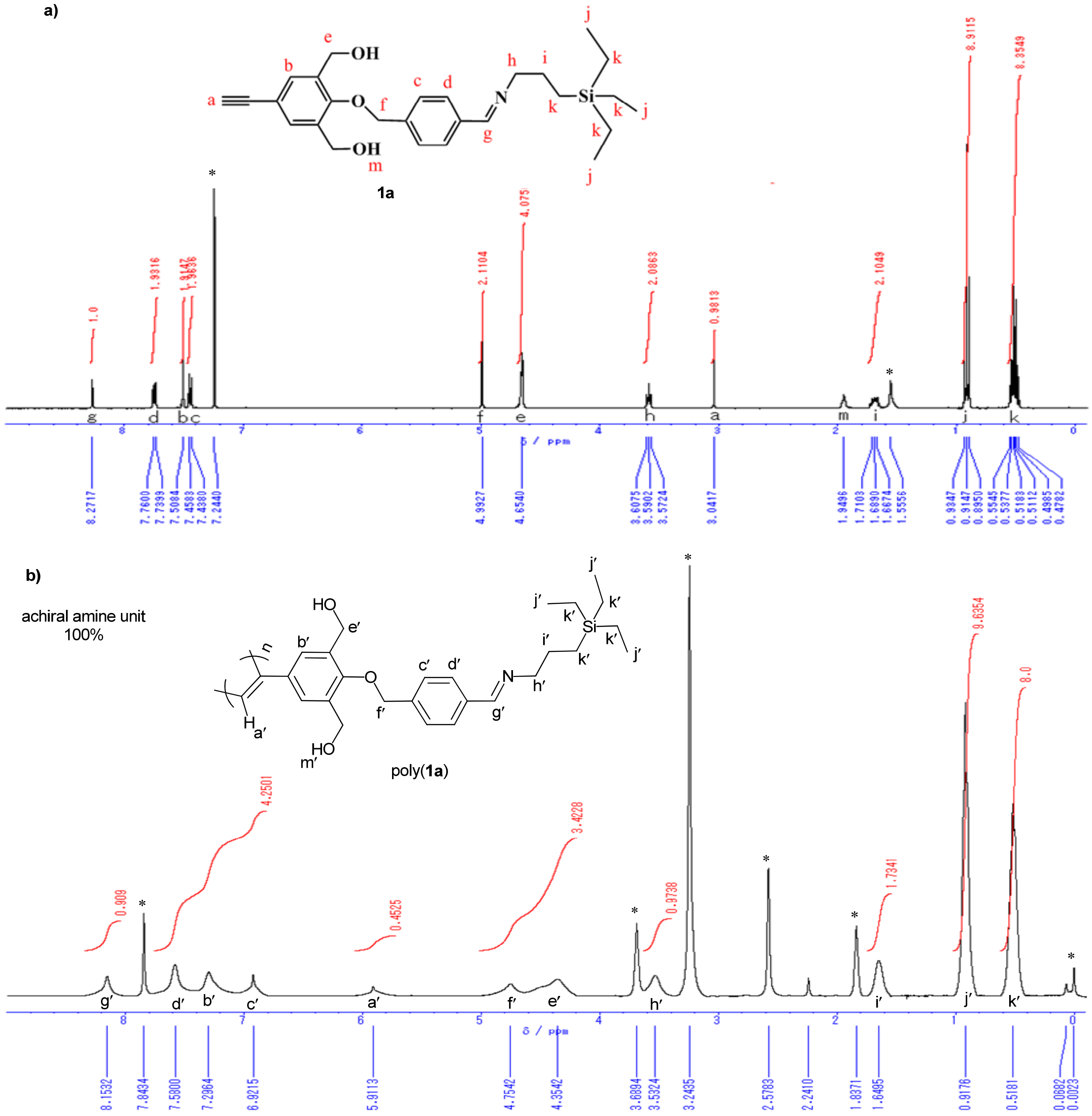


Fig. S5 ^{1}H-NMR spectra of **a**) monomer (**1a**), **b**) helix-sense-selective polymerisation (**HSSP**) of monomer (**1a**) by using (*R*)- or (*S*)-DMPEA as a cocatalyst, **c**) pseudo helix-sense-selective polymerisation (**PHSSP**) of monomer (**1a**) by using (*R*)- or (*S*)-PEA as a chiral source (No. 2 in table 3), **d**) pseudo helix-sense-selective polymerisation (**PHSSP**) of monomer (**1a**) by using (*R*)- or (*S*)-PEA as a chiral source (No. 1 in table 1), **e**) monomer (**PE*P**), **f**) asymmetric-induced polymerisation (**AIP**) of chiral monomer **PE*P**, **g**) the enlargement of b), c) and d).

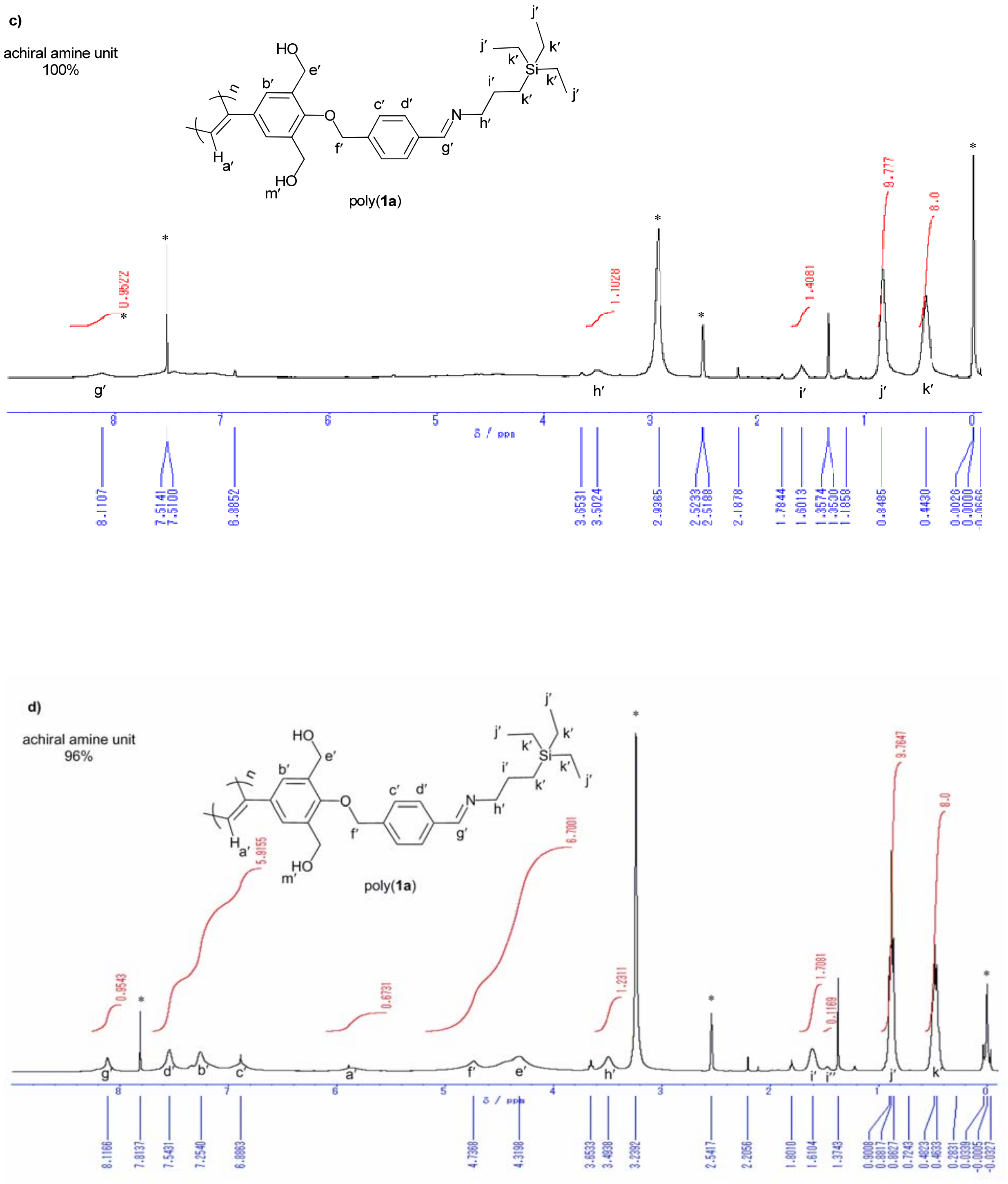


Fig. S5 (Continued).

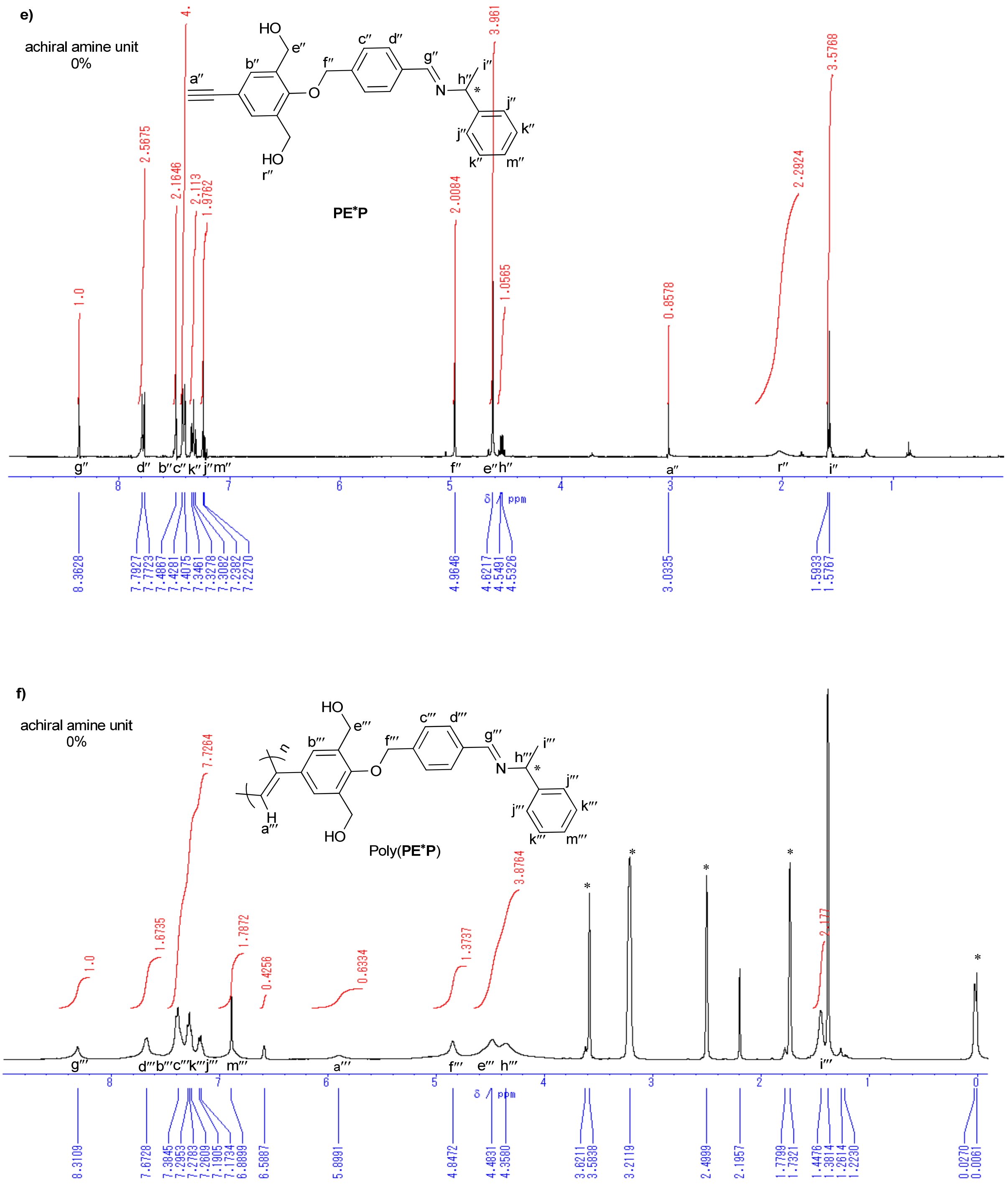


Fig. S5 (Continued).

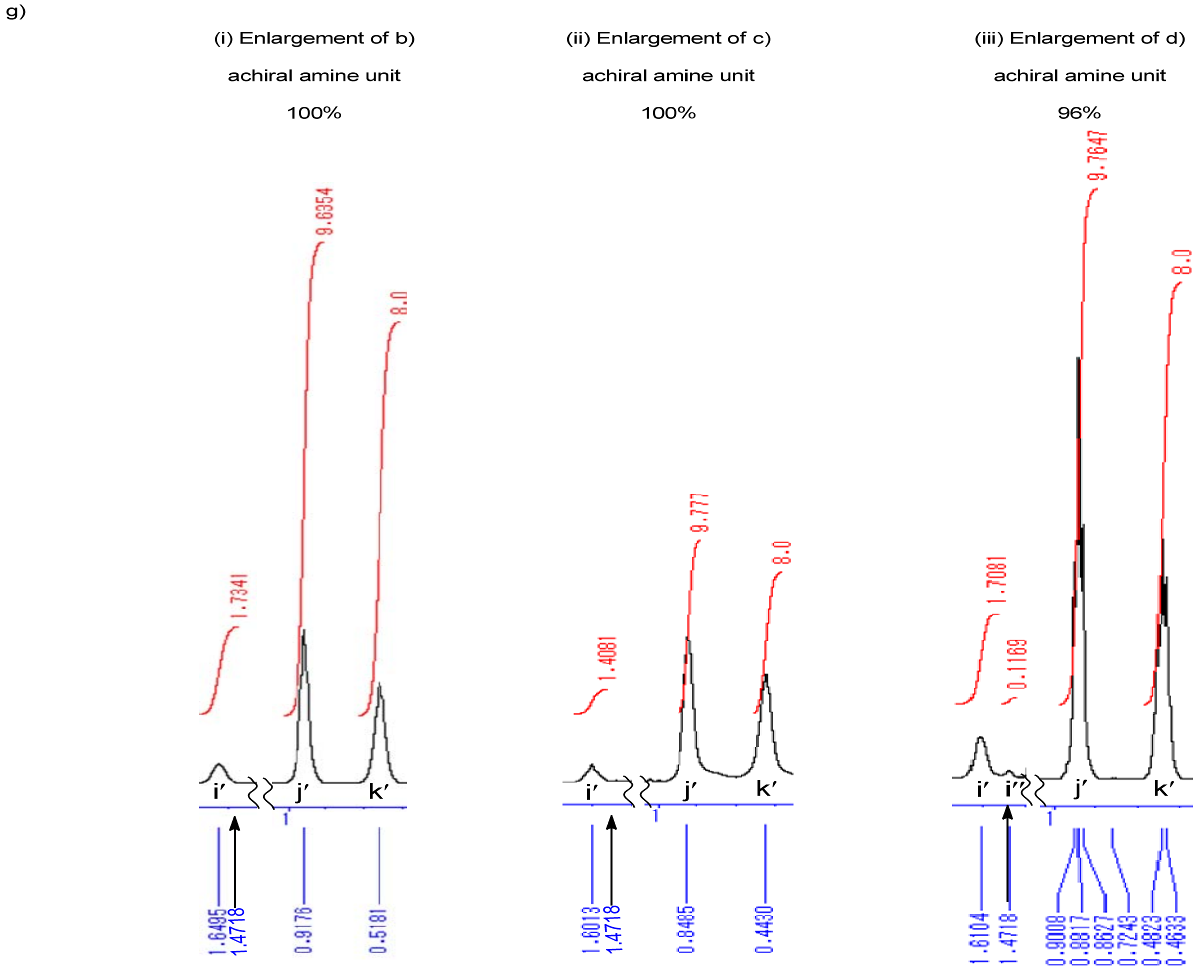


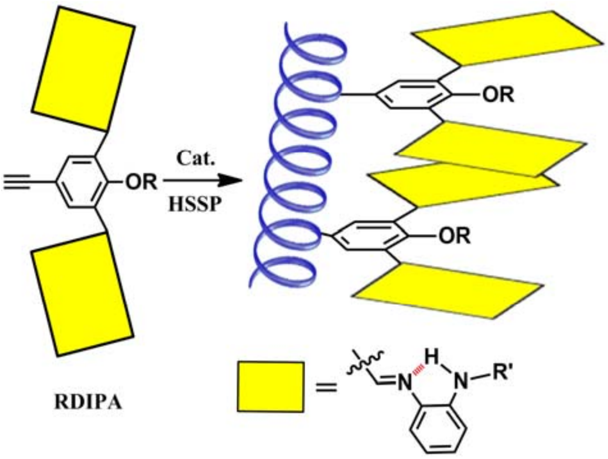
Fig. S5 (Continued).

Chapter 2

Helix-Sense-Selective Polymerization Using Catalytic Amount of Chiral Cocatalyst of Substituted Acetylenes Containing Bulky π-Conjugated Planar Substituents Yielding Highly Stable One-Handed Helical Polymers

2.1 Abstract

The helix-sense-selective polymerization (HSSP) has been achieved of three achiral substituted acetylene monomers synthesized which contained two bulky π-conjugated planar substituents via imine groups by using the chiral catalytic system we developed before. One-handed helical main chains of the resulting polymers were stabilized by intramolecular steric hindrance, not by intramolecular hydrogen bonds. Therefore the chiral main chains were very stable to polar solvent and heating. In addition, the efficiency of the chiral induction was much higher than that in the case of the previous monomers having hydoroxy groups we reported, *i.e.*, it needs only catalytic amount of chiral cocatalysts. Therefore we found more valuable and general monomers which were more suitable for the HSSP. The monomers have enhanced the value of our HSSP because the range of the molecular design has been enlarged.



RDIPA

2.2 Introduction

π-Conjugated polymers like polyacetylenes have aroused interest because of their noteworthy physical properties such as conductivity, organomagnetism, and optical non-linear susceptibility. Recently chiral polyacetylenes [1] have attracted much attention since the chiral structure can enhance the unique properties and add new functions.

Several kinds of asymmetric polymerizations of achiral monomers to obtain chiral polymers having their chiral structures in their main chains have been reported. Among them, a direct synthetic method of soluble chiral π-conjugated polymers whose chiral structures arise solely from the one-handed helical conformation of the conjugated main chains (therefore, they have no asymmetric carbons) and are stable alone in solution was so far only the helix-sense-selective polymerization (HSSP) of an achiral phenylacetylene monomer by using a chiral catalytic system developed in our laboratory. [2]

In general, there exist two methods to synthesize soluble chiral polymers whose chiral structures are present alone in the main chain as asymmetric carbons and/or as a one-handed helical conformation. One is HSSP [3] of an achiral monomer by using a chiral catalyst as a chiral source and the other is asymmetric-induced polymerization, by using achiral catalysts, of monomers having a chiral group as a chiral source, followed by removing the chiral groups by a polymer reaction in solution where the chiral groups were desubstituted from the resulting one-handed helical polymers (AIP-R). [4]

However, the examples where the two methods, HSSP and AIP-R, have been applied to π-conjugated polymers are very few. [2, 5] In fact there has been only one example by using HSSP by our group [2] and only one example by the use of AIP-R by our group [4] for obtaining soluble chiral conjugated polymers. Therefore, so far our HSSP and AIP-R synthesis were the only two methods available to obtain soluble chiral conjugated polymers whose chiral structures arise only from the one-handed helical conformation of their conjugated main chains.

The HSSP is more simple procedure than AIP-R. However, in the HSSP suitable monomers were limited and typical monomers needed two functional groups which could make hydrogen bonds like hydroxyl groups (Chart 1, DoDHPA). [2] The one-handed helical backbone was not stable to polar solvents and heating because it was maintained by intramolecular hydrogen bonds. In addition, the efficiency of the chiral induction was not high, *i.e.*, a large ratio of the chiral cocatalyst to the monomer (Chart 1, (*R*)- or (*S*)-PEA) was needed.

In this chapter, we report novel and more general monomers having no groups making hydrogen bonds such as hydroxyl groups [1a] and amide groups [1g] but having bulky planar conjugated groups via imino groups (Chart 1, DoDIPA) suitable for the HSSP. In addition, we report the absolute stability of the resulting one-handed helicity of poly(DoDIPA) kept by intramolecular steric interaction and higher efficiency of chiral induction of HSSP of DoDIPA, *i.e.*, it needed only catalytic amounts of the chiral source. Finally the reason for the suitability of DoDIPA for the HSSP is discussed.

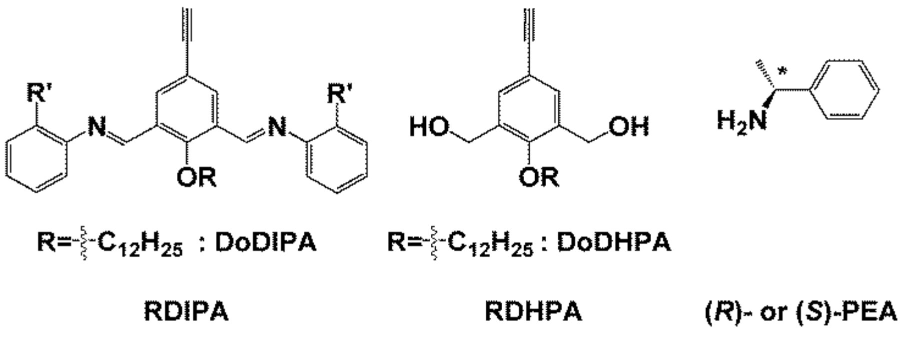


Chart 1. Chemical structures of monomers and a chiral amine.

2.3 Experimental

2.3.1 Materials

All the solvents used for synthesis and polymerization of the monomers were distilled as usual. The polymerization initiator, [Rh(nbd)Cl]$_2$ (nbd = 2,5 norbornadiene), purchased from Aldrich Chemical was used as received. 4-

Dodecyloxy-3,5-bis(hydroxymethyl)phenylacetylene (**4**) was synthesized from 4-bromophenol according to our previous report. [1a]

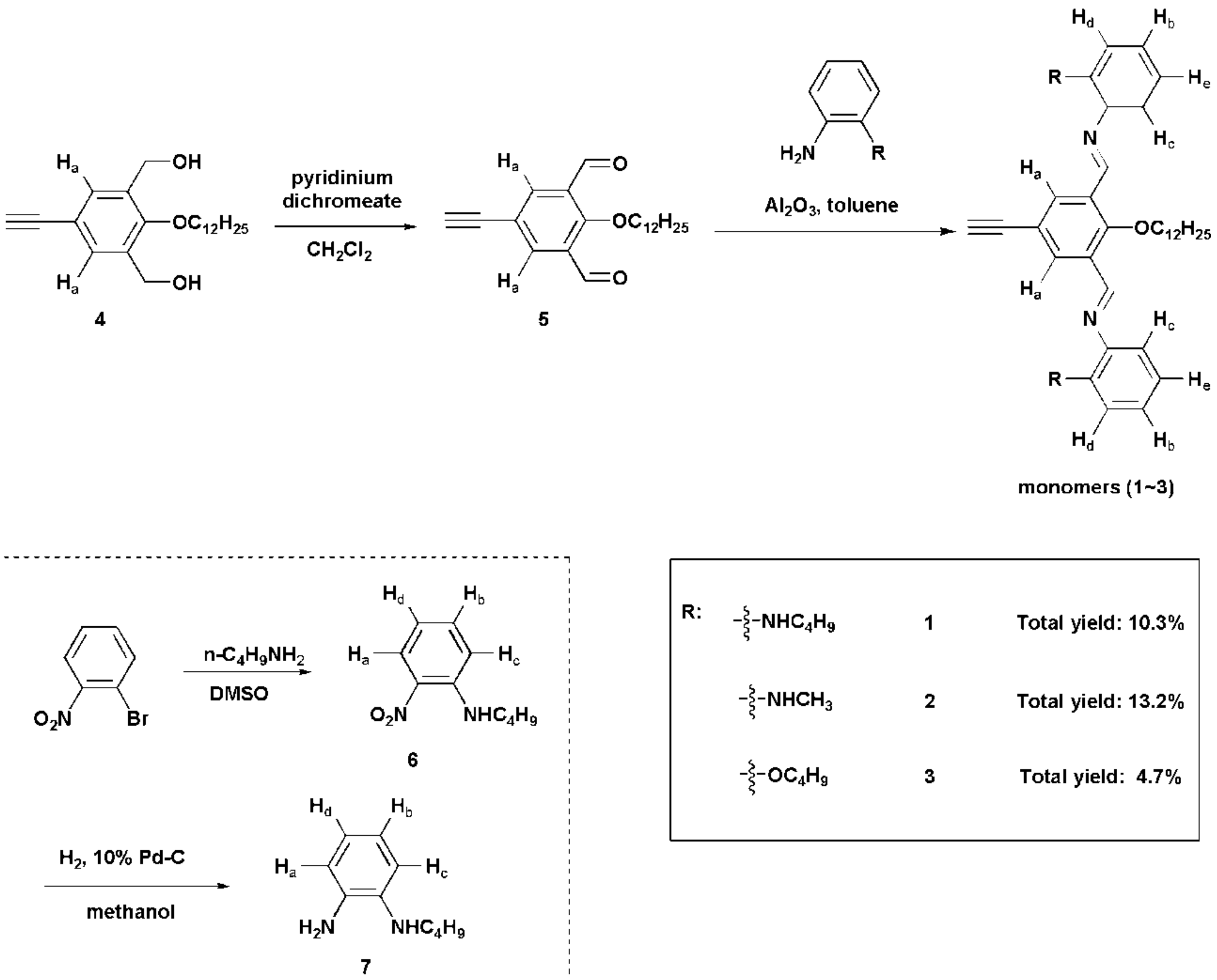
2.3.2 Measurements

^{1}H NMR (400MHz) spectra were recorded on a JEOL LEOLEX-400 spectrometer. The average molecular weights (M_n and M_w) were evaluated by gel permeation chromatography (GPC) by using JASCO liquid chromatography instruments with PU-2080, DG-2080-53, CO-2060, UV-2070, CD-2095, and two polystyrene gel columns (Shodex KF-807 L, THF eluent, polystyrene calibration). We recorded CD spectra by using a JASCO J-720WI spectropolarimeter with a Peltier controller for temperatures at 20℃ (a quartz cell of 1 mm path length; sample concentration: 0.100 to 2.00 mM based on the monomer unit). The infrared spectra were recorded on FT/IR-4200 (JASCO).

2.3.3 Synthesis of the monomers (1~3) (Scheme 1)

2.3.3.1 4-Dodecyloxy-3,5-diformylphenylacetylene (**5**)

To a mixture of pyridinium dichromate (PDC) (63.0 g, 231 mmol) and dichloromethane (500 mL), a dichloromethane solution (200 mL) of **4** (8.00 g, 23.0 mmol) was added dropwise at 0℃. After the mixture was stirred for 48 h at room temperature, the mixture was filtered, and dichloromethane was removed by evaporation. The crude product was purified by silica-gel column chromatography to give **5** as a yellow solid. Yield: 95.3% (7.50 g). R_f = 0.460 (ethyl acetate / hexane = 1 / 2). ^{1}H NMR (400MHz, $CDCl_3$, TMS, δ): 10.36 (s, 2H, CHO), 8.17 (s, 2H, Ar H_a), 4.12 (t, J =6.6 Hz, 2H, OCH_2CH_2), 3.14 (s, 1H, HC≡C), 1.91 (m, 2H, $OCH_2CH_2CH_2$), 1.82~1.26 (m, 18H, $OCH_2CH_2(CH_2)_9CH_3$), 0.86 (t, J = 6.8 Hz, 3H, CH_2CH_3). IR (KBr): 3270 (H-C≡), 2920 (CH), 2320 (C≡C), 1380 cm^{-1} ((H)C=O).



Scheme 1. Synthetic route to the monomers (**1~3**)

2.3.3.1 *N*-*n*-Butyl-2-nitroaniline (**6**)

To a mixture of 2-bromonitrobenzene (10.0 g, 50.0 mmol) and dimethyl sulfoxide (DMSO) (50.0 mL), *n*-butylamine (18.0 mL, 0.180 mol) was added. After the mixture was stirred for 18 h at 80℃, water (150 mL) was added. The mixture was extracted with dichloromethane, and the organic layer was dried over anhydrous $MgSO_4$. The crude product was purified by silica-gel column chromatography to give **6** as an orange liquid. Yield: 95.1% (9.10 g). $R_f = 0.360$ (ethyl acetate / hexane = 1 / 2). ^{1}H NMR (400MHz, $CDCl_3$, TMS, δ): 8.16 (dd, J_1 = 1,6 Hz, J_2 = 8.7 Hz, 1H, Ar H_a), 8.05 (br, 1H, Ar N*H*), 7.42 (m, 1H, Ar H_b), 6.83 (d, *J* = 8.6 Hz, 1H, Ar H_c), 6.61 (m, 1H, Ar H_d), 3.29 (m, 2H, NCH_2CH_2), 1.71 (m, 2H, $CH_2CH_2CH_2$), 1.47 (m, 2H, $CH_2CH_2CH_3$), 0.98 (t, *J* = 7.4 Hz, 3H, CH_2CH_3).

2.3.3.2 *N*-*n*-Butyl-1, 2-phenylenediamine (**7**)

A mixture of **6** (4.30 g, 22.0 mmol) and 10% Pd-C (0.470 g, 0.440 mol) in methanol (25.0 mL) was stirred at room temperature for 10 h. The formed solid was filtered out, and methanol was removed from the resulting solution by evaporation. The crude product was purified by silica-gel column chromatography to give **7** as a purple solid. Yield: 78.0% (2.86 g). $R_f = 0.360$ (ethyl acetate / hexane = 1 / 3). ^{1}H NMR (400MHz, $CDCl_3$, TMS, δ): 6.83 (m, 1H, Ar H_b), 6.73~6.64 (m, 3H, Ar H_a, Ar H_c, Ar H_d), 3.29 (br, 3H, N*H* and NH_2), 3.10 (m, 2H, NCH_2CH_2), 1.63 (m, 2H, $CH_2CH_2CH_2$), 1.45 (m, 2H, $CH_2CH_2CH_3$), 0.97 (t, *J* = 7.4 Hz, 3H, CH_2CH_3).

2.3.3.3 4-Dodecyloxy-3,5-bis(2'-*n*-butylaminophenyliminomethyl)phenylacetylene (**1**)

A mixture of **5** (0.200 g, 0.580 mmol), **7** (0.220 g, 1.33 mmol) and Al_2O_3 (0.300 g, 2.90 mmol) in dry toluene (20.0 mL) was stirred for 18h at room temperature. After the mixture was filtered, the solvent was removed to yield a yellow solid. The crude product was purified by recrystalization in dry hexane to give **1** as a yellow solid. Yield: 64.9% (0.240 g). ^{1}H NMR (400MHz, $CDCl_3$, TMS, δ): 8.86 (s, 2H, *H*C=N), 8.37 (s, 2H, Ar H_a), 7.19 (t, *J* = 7.4 Hz, 2H, Ar H_b), 7.06 (d, *J* = 7.6 Hz, 2H, Ar H_c), 6.71(d, *J* = 7.9 Hz, 2H, Ar H_d), 6.67 (t, *J* = 7.5 Hz, 2H, Ar H_e), 5.06 (s, 2H, N*H*), 3.95 (t, *J* = 6.6 Hz, 2H, OCH_2CH_2), 3.23 (m, 4H, $NHCH_2CH_2$), 3.14 (s, 1H, *H*C≡C), 1.84 (m, 2H, $OCH_2CH_2CH_2$), 1.71 (m, 4H, $NHCH_2CH_2CH_2$), 1.50~1.47 (m, 4H, $NH(CH_2)_2CH_2CH_3$), 1.33~1.25 (m, 18H, $CH_2(CH_2)_9CH_3$), 0.99 (t, *J* = 7.4 Hz, 6H, $NH(CH_2)_3CH_3$), 0.88 (t, *J* = 6.8 Hz, 3H, $O(CH_2)_{11}CH_3$); IR (KBr): 3317 (H-C≡), 2926 (CH), 2359 (C≡C), 1597 (C=N), 1446 cm^{-1} (N-C); UV–vis ($CHCl_3$): λ_{max} (ε) = 262 (3300), 313 (1300), 436 nm (1150); Anal. calcd for $C_{42}H_{58}N_4O$: C 79.4, H 9.21, N 8.82, O 2.52; found: C 79.0, H 9.48, N 8.93, O 2.58.

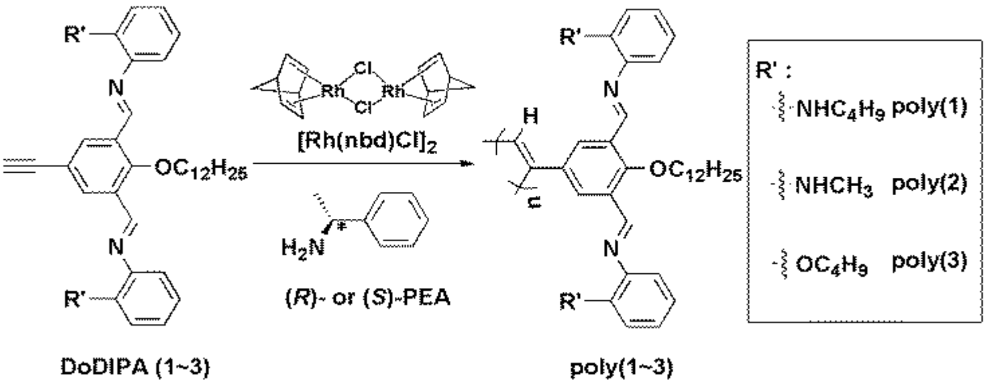
2.3.3.4 4-Dodecyloxy-3,5-bis(2'-methylaminophenyliminomethyl)phenylacetylene (**2**)

A mixture of **5** (0.200 g, 0.580 mmol), *N*-methyl-phenylenediamine (0.140 mL, 1.2 0mmol) and Al_2O_3 (0.530 g, 5.20 mmol) in dry toluene (20.0mL) was stirred for 18h at room temperature. After the mixture was filtered, the solvent was removed to yield a yellow solid. The crude product was purified by recrystalization in dry hexane to give **2** as a yellow solid. Yield: 83.8% (0.270 g). ^{1}H NMR (400MHz, $CDCl_3$, TMS, δ): 8.87 (s, 2H, *H*C=N), 8.39 (s, 2H, Ar H_a), 7.20 (t, *J* = 7.5 Hz, 2H, Ar H_b), 7.07 (d, *J* = 6.7 Hz, 2H, Ar H_c), 6.72(d, *J* = 5.1 Hz, 2H, Ar H_d), 6.67 (t, *J* = 8.0 Hz, 2H, Ar H_e), 5.08 (br, 2H, N*H*), 3.93 (t, *J* = 6.6 Hz, 2H, OCH_2CH_2), 3.13 (s, 1H, *H*C≡C), 2.95 (s, 6H, NCH_3), 1.81 (m, 2H, $OCH_2CH_2CH_2$), 1.40~1.15 (m, 18H, $CH_2(CH_2)_9CH_3$), 0.85 (t, *J* = 6.8 Hz, 3H, CH_2CH_3); IR (KBr): 3313 (H-C≡), 2924 (CH), 2345 (C≡C), 1597 (C=N), 1446 cm^{-1} (N-C); Anal. calcd for $C_{36}H_{46}N_4O$: C 78.5, H 8.42, N 10.2, O 2.90; found: C 78.3, H 8.43, N 10.2, O 2.79.

2.3.3.5 4-Dodecyloxy-3,5-bis(2'-*n*-butylaminophenyliminomethyl)phenylacetylene (**3**)

A mixture of **5** (0.200 g, 0.580 mmol), 2-butoxyaniline (0.210 g, 1.30 mmol) and Al_2O_3 (0.300 g, 2.90 mmol) in dry toluene (20.0mL) was stirred for 18h at room temperature. After the mixture was filtered, the solvent was removed to yield a yellow solid. The crude product was purified by recrystalization in dry hexane to give **3** as a yellow solid. Yield: 84.1% (0.310 g). ^{1}H NMR (400MHz, $CDCl_3$, TMS, δ): 8.82 (s, 2H, *H*C=N), 8.45 (s, 2H, Ar H_a), 7.16 (m, 2H, Ar H_b), 7.06 (m, 2H, Ar H_c), 6.98 (m, 4H, Ar H_d and H_e), 4.04 (t, J = 6.6 Hz, 4H, $OCH_2CH_2CH_2CH_3$), 3.97 (t, J = 6.6 Hz, 2H, OCH_2CH_2), 3.07 (s, 1H, *H*C≡C), 1.78 (m, 4H, $OCH_2CH_2CH_2CH_3$), 1.49 (m, 2H, $OCH_2CH_2CH_2$), 1.47 (m, 4H, $O(CH_2)_2CH_2CH_3$), 1.30~1.22 (m, 18H, $CH_2(CH_2)_9CH_3$), 0.93 (t, J = 7.4 Hz, 6H, $O(CH_2)_3CH_3$), 0.86 (t, J = 6.8 Hz, 3H, $O(CH_2)_{11}CH_3$); UV–vis ($CHCl_3$): λ_{max} (ε) = 252 (3500), 279 (2200), 360 nm (1200); Anal. calcd for $C_{42}H_{56}N_2O_3$: C 79.2, H 8.86, N 4.40, O 7.54; found: C 79.0, H 9.03, N 4.38, O 7.56.

2.3.4 Polymerization of the monomers (1~3) (Scheme 2, Table 1)



Scheme 2. Helix-sense-selective polymerization (HSSP) of DoDIPA monomers (**1**~**3**) using (*R*)- or (*S*)-PEA as a cocatalyst in toluene at room temperature.

A typical polymerization procedure for **1** was as follows: A solution of $[Rh(nbd)Cl]_2$ (0.220 mg, 0.470 μmol) and (*S*)-phenylethylamine (PEA) (15.0 μl, 0.120 mmol) in dry toluene (0.240 mL) was added to a dry toluene (0.240 mL) solution of **1** (30.0 mg, 47.0 μmol). The reaction solution was stirred at room temperature for 18 h. The crude polymer was purified by reprecipitation of the toluene solution into a large amount of methanol and the formed solid was dried in *vacuo* to give an orange solid. Poly(**1**):Yield: 94.0% (28.2 mg). $M_w = 3.60\times10^6$. M_w/M_n = 6.70 (Table 1, no. 1). ^{1}H NMR (400MHz, $CDCl_3$, TMS, δ): 1.27 (br, $\Delta W_{1/2}$ (half width) = 0.13 ppm, 18H, $CH_2(CH_2)_9CH_3$), 0.89 (br, $\Delta W_{1/2}$ (Half width) = 0.067 ppm, 3H, $O(CH_2)_{11}CH_3$), the other peaks were not detectable; IR (KBr): 2924 (CH), 1593 (C=N), 1445 cm^{-1} (N-C); UV–vis ($CHCl_3$): λ_{max} (ε) = 425 nm (1300).

The other polymerizations of the monomers **2** and **3** were also carried out similarly.

Poly(**2**): ^{1}H NMR (400MHz, $CDCl_3$, TMS, δ): 1.25 (br, $\Delta W_{1/2}$ = 0.15 ppm, 18H, $CH_2(CH_2)_9CH_3$), 0.88 (br, $\Delta W_{1/2}$ = 0.083 ppm, 3H, $O(CH_2)_{11}CH_3$), the other peaks were not detectable; IR (KBr): 2923 (CH), 1594 (C=N), 1448 cm^{-1} (N-C).

Poly(**3**): ^{1}H NMR (400MHz, $CDCl_3$, TMS, δ): ^{1}H NMR (400MHz, $CDCl_3$, δ): 1.25 (br, $\Delta W_{1/2}$ = 0.11 ppm, 18H, $CH_2(CH_2)_9CH_3$), 0.88 (br, $\Delta W_{1/2}$ = 0.040 ppm, 6H, $O(CH_2)_3CH_3$), 0.70 (br, $\Delta W_{1/2}$ = 0.080 ppm, 3H, $O(CH_2)_{11}CH_3$), the other peaks were not detectable; IR (KBr): 2920 (CH), 1621(C=N), 1455 cm^{-1} (C-O).

2.4 Results and discussion

2.4.1 Achievement of HSSP of new monomer DoDIPA

As described in the introduction, the chemical structures of monomers suitable for the HSSP were limited. Therefore, to develop new monomers having more general structures for the HSSP than RDHPA (Chart 1) we reported previously,[1a] we designed and synthesized a new type of three achiral substituted phenylacetylene monomers (DoDIPA: **1~3** in Scheme 2) which contained two bulky π-conjugated planar substituents via imine bonds and an alkyl group. The monomers were polymerized by using the chiral catalytic system, $[Rh(nbd)Cl]_2$ and chiral phenylethylamine ((*R*)- or (*S*)-PEA) that we previously developed for the HSSP of DoDHPA[1a] as shown in Table 1.

The resulting polymers of **1**~**3** having ca. 10^6 of MW were chiral because they had CD absorption bands although the starting monomers were achiral (Figures 1~3). Since the CD bands were observed at the wavelength assigned to the main chain**,** the polymers had chirality in the main chain, that is, one handed helical backbone. In addition, the sense of the helicity was controlled by the sign of the chiral amine ((*R*)- or (*S*)-PEA) as shown in No.1 and 2 in Figure 1 and Table 1, and Figures 2 and 3. Therefore, the HSSP of DoDIPA (**1**~**3**) with no hydroxyl groups has been successfully achieved.

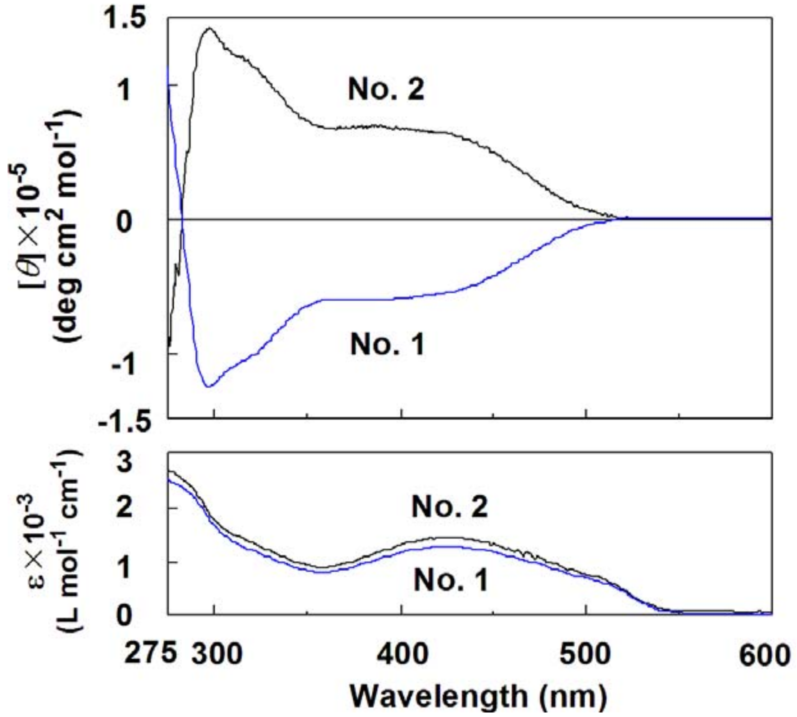


Figure 1. CD and UV-vis spectra of poly(**1**) (Nos. 1 and 2 in Table 1) in THF.

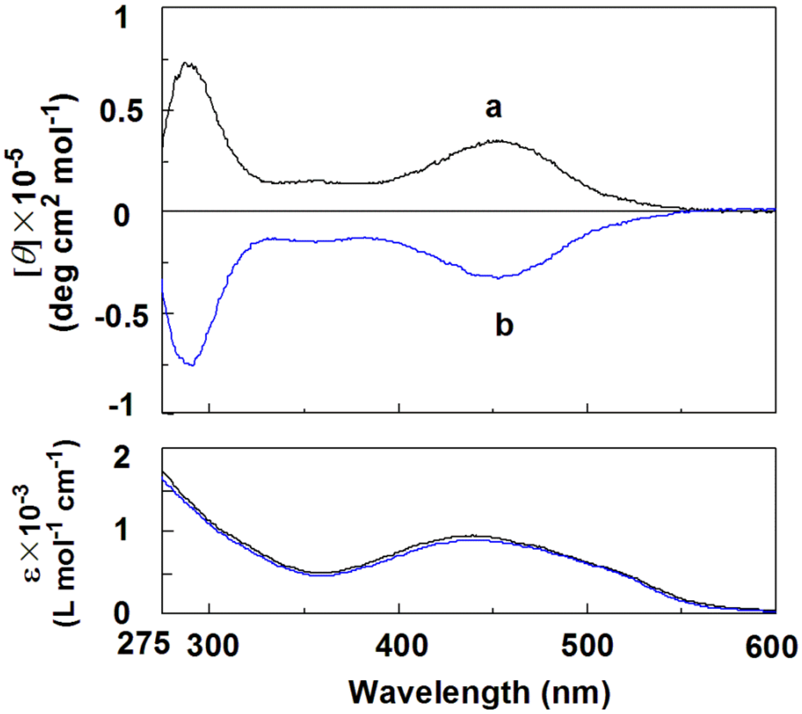


Figure 2. CD and UV-vis spectra of poly(**2**) by using (*R*)-PEA (a) and (*S*)-PEA (b) as a cocatalyst.

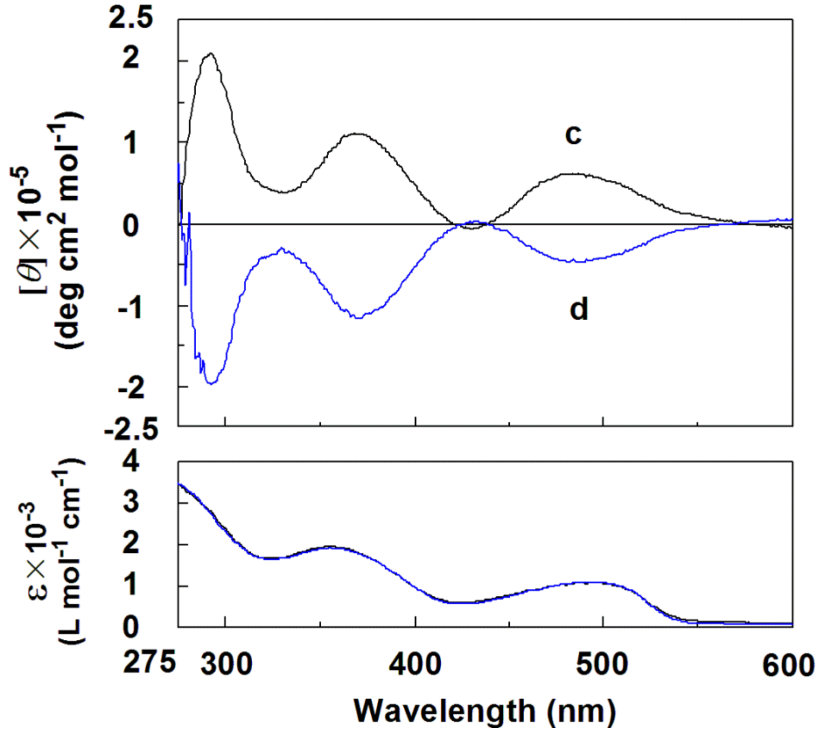


Figure 3. CD and UV-vis spectra of poly(**3**) by using (*R*)-PEA (c) and (*S*)-PEA (d) as a cocatalyst in THF.

Table 1. Helix-sense-selective polymerization (HSSP) of DoDIPA monomers (**1**~**3**) using (*R*)- or (*S*)-PEA as a cocatalyst in toluene at room temperature.

No.[a]	**DoDIPA**[b]	**Cocatalyst**[b]	**[Cocatalyst]/ [DoDIPA]**	**Yield**[c] **[%]**	M_w[d] **[$\times 10^6$]**	M_w/M_n[d]	g_{297nm}[e] **[$\times 10^{-5}$]**
1	**1**	(*S*)-PEA	2.50	94	3.6	6.7	-2.1
2		(*R*)-PEA	2.50	89	4.5	2.3	2.4
3		(*R*)-PEA	1.00	89	3.8	12	2.3
4		(*R*)-PEA	0.0200	72	1.8	11	1.7
5		(*R*)-PEA	0.00500	76	2.0	6.6	1.4
6		(*R*)-PEA	0.00300	67	1.5	6.0	0.58
7	**2**	(*R*)-PEA	2.50	69	0.77	5.8	1.6
8		(*R*)-PEA	1.00	53	0.26	4.1	0.82
9		(*R*)-PEA	0.0200	4.2	0.030	2.2	0[f]
10	**3**	(*R*)-PEA	2.50	83	0.36	4.0	2.2
11		(*R*)-PEA	1.00	65	0.52	3.0	0.90
12		(*R*)-PEA	0.0200	56	1.0	5.0	0.060
13[g]	DoDHPA	(*R*)-PEA	2.50	77	5.1	9.9	1.3[h]
14[g]		(*R*)-PEA	1.25	62	1.2	3.2	0.76[h]
15[g]		(*R*)-PEA	0.250	70	3.4	2.0	0.052[h]

[a] For 18h, [DoDIPA]=0.1mol/L, [DoDIPA] /[[Rh(nbd)Cl]$_2$]=100; [b] For the codes, see Chart 1 and Scheme 1; [c] Methanol insoluble part; [d] Determined by GPC (polystyrene, THF); [e] $g=([\theta]/3300/\varepsilon)\times 0.001$, in THF(0.001mol/L); [f] Less than 10^{-8}; [g] For 4h, [DoDHPA]=0.1mol/L, [DoDHPA]/[[Rh(nbd)Cl]$_2$]=200; [h] Calculated from the peak at 310nm.

2.4.2 High stability of the one-handed helical conformation of poly(DoDIPA) (poly(1)~poly(3)) in solution prepared by the HSSP

To estimate the stability of one-handed helical conformation of poly(DoDIPA) prepared by the HSSP to polar solvents, a polar solvent, dimethyl sulfoxide (DMSO) was added to the chloroform solution of poly(**1**) (Figure 4 (a)). The CD spectrum made almost no change as shown in Figure 4 (b) and (c), that is, the one-handed helical conformation of poly(**1**) was very stable and much more stable than that of poly(DoDHPA) whose one handed helicity was kept by intramolecular hydrogen bonds and disappeared completely by adding DMSO to the chloroform solution showing CD peaks.[1a] The other two poly(DoDIPA), poly(**2**) and poly(**3**) were also very stable to polar solvents because the CD peaks had no changes by adding DMSO as shown in Figures 5 and 6. In addition, no change happened in the CD of poly(DoDIPA) by heating at 50°C where the CD peaks of poly(DoDHPA) decreased. In summary, poly(DoDIPA) had an intrinsically stable helical backbone which was completely different from poly(DoDHPA) (Figure 7).

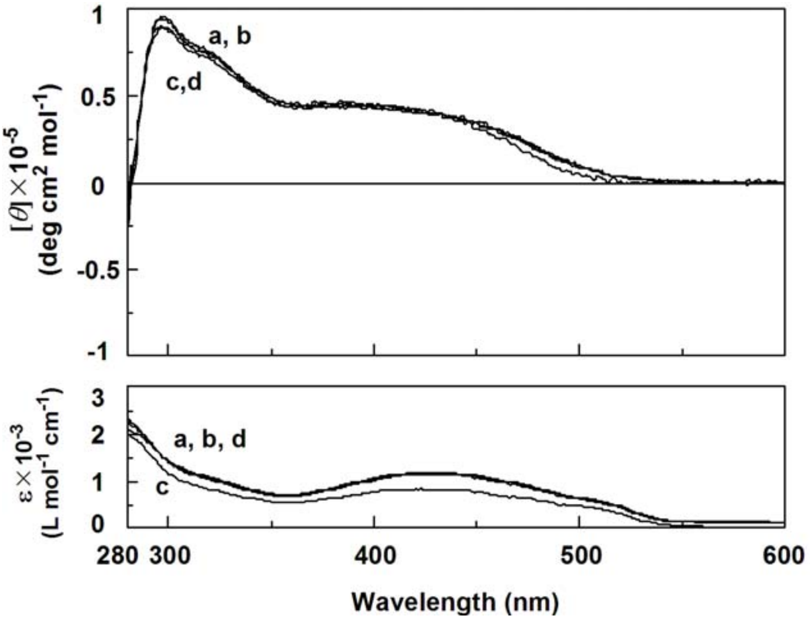


Figure 4. CD and UV-vis spectra of poly(**1**) in (a) $CHCl_3$; (b) $CHCl_3$ / DMSO = 95 / 5 (v / v); (c) $CHCl_3$ / DMSO = 90 / 10 (v / v); (d) $CHCl_3$ / DMSO = 95 / 5(v / v) ((d) was the solution prepared by addition of $CHCl_3$ to the solution of (c)).

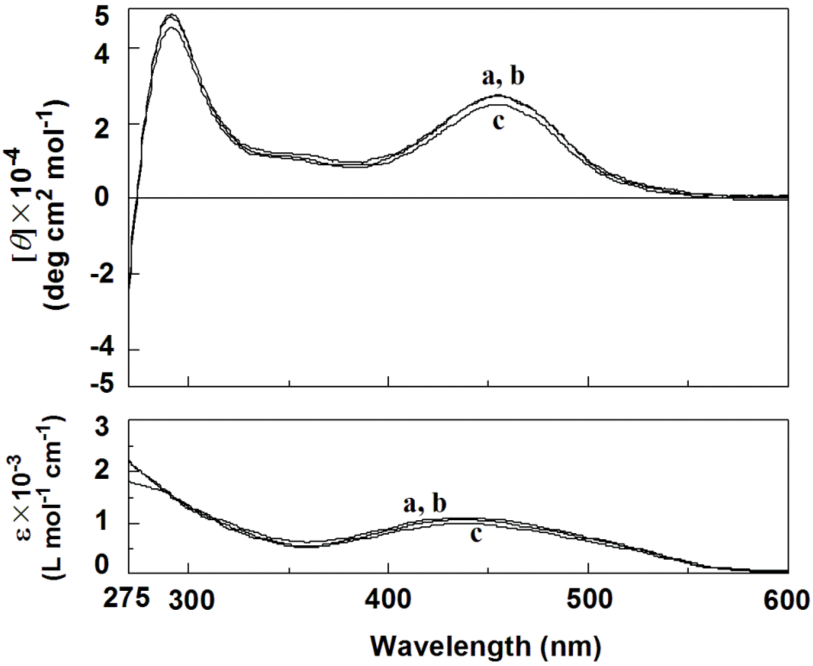


Figure 5. CD and UV-vis spectra of poly(**2**) in (a) THF; (b) THF / DMSO = 95 / 5 (v / v); (c) THF / DMSO = 90 / 10 (v / v).

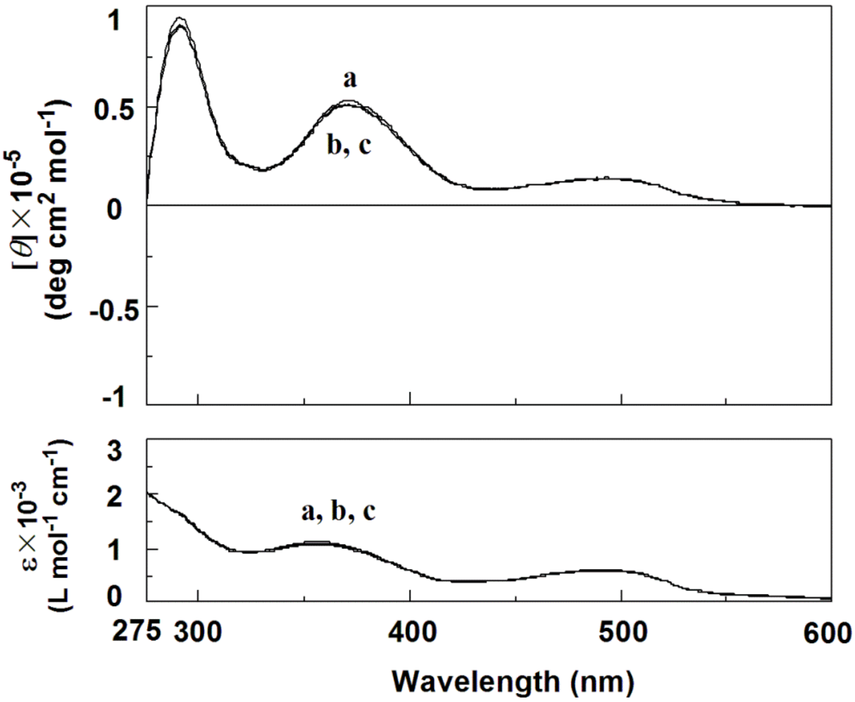


Figure 6. CD and UV-vis spectra of poly(**3**) in (a) THF; (b) THF / DMSO = 95 / 5 (v / v); (c) THF / DMSO = 90 / 10 (v / v).

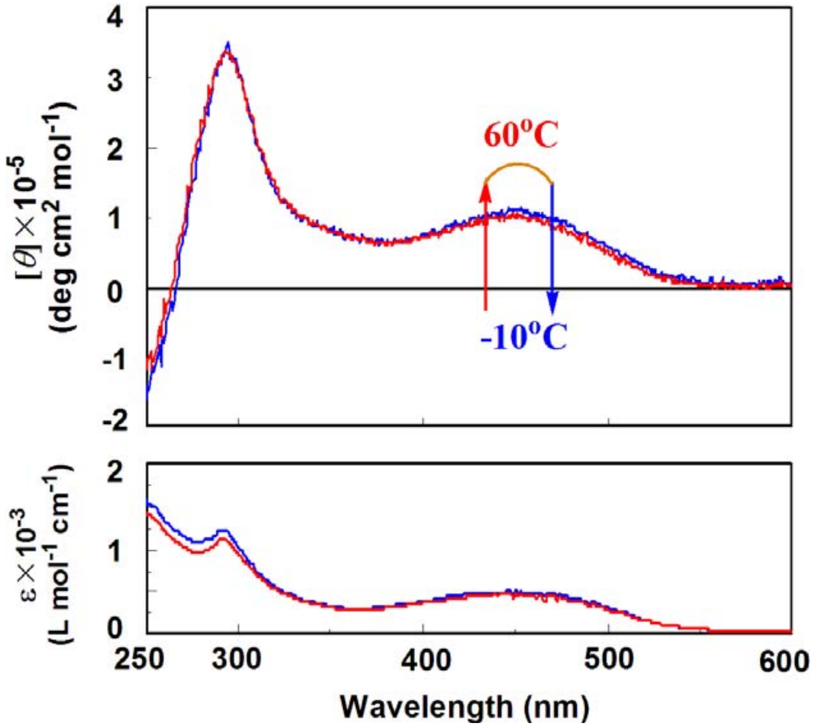


Figure 7. Dependence of temperature on [*θ*] of poly(**2**) in THF.

Since the one handed helicities of the three poly(DoDIPA), poly(**1**) ~ poly(**3**) were not affected by change of the polarity of the solvent, the helicity was thought to be maintained not by intramolecular hydrogen bonds but by steric interactions. This was directly proved by the fact that monomer **3** having no functional groups which could make hydrogen bonds was also suitable to the HSSP to give a one-handed helical polymer (Figures 2 and 3), and poly(**3**) was also stable to polar solvents (Figures 5 and 6). Therefore, we successfully found a new type of monomers having no groups making hydrogen bonds suitable to the HSSP. Since this type of monomers does not need to have groups making hydrogen bonds, the monomers RDIPAs are more general and valuable than RDHPAs.

The stability of the one-handed helical conformation was thought to be based on the rigidity of the main chain which was estimated by NMR. Judging from the half width of the NMR peaks, the backbone of poly(DoDIPA) in polar and nonpolar solvent was thought to be very rigid similarly to that of poly(DoDHPA) in nonpolar solvent. The one-handed helicity of poly(DoDHPA) was not affected by polar solvents and heating and therefore eternally stable.

2.4.3 High efficiency of the chiral induction of the HSSP of RDIPA

The efficiency of the chiral induction during the HSSP of the new monomers (DoDIPA) was much higher than that of the previous monomers having two hydroxyl groups(DoDHPA) (*i.e.,* the minimum amounts of the chiral source needed to obtain CD active polymers by the HSSP of DoDIPA were much lower than those of DoDHPA) as shown in Table 1. For example, monomer **1** needed only more than [chiral cocatalyst] / [monomer] = 0.00500 to obtain chiral polymers having more than $g = 1.0$, while DoDHPA needs [chiral cocatalyst] / [monomer] = 2.50 to obtain chiral polymers having more than $g = 1.0$. In the case of DoDHPA, to obtain CD-active polymers ($g > 0.05$), more than 0.250 of [chiral cocatalyst] / [monomer] was necessary, while monomers **1** and **3** needed only 0.00300 and 0.0200 of [chiral cocatalyst] / [monomer], respectively. Therefore, the monomers (**1**~**3**) needed only catalytic amounts of chiral source. Since they had higher efficiency in chiral induction during the HSSP, they were more suitable to the HSSP than DoDHPA. Since they did not need functional groups which could make hydrogen bonds such as hydroxyl groups, the finding enlarged the range of design of monomers having possibility to be suitable for the HSSP. Therefore, RDIPA is more general and valuable than RDHPA as a HSSP monomer.

In conclusion, we found a new type of monomers which were more suitable and more general and more valuable to the HSSP because it produced an intrinsically stable one-handed helical polymer by using a catalytic amount of chiral source. It will be able to make the HSSP method more valuable and more useful in the field of asymmetric polymerization.

2.4.4 Comparison of the suitability of 1~3 for the HSSP

All the three RDIPA monomers (**1**~**3**) we newly synthesized in this study were found to be suitable to the HSSP as described above. When we compare them in the same condition (the same ratio of the chiral cocatalyst to the monomer =1.00) (Table 1, no. 3, 8, 11), monomer **1** gave polymers having the highest *g* value (Table 1, no. 3). In addition, the smallest ratio of the cocatalyst to the monomer (= 0.00300) was sufficient for **1** to give the resulting polymers clear CD signals (Table 1, no. 6). Therefore, **1** was the best monomer which had the highest efficiency of chiral induction among the three monomers.

2.4.5 Reason for the suitability of RDIPA and monomer 1 to the HSSP

Semiempirical calculations were carried out on a PC equipped with an Inter (R) Core (TM) 2 processor (1.87 GHz) using Spartan Student v 5.0.0.0. All the conformations of monomers were calculated by MMFF.

The initial condition for the calculation of monomer energies and structures was as follows: the dihedral angles of C=N-Ar of monomers were constrained at 180°, 0° and -180° in advance, then the MMFF was used for optimization of monomer energies and structures. The results are shown in Table 2.

Table 2. Calculation data of π-conjugated planar structures of DoDIPA monomers (**1**~**3**) by MMFF.

Monomer	**Energy [kJ/mol]**				**Δ E** [b]
	trans-trans [a]	**trans-cis** [a]	**cis-cis** [a]	**cis-trans** [a]	**[kJ/mol]**
1	331.42	410.04	591.64	480.29	79
2	352.35	437.45	495.32	405.43	53
3	412.55	393.45	452.29	475.51	19

[a] For the conformation, see Chart 2; [b] The energy difference between conformation having the lowest energy and the second lowest energy.

The initial condition for calculation of polymer energies and structures was as follows: the dihedral angles of polymer main chain were constrained at a different degree in advance, the MMFF level was used for optimization of polymers structures. Then, the dihedral angles of the polymer main chain were unconstrained, the MMFF calculation was carried out once again. The results are shown in Table 3.

Table 3. Calculation data of 3D structures of poly(**1**) by MMFF.

Conformation [a)]	**Dihedral angle [º]** [b)] (constrained)		**Energy [kJ/mol]**	**Dihedral angle [º]** [b)] (unconstrained)		**Energy [kJ/mol]**
	A	**B**		**A**	**B**	
trans-trans	110	-58.16	2350	123.27	-70.10	2310
trans-cis	120	-65.54	6540	111.67	-54.46	2679

[a)] See Chart 2; [b)] See Chart 3.

As mentioned above, RDIPAs were much better monomers than RDHPAs and **1** was the best in the three RDIPAs. Since RDIPAs had a bulky π-conjugated planar substituent, the one-handed helical main chains were thought to be stabilized by the steric hindrance. Therefore, the main chains were thought to be intrinsically stable.

In order to know more information of the reason for the best suitability of **1** for the HSSP, we calculated the energy of the four possible π-conjugated planar conformations, trans-trans, trans-cis, cis-cis, and cis-trans as shown in Chart 2 of the three DoDIPA monomers (**1**~**3**) using MMFF (Table 2). There seems to be mainly two factors determinate the energy: steric repulsion between the dodecyl group and the N- or O-alkyl groups for the three monomers (**1**~**3**) and hydrogen bonds between the amino groups and imino group for the monomers **1** and **2**. Since the ether-containing monomer **3** can't make hydrogen bonds, the stability must be determined only by the steric repulsion. The increasing order of the energy of the conformation of monomer **3** was trans-cis < trans-trans < cis-cis < cis-trans as shown in Table 2. On the other hand, in the case of the amine-containing monomers **1** and **2** which can make intramolecular hydrogen bonds at trans-trans and cis-trans conformations as shown in Chart 2, the orders were trans-trans < trans-cis and cis-trans < cis-cis which were different from those of **3**. The energy may be lowered by the hydrogen bonds in trans-trans and cis-trans as shown in Figure 8. Therefore, the orders between trans-trans and trans-cis, and cis-trans and cis-cis were different between monomers **1**, **2** and **3**. As a result, trans-trans had the lowest energy in the amine-containing monomers, **1** and **2**.

To stabilize one handed helical conformation of the resulting polymers of the HSSP of RDIPA, the conformer trans-trans of a monomer unit is thought to be the best, because the trans-trans conformer (Figure 8a)) can keep sterically the helicity more easily than the other conformers like cis-trans (Figure 8b)). Therefore, the amine-containing monomers **1** and **2** having trans-trans conformation as the most stable conformer were better monomers than **3**. When we compared **1** with **2**, the energy difference (ΔE) of **1** between the lowest and the second lowest was higher than **2** (Table 2). Therefore, monomer **1** may be the best.

To confirm this speculation, that is, the conformer trans-trans was the best, the energies of the polymers of trans-trans and trans-cis of **1** were calculated (Table 3). As a result, the former one was more stable. Therefore, monomer **1** was the best. It was supported by the experimental facts that **1** showed the best results in the HSSP.

In summary, chiral induction efficiency during of the HSSP of monomer **1** having two longer alkyl groups via imino and amino groups was the highest because the monomer can take a conformation (trans-trans) which are favorable to stabilize satirically the one-handed helical conformation of the resulting polymers.

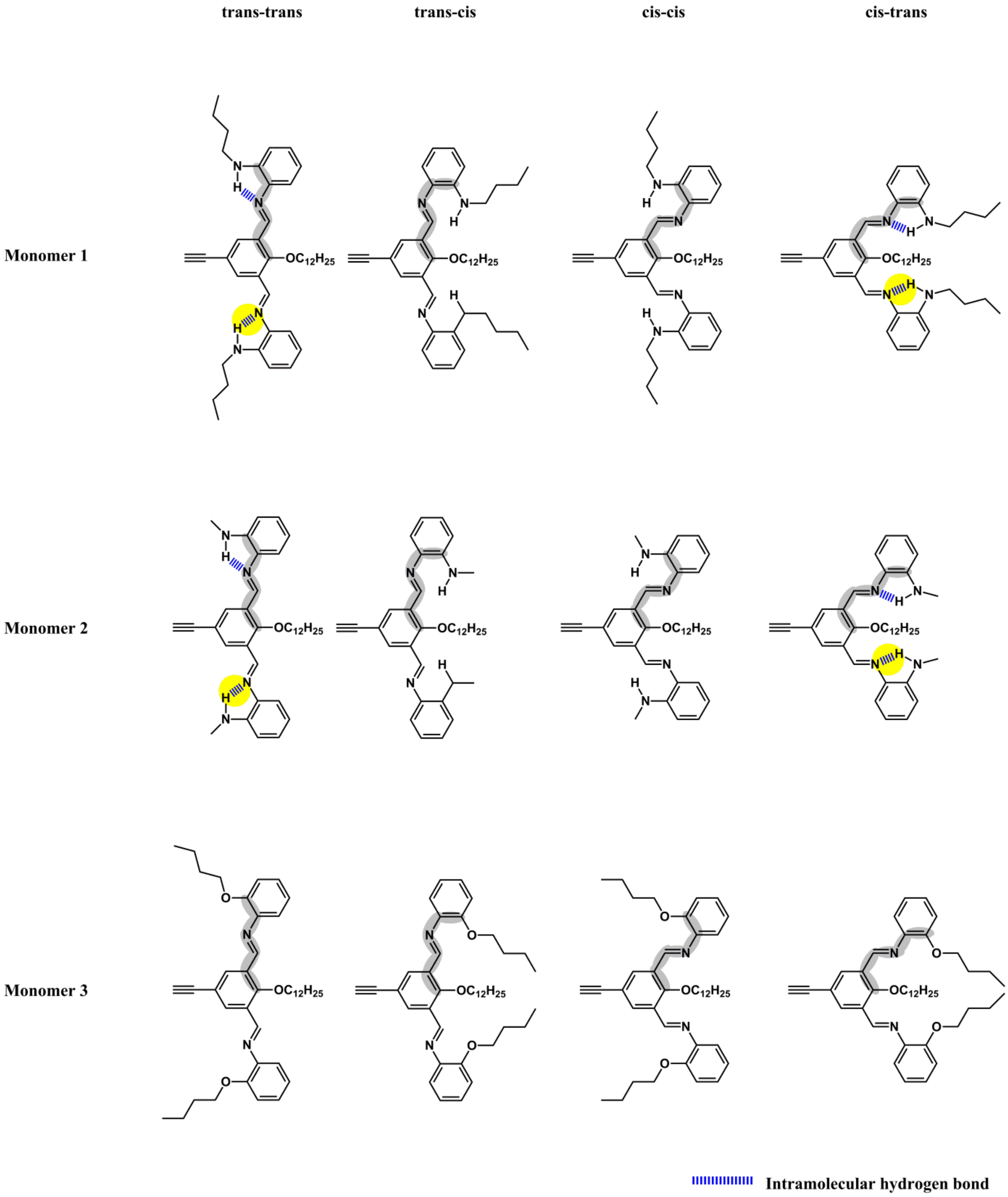


Chart 2. Possible π-conjugated planar conformations of DoDIPA monomers (**1**~**3**).

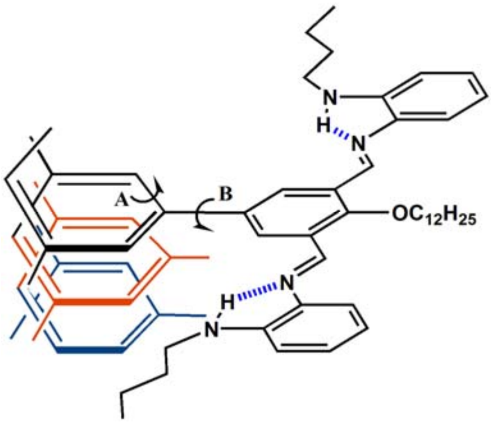


Chart 3. Dihedral angles of A (main chain) and B (side chain) of poly(**1**).

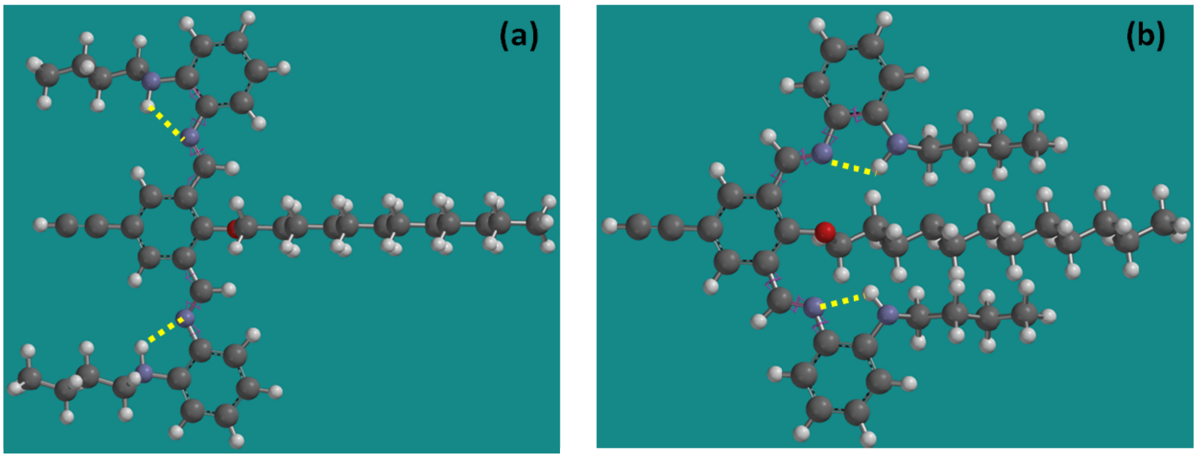


Figure 8. MMFF-optimized conformation of monomer (**1**) (a) suitable conformation (trans-trans) to HSSP and (b) unsuitable conformation (cis-trans) to HSSP (┈: hydrogen bonds). (See Chart 2).

2.5 Conclusions

In conclusion, we synthesized and polymerized a new type of three achiral substituted acetylene monomers (RDIPA), suitable to the helix-sense-selective polymerization (HSSP), which contained two bulky π-conjugated planar substituents via imine bonds and an alkyloxy group, by the chiral catalytic system for the HSSP. The resulting polymers had a one-handed helical main chain stabilized by intramolecular steric hindrance. The chiral main chains were very stable and the minimum amounts of the chiral source needed to obtain CD active polymers were much smaller than that of the previous monomers having two hydroxyl groups. Therefore we found new valuable monomers which were more suitable and more general to the HSSP. Monomer **1** having amino groups and longer alkyl groups via imino bonds showed higher efficiency of the chiral induction than the corresponding monomer having ether bonds instead of amino groups. The higher chiral induction efficiency during the HSSP of the monomer **1** was caused by the fact that the monomer can take a conformation (trans-trans) which was favorable to stabilize the one-handed helical conformation of the resulting polymers.

References and Notes

[1] For helical polyacetylenes: (a) Akagi, K. *Chem. Rev.* **2009**, *109*, 5354; (b) Liu, J.; Lam, J. W. Y.; Tang, B. Z. *Chem. Rev.* **2009**, *109*, 5799; (c) Yashima, E.; Maeda, K.; Lida, H.; Furusho, Y.; Nagai, K. *Chem. Rev.* **2009**, *109*, 6102; (d) Rosen, B. M.; Wilson, C. J.; Wilson, D. A.; Peterca, M.; Imam, M. R.; Percec, V. *Chem. Rev.* **2009**, *109*, 6275.

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Chapter 3

Helix-Sense-Selective Polymerization of Fluorine-Containing Achiral Phenylacetylenes

3.1 Abstract

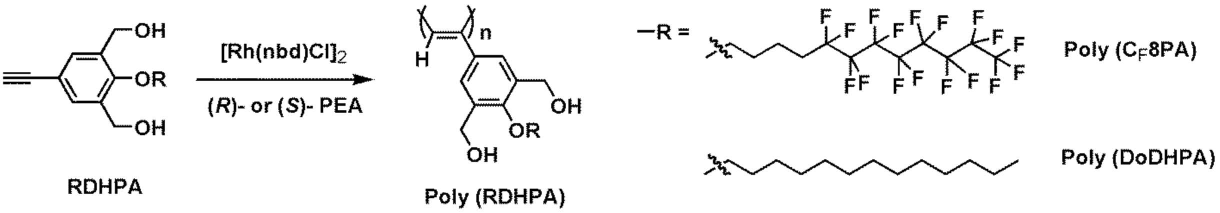
To develop new phenylacetylene monomers suitable for helix-sense-selective polymerization (HSSP) we reported previously and to improve the efficiency and ability of chiral induction of HSSP of C_F8DHPA, *i.e.*, it needed only catalytic amounts of the chiral source and the resulting polymer having higher relative optical purity, a novel phenylacetylene monomer having a perfluorinated alkanes side group was synthesized and polymerized by a chiral catalytic system. The efficiency and ability of the chiral induction were much higher than that in the case of the previous monomers having perhydrogenated alkanes side group we reported. In addition, the fluorine containing polymers membrane showed high selectivity of selective photocyclicaromatization (SCAT). The SCAT product of poly(C_F8DHPA) was used as surface modifier for PDPA, and the resulting blend membrane T-F / PDPA showed higher oxygen permselectivity than T-Do / PDPA membrane which was modified by SCAT product of poly(DoDHPA).

3.2 Introduction

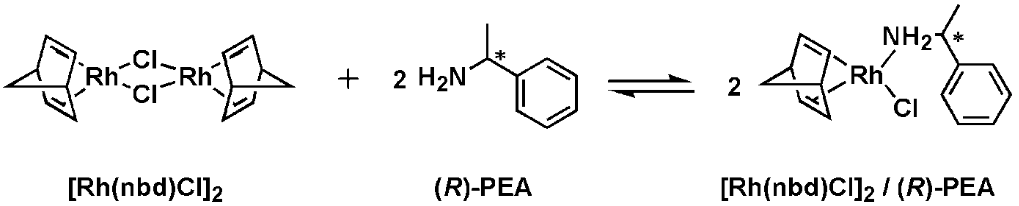
π-Conjugated polymers like polyacetylenes have aroused interest because of their noteworthy physical properties such as conductivity, organomagnetism, and optical non-linear susceptibility. Recently chiral polyacetylenes [1] have attracted much attention since the chiral structure can enhance the unique properties and add new functions.

Now, two methods major synthetic strategies have been developed to synthesize soluble chiral polymers whose chiral structures are present alone in the main chain as asymmetric carbons and/or as a one-handed helical conformation. One is HSSP [2] of an achiral monomer by using a chiral catalyst as a chiral source and the other is asymmetric-induced polymerization, by using achiral catalysts, of monomers having a chiral group as a chiral source, followed by removing the chiral groups by a polymer reaction in solution where the chiral groups were desubstituted from the resulting one-handed helical polymers (AIP-R). [3]

HSSP is a direct synthetic method of soluble chiral π-conjugated polymers whose chiral structures arise solely from the one-handed helical conformation of the conjugated main chains (therefore, they have no asymmetric carbons) and are stable alone in solution was so far only the helix-sense-selective polymerization (HSSP) of an achiral phenylacetylene monomer DoDHPA (Scheme 1) by using a chiral catalytic system $[Rh(nbd)Cl]_2$ / (*R*)-phenylethylamine ((*R*)-PEA) developed in our laboratory. [4] However, in the HSSP suitable monomers were limited. In addition, the efficiency of the chiral induction was not high, *i.e.*, a large ratio of the chiral cocatalyst to the monomer (Chart 1, (*R*)- or (*S*)-PEA) was needed. In order to estimate performance of the chiral initiators, we define the efficiency and ability of them in the HSSP. The efficiency was estimated by the value of [Chiral ligand] / [Monomer]. When the value is smaller, the efficiency is higher. The ability was estimated by a relative optical purity(%) = (a [θ] value of an obtained polymer / the highest [θ] value among all of the polymers) × 100. For the previous HSSP [4], a stoichiometric amount of chiral cocatalyst, (*R*)-PEA ([chiral ligand] / [Monomer] = 0.25) was needed in the initiator system (Scheme 2).



Scheme 1. Helix-sense-selective polymerization (HSSP) of **RPA**.



Scheme 2. Two component chiral initiator system in our previous study.

The fluorinated polymers represent a class of very interesting and versatile polymeric materials and have attracted much attention because of their outstanding properties such as low dielectric constant, low friction, low refractive index, high transparency and low surface energy, as well as excellent chemical and thermal resistance. [5] It is well-known that perfluorinated alkanes are more rigid and less miscible (fluorophobic effect) than the corresponding perhydrogenated alkanes. [6] As fluorine-containing compounds have an oxygen affinity, it is expected to enhance oxygen permselectivity.

Recently, a valuable reaction selective cycloaromatization (SCAT) was reported by our group. [7] The SCAT reaction had many unique characteristics, such as unusual selectivities, as follows. 1) It is a quantitative reaction: it gave only the corresponding cyclic trimer, *i.e.*, a 1,3,5-trisubstituted benzene derivative, quantitatively(= 100%). No by-products were produced under the best condition. 2) It is an intramolecular reaction: it occurred between adjacent three monomer units in one macromolecule. 3) It is a stereospecific and topochemical or template reaction: the reactivity strongly depended on the configuration and conformation of the starting polymer substrates. 4) It is a photoreaction: high selectivity (= 100%) was observed only by the use of visible light irradiation, not by heating. 5) It is a solid state reaction: high selectivity(=100%) was observed only in the solid state, not in solution. *In addition*, 6) the resulting cyclic trimers had the ability to form a self-supporting membrane, in spite of their low molecular weights. This new approach resulted in a new class of supramolecular polymers consisting of a 1,3,5-trisubstituted benzene derivative, numbers of which were linearly linked by hydrogen bonds and stacked benzenes. Since SCAT has such high selectivities and is useful for the preparation of a self-supporting supramolecular polymer membrane, many kinds of applications can be expected.

In this chapter, a novel fluorine-containing achiral phenylacetylene monomer having two hydroxyl groups making hydrogen bonds (Scheme 1) suitable for the HSSP was reported. In addition, the higher efficiency and ability of chiral induction of HSSP of C_F8DHPA were reported as well, *i.e.*, it needed only catalytic amounts of the chiral source and the resulting polymer having higher relative optical purity. The fluorine-containing polyphenylacetylene was SCAT active polymer. The SCAT product 1,3,5-trisubstituted benzene derivative was used as a surface modifier to enhance the O_2 permselectivity of poly(1-phenyl-2-[*p*-(trimethylsilyl)phenyl]acetylene) (PDPA) membranes.

3.3 Experimental

3.3.1 Materials

All the solvents used for synthesis and polymerization of the monomers were distilled as usual. The polymerization initiator, $[Rh(nbd)Cl]_2$ (nbd = 2,5 norbornadiene), purchased from Aldrich Chemical was used as received. 4-Dodecyloxy-3,5-bis(hydroxymethyl)phenylacetylene (**4**) was synthesized from 4-bromophenol according to our previous report.[4a] Poly(DoDHPA) and T-DO were prepared according to our previous report. [7]

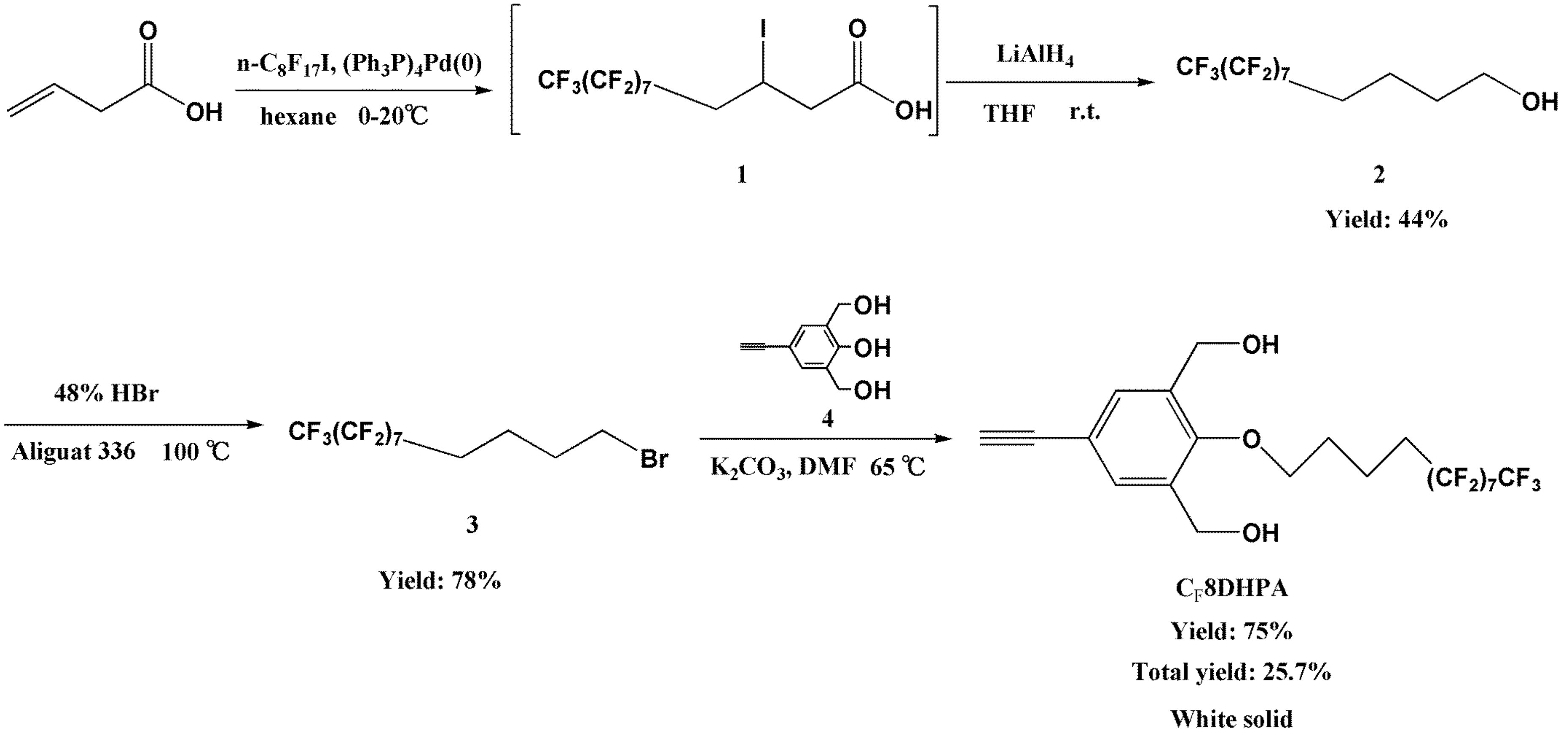
3.3.2 Measurements

^{1}H NMR (400MHz) spectra were recorded on a JEOL LEOLEX-400 spectrometer. The average molecular weights (M_n and M_w) were evaluated by gel permeation chromatography (GPC) by using JASCO liquid chromatography instruments with PU-2080, DG-2080-53, CO-2060, UV-2070, CD-2095, and two polystyrene gel columns (Shodex KF-807 L, THF eluent, polystyrene calibration). We recorded CD spectra by using a JASCO J-720WI spectropolarimeter with a Peltier controller for temperatures at 20℃ (a quartz cell of 1 mm path length; sample concentration: 0.100 to 2.00 mM based on the monomer unit). The infrared spectra were recorded on FT/IR-4200 (JASCO).

3.3.3 Synthesis of the monomer C_F8DHPA (Scheme 3)

3.3.3.1 1*H*, 1*H*, 2*H*, 2*H*, 3*H*, 3*H*, 4*H*, 4*H*-Perfluorododecyl bromide (**3**)

Compound **3** was synthesized according to the Percec's report, [6] a white needle-like crystal was obtained with the total yield of 44.0% (0.426 g). ^{1}H NMR (400MHz, $CDCl_3$, TMS, δ): 3.44 (t, 2H, J =6 Hz, CH_2CH_2Br), 1.75~2.16 (overlapped peaks, 6H, $CF_2CH_2CH_2CH_2$).



Scheme 3. Synthetic route of C_F8DHPA.

3.3.3.2 2, 6-Bis(hydroxymethyl)-4-ethynylphenol (**4**)

Compound **4** was synthesized according to the previous report [4a], a white solid was obtained with the total yield of 40.4% (3.8 g). ^{1}H NMR (400MHz, DMSO-d_6, δ): 8.98 (s, H, PhO*H*), 7.27 (s, 2H, Ph*H*), 5.29 (s, 2H, Ph(CH_2OH)$_2$), 3.91 (s, 1H, C*H*≡C).

3.3.3.3 4- (1*H*, 1*H*, 2*H*, 2*H*, 3*H*, 3*H*, 4*H*, 4*H*-Perfluorododecyloxy)-3,5-bis(hydroxymethyl)phenylacetylene (C_F8DHPA)

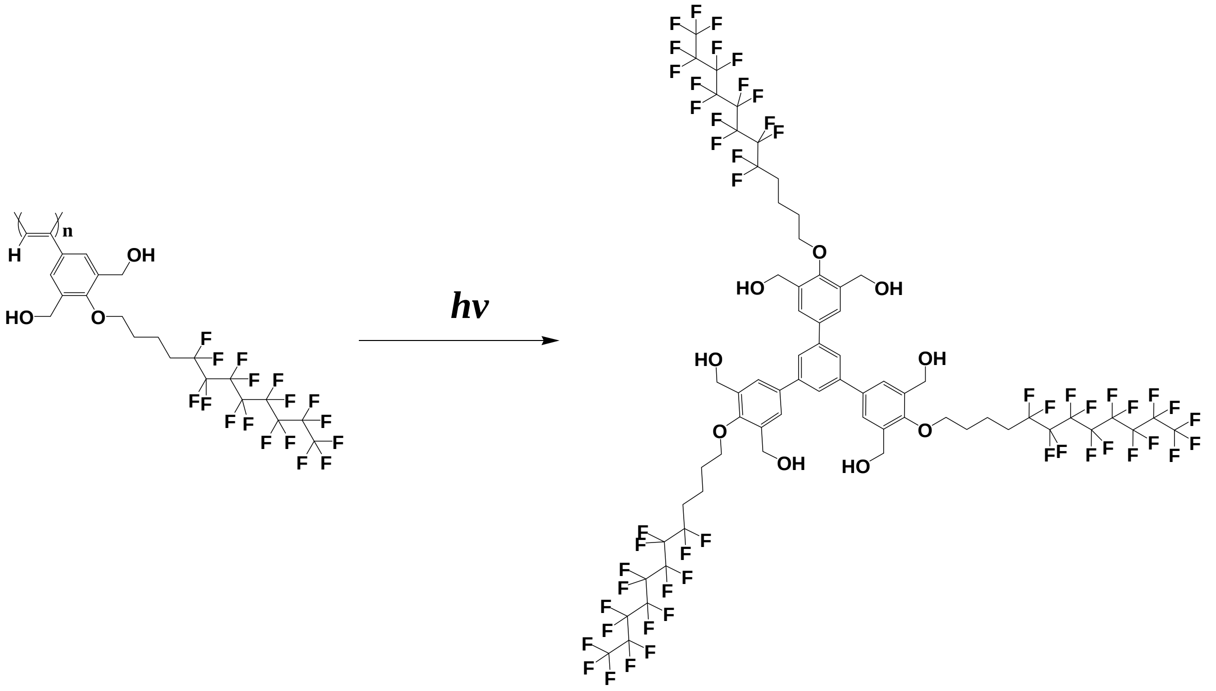
A mixture of **3**(536 mg, 0.970 mmol), **4** (157 mg, 0.880 mmol) and K_2CO_3 (346 mg, 2.46 mmol) in DMF (5 mL) was stirred for 40h at 65℃.After the mixture was filtered, the solvent was removed. The residue was washed with water and extracted with ethyl acetate. The organic layer was dried over MgSO4 and concentrated. The crude product was purified by silica-gel column chromatography to give aim product C_F8DHPA. Rf = 0.42 (hexane/ethyl acetate = 2/1). ^{1}H NMR (400MHz, $CDCl_3$, TMS, δ): 7.44 (s, 2H, C≡CPh*H*), 4.65 (d, 4H, *J* = 6Hz, Ph(CH_2OH)$_2$), 3.89 (t, 2H, *J* = 6 Hz, OCH_2CH$_2$), 2.98 (s, 1H, *H*C≡C), 2.12 (m, 2H, CH$_2$CH_2CF$_2$), 1.84 (m, 4H, OCH$_2$(CH_2)$_2$CH$_2$CF$_2$). ^{19}F NMR ($CDCl_3$, C_6F_6, δ): -83.88 (t, 3F, C*F*$_3$, *J*=11Hz), -117.48 (m, 2F, CH$_2$CF_2), -124.81 (m, 6F, (CF_2)$_3$CF$_2$CH$_2$), -125.81 (s, 2F, CF_2CF$_2$CF$_2$CF$_3$), -126.58 (s, 2F, CF$_2$CF_2CF$_2$CF$_3$), -129.21 (s, 2F, CF$_2$CF$_2$CF_2CF$_3$). IR (cm^{-1}, KBr): 3361 (OH), 3294 (HC≡C), 1240 (CF_3), 1207 (CF_2), 656 (CF_3). Anal. Cacld for $C_{22}H_{17}F_{17}O_3$: C, 40.51; H, 2.63; F, 49.40. Found: C, 40.28; H, 2.64; F, 49.40.

3.3.4 Polymerization of monomers (Scheme 1)

A typical procedure for monomer C_F8DHPA was as follows: A solution of [Rh(nbd)Cl]$_2$ (0.280 mg, 0.613 μmol) and (*S*)- or (*R*)- phenylethylamine (PEA) (15.7 μl, 0.123 mmol) in dry perfluorobenzene (0.154 mL) was added to a dry perfluorobenzene (0.154 mL) solution of C_F8DHPA (20.0 mg, 30.7 μmol). The reaction solution was stirred at room temperature for 4h. The crude polymer was purified by reprecipitation of perfluorobenzene solution into a large amount of methanol and the formed solid was dried *in vacuo* to give a red solid.

Other helix-sense-selective polymerization (HSSP) of the monomers C_F8DHPA and DoDHPA were carried out similarly.

3.3.5 Preparation of T-F (Scheme 4) [7]



poly(C_F8DHPA) T-F

Scheme 4. SCAT of poly(C_F8DHPA).

A solution of poly(C_F8DHPA) in perfluorobenzene (13 mg/mL) was cast on a poly(tetrafluoroethylene) sheet (100 cm^2), and the solvent was evaporated for 24 h at room temperature. The membrane (thickness 20.0 μm) was irradiated under nitrogen by visible light (400-500 nm, 2.54 mW/cm^2) for 3 days. The reaction was monitored by GPC detected by UV and CD. Visible light (400-500 nm) irradiation was carried out by using a 300 W of Xe lamp (Asahi Spectra, MAX-302 with vis mirror module) through a cutoff filter (Asahi Spectra, LUX400 ($\lambda > 400$ nm), XF541 ($\lambda < 510$ nm), and XF546 ($\lambda < 610$ nm). All the resulting products were totally soluble and no insoluble parts were obtained.

Yield: 99.8%. ^{1}H NMR ($CDCl_3$, TMS, ppm): δ = 7.41~6.93 (m, 9H, PhPh*H* and Ph*H*($CH_2OH)_2$)), 5.01 (t, 6H, Ph(CH_2O*H*$)_2$), 4.62 (d, 12H, Ph(C*H*$_2$OH$)_2$), 3.97 (m, 6H, OC*H*$_2CH_2CH_2CH_2$), 2.12 (m, 6H, $OCH_2CH_2CH_2$C*H*$_2CF_2$), 1.92 (m, 12H, OCH_2C*H*$_2$C*H*$_2CH_2CF_2$). IR (film): 3375cm^{-1} (OH), 2955cm^{-1} (CH), 1207cm^{-1} (CF). TOF-MS m/z (M + Na$^+$): Calcd. 1979.26, Found.

3.3.6 Membrane preparation

A typical blend membrane fabrication method for T-F/PDPA was as follows: A solution of the T-F in $CHCl_3$ and a solution of the base polymer PDPA in toluene were blended together, and then the resulting blend solution was cast on a poly(tetrafluoroethylene) sheet. After evaporating the solvent for 24h at room temperature, the membranes were detached from the sheet and dried in *vacuo* for 24 h. Thickness (*L*) of the membranes was 7.00~12.0 μm.

3.4 Results and discussion

3.4.1 Achievement of HSSP of new monomer C_F8DHPA

As described in the introduction, the monomers suitable for the HSSP were limited. Therefore, to develop new monomers more suitable for the HSSP than DoDHPA (Chart 1) we reported previously,[4a] a novel fluorine-containing achiral phenylacetylene monomer C_F8DHPA was synthesized. The monomer was polymerized by using the chiral catalytic system, $[Rh(nbd)Cl]_2$ and chiral phenylethylamine ((*R*)- or (*S*)-PEA) that we previously developed for the HSSP of DoDHPA[1a] as shown in Table 1. All the polymerizations were carried out in perfluorobenzene because the fluorine-containing polymers poly(C_F8DHPA) are insoluble except in perfluorobenzene.

The resulting polymers of C_F8DHPA showed a large Cotton signal in the range of main chain absorption (Figures 1), indicating that all the polymers exist in excess one-handed helical conformation. Therefore, the HSSP of C_F8DHPA has been successfully achieved.

Table 1. HSSP of C$_F$8DHPA and DoDHPA at room temperature [a)]

No.	Monomer	Solvent	[Chiarl cocatalyst] /[Monomer]	Yield (%)	g_{308} [b] ($\times 10^{-5}$)
1	C$_F$8DHPA	toluene	4.0	67	0
2		perfluorobenzene	4.0	80	-0.75
3		perfluorobenzene	2.0	80	-0.21
4	DoDHPA	toluene	4.0	92	0.22

[a] [M]=0.1mol/L; [chiral amine]/[Rh(nbd)Cl]$_2$]= 200; [M]/[[Rh(nbd)Cl]$_2$]= 50, for 4h. [b] g value at 308nm, $g = ([\theta]/3300/\varepsilon)\times 0.001$.

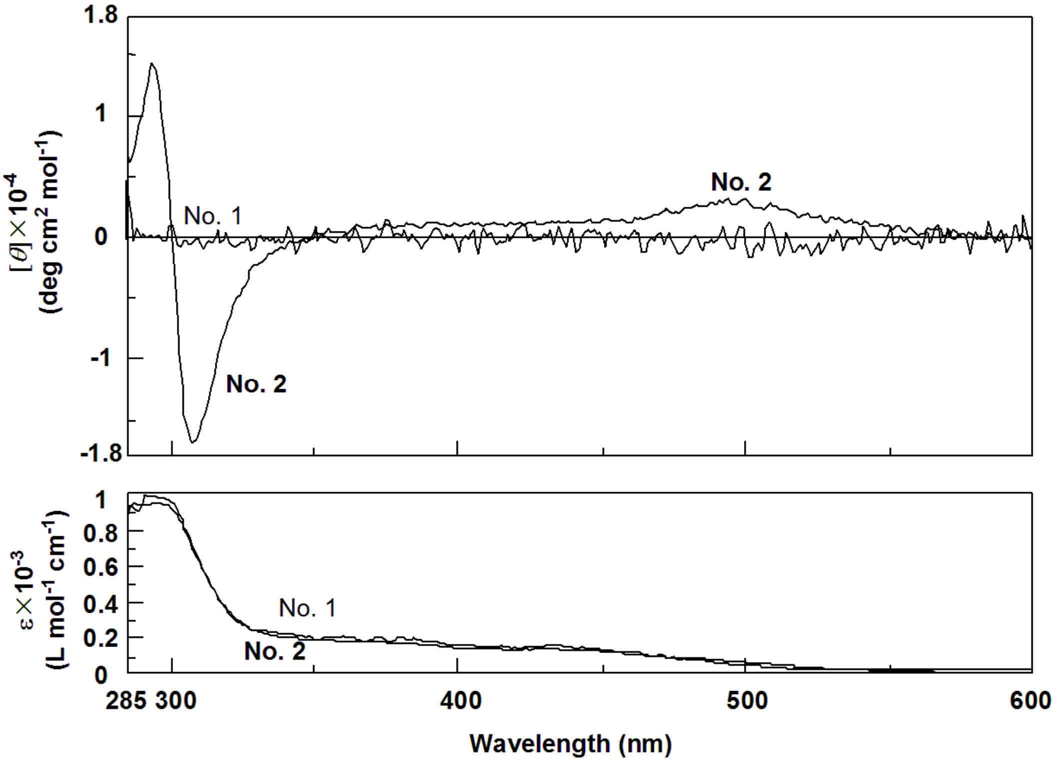


Figure 1. CD and UV spectra of poly(C$_F$8DHPA) in perfluorobenzene (Table 1, nos. 1 and 2).

The efficiency of the chiral induction during the HSSP of C$_F$8DHPA was much higher than that of the previous monomer DoDHPA. For example, monomer C$_F$8DHPA need only [Chiral cocatalyst]/[Monomer] = 2.0 to obtain chiral polymers having *g* = -0.21 (Table 1, no. 3), while DoDHPA needs [Chiral cocatalyst]/[Monomer] = 4.0 (Table 1, no. 4) to obtain chiral polymer having the similar *g* value. By using the same amount of [Chiral cocatalyst]/[Monomer] = 4.0, *g* value of poly(C_F8DHPA) showed 3.4 times higher ((Table 1, no. 2, g = -0.75)) than that poly(DoDHPA) ((Table 1, no. 4, g = -0.22). Therefore, C_F8DHPA is more suitable for HSSP than DoDHPA.

3.4.2 Synthesis of T-F by SCAT

A highly selective photocyclicaromatization reaction (SCAT in Scheme 4) of a red π-conjugated poly(C_F8DHPA) from a phenylacetylene having two hydroxyl groups and a perfluorinated alkanes to exclusively yield a non-colored 1,3,5-trisubstituted benzene derivative T-F was found and confirmed by GPC (Figure 2), ^{1}H-NMR. It was an almost quantitative reaction because it gave only the corresponding cyclic trimer, *i.e.*, a 1,3,5-trisubstituted benzene derivative without any by-products under the best condition, visible light irradiation in the membrane state.

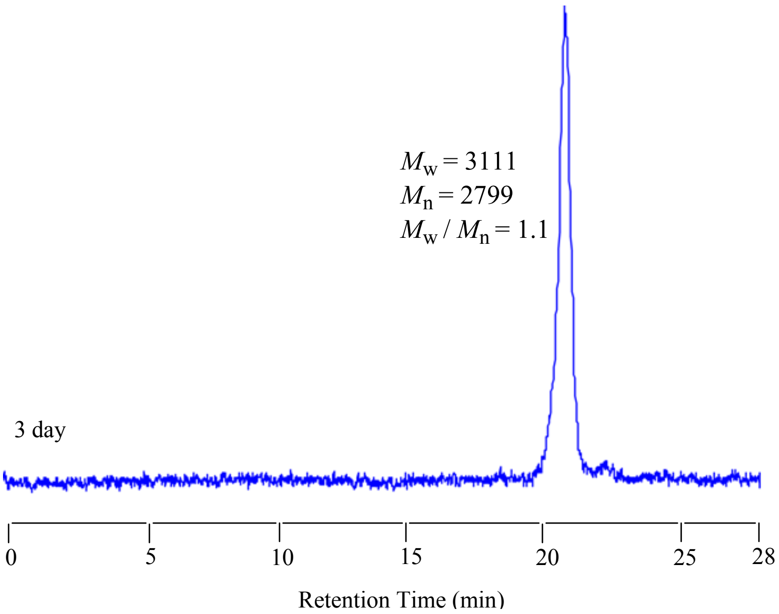


Figure. 2. GPC chromatograms of Poly(C_F8DHPA) membrane (thickness:15μm) after visible light irradiation under N_2 room temperature (LED (100000 lx)).

Amphiphilic molecule T-F was designed, the chemical structures were shown in Scheme 4. T-F contain three parts: (1) a rigid and hydrophobic disc-like 2D center; (2) three hydrophobic perfluorinated alkanes side chains at p-positions as an anchor; (3) six hydroxyl groups making intermolecular hydrogen bonds. The hydrophobic perfluorinated alkanes side chains anchored to the hydrophobic substrate polymer, the rigid and hydrophobic disc-like 2D center appeared on the surface of the substrate polymer and then the resulting 2D structures were fixed by intermolecular hydrogen bonds.

The surface modifications of PDPA substrate polymer membranes were achieved by using 5 wt% of amphiphilic molecule T-F and T-Do, respectively. The contact angles of water on blend membranes were shown in Tables 2. The contact angles of the blend membranes decreased notably by adding the additives to the membranes. The decreasing on contact angles may be coursed by the existence of free OH of T-F and T-Do which didn't make the intermolecular bond. As a result the surface of blend membranes were not perfect 2D structure.

O_2/N_2 permselectivity of the modified PDPA blend membranes were

Table 2. Contact angles of water and oxygen permeation of polymer or supramolecular polymer membranes of additives or substrates.

No.	Membrane	Content of additives in membranes (wt %)	Contact angle[b] (deg)	P_{O_2}[c] (barrer)	α[d]
1	T-F / PDPA	5	83.0 ± 1.6	937	2.28
2	T-Do / PDPA	5	65.0 ± 2.3	494	2.36
3	PDPA	-	110 ± 1.3	1510	1.96
4	Poly(C_F8DHPA)	-	104 ± 1.5	-	-
5	Poly(DoDHPA)	-	86.5 ± 1.1	141	2.61

[a] Contact angles for water droplets; [b] In $10^{-10}\cdot cm^3\cdot$ (STP)$\cdot cm\cdot cm^{-2}\cdot s^{-1}\cdot cmHg^{-1}$ (= 1 barrer); [d] $\alpha = P_{O_2}/P_{N_2}$.

measured and the results were list in the Table 2 and Figure 3. By the surface modification of the T-F (Table 2, no. 1), the O_2/N_2 permselectivity - α values of substrate PDPA membranes increased largely from 1.96 (Table 2, no. 3) to 2.28 (Table 2, no. 1) with a small drop in P_{O_2}. It may be caused by formation of a supromolecular structure of the amphiphilic molecules T-F having 2D regular size pores and thinner thickness in molecular level on the PDPA membrane surface. When the T-Do was used to modify the PDPA membrane, the α value increased highly, however, a large drop in P_{O_2} was happened simultaneously (Table 2, no. 2). This phenomenon may be caused by the T-Do/PDPA membrane exist more defects on the blend membrane than T-F/PDPA.

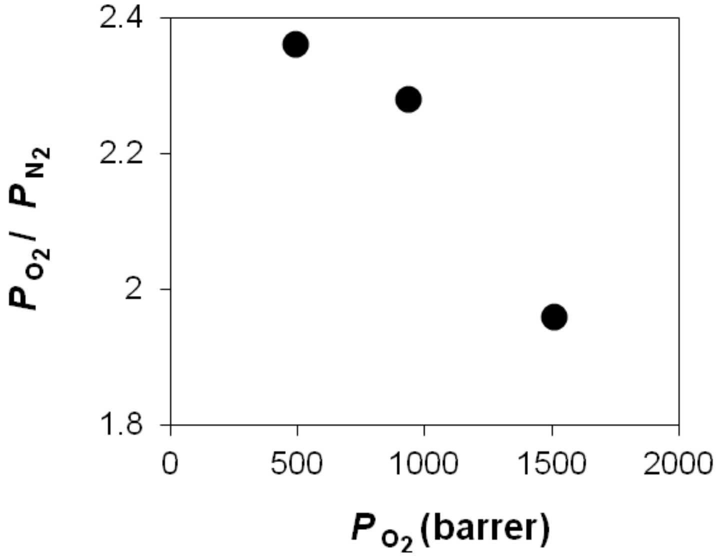


Figure 3. Oxygen permeation through blend membranes (the numbers in the figure correspond to those in Table 2).

8.5 Conclusions

A novel phenylacetylene monomer having a perfluorinated alkanes side group was synthesized and polymerized by a chiral catalytic system. The efficiency and ability of the chiral induction were much higher than that in the case of the previous monomers having perhydrogenated alkanes side group we reported. In addition, the fluorine containing polymers membrane showed high selectivity of selective photocyclicaromatization (SCAT). The SCAT product of poly(C_F8DHPA) was used as surface modifier for PDPA, and the resulting blend membrane T-F/PDPA showed higher oxygen permselectivity than T-Do/PDPA membrane, which was modified by SCAT product of poly(DoDHPA).

References and Notes

[1] For helical polyacetylenes: (a) Akagi, K. *Chem. Rev.* **2009**, *109*, 5354; (b) Liu, J.; Lam, J. W. Y.; Tang, B. Z. *Chem. Rev.* **2009**, *109*, 5799; (c) Yashima, E.; Maeda, K.; Lida, H.; Furusho, Y.; Nagai, K. *Chem. Rev.* **2009**, *109*, 6102; (d) Rosen, B. M.; Wilson, C. J.; Wilson, D. A.; Peterca, M.; Imam, M. R.; Percec, V. *Chem. Rev.* **2009**, *109*, 6275.

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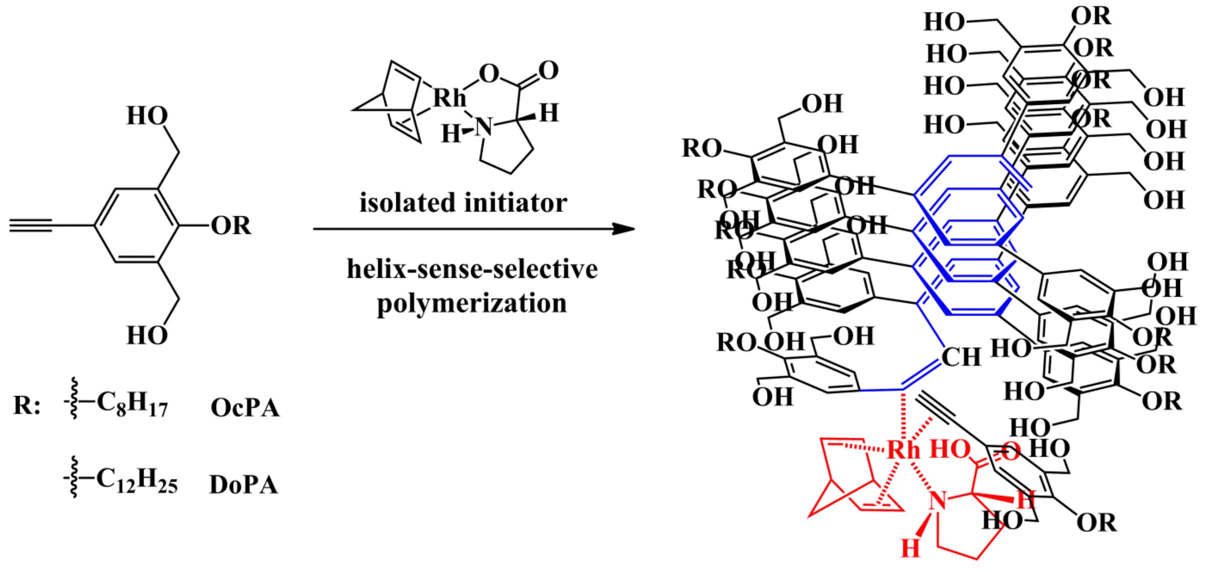
Chapter 4

Helix-Sense-Selective Polymerization of Substituted Acetylenes by Using an Isolated Rh Chiral Initiator with an Amino Acid Ligand

4.1 Abstract

Helix-sense-selective polymerization (HSSP) of substituted acetylenes by using an isolated chiral Rh initiator with an amino acid ligand has been achieved. The sense of the helix of the main chain of the resulting polymer was controlled by the sign of the chirality of the ligand. The isolated initiator needed less amount of the chiral ligand and gave polymers having a higher [θ] value than the two component chiral initiator systems we reported previously. The resulting polymers had a higher M_w.

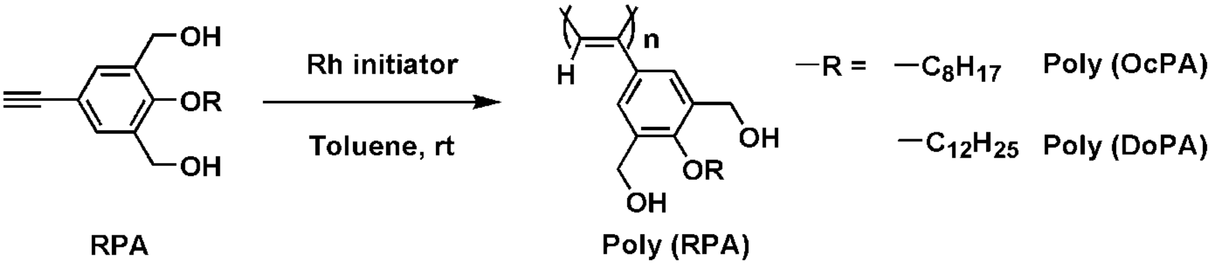


RPA

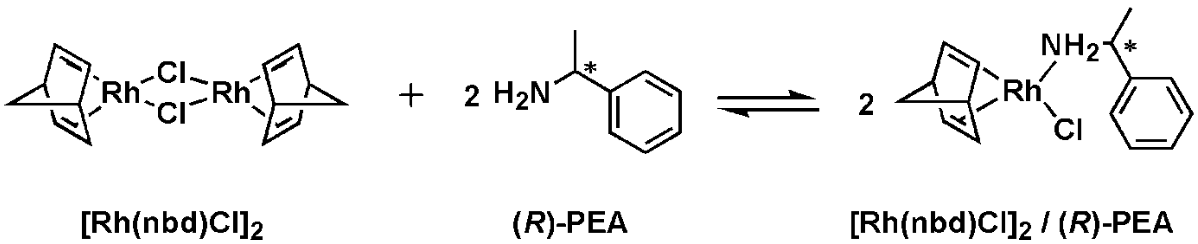
Poly(RPA)

4.2 Introduction

π-Conjugated polymers like polyacetylenes have aroused interest because of their noteworthy physical properties such as conductivity, organomagnetism, and optical non-linear susceptibility. Recently chiral polyacetylenes [1] have attracted much attention since the chiral structure can enhance the unique properties and add new functions. Several kinds of asymmetric polymerizations of achiral monomers to obtain chiral polymers having their chiral structures in their main chains have been reported. [2] Among them, a direct synthetic method of soluble chiral π-conjugated polymers whose chiral structures arise solely from the one-handed helical conformation of the conjugated main chains (therefore, they have no asymmetric carbons) and are stable alone in solution was so far only the helix-sense-selective polymerization (HSSP) of an achiral phenylacetylene monomer such as **DoPA** (Scheme 1) by using a chiral catalytic system $[Rh(nbd)Cl]_2$ / (*R*)-phenylethylamine ((*R*)-PEA)(Scheme 2) developed in our laboratory. [3]



Scheme 1. Helix-sense-selective polymerization (HSSP) of **RPA**.



Scheme 2. Two component chiral initiator system in our previous study.

In order to estimate performance of the chiral initiators, we define the efficiency and ability of them in the HSSP. The efficiency was estimated by the value of [Chiral ligand] / [Monomer]. When the value is smaller, the efficiency is higher. The ability was estimated by a relative optical purity(%) = (a [θ] value of an obtained polymer / the highest [θ] value among all of the polymers) x 100. For the previous HSSP [3], a stoichiometric amount of chiral cocatalyst, (*R*)-PEA ([chiral ligand] / [Monomer] = 0.25) was needed in the initiator system (Scheme 2).

However, we could not exclude the possibility that the chiral induction was partly caused by the interaction between chiral amines and two hydroxyl groups of the monomer because of the presence of the free (*R*)-PEA (Scheme 2). The coexistence of the chiral amine may lower the efficiency of the chiral induction during the HSSP. Therefore, isolation of the real active species from the $[Rh(nbd)Cl]_2$ / (*R*)-PEA was desired, but it was difficult due to the low stability. Only one chiral Rh initiator suitable for HSSP was reported by Hayashi [4e], but the synthetic route contained several steps and the total yield was not high.

In this communication, we report isolated chiral Rh initiators **1-3** (Scheme 3) which can be very easily obtained and suitable for HSSP of **RPA** (Scheme 1). The efficiency of the chiral induction during the HSSP was enhanced by using the isolated chiral Rh initiators **1-3**, and the resulting polymers had a higher optical purity and M_w.

4.3 Experimental

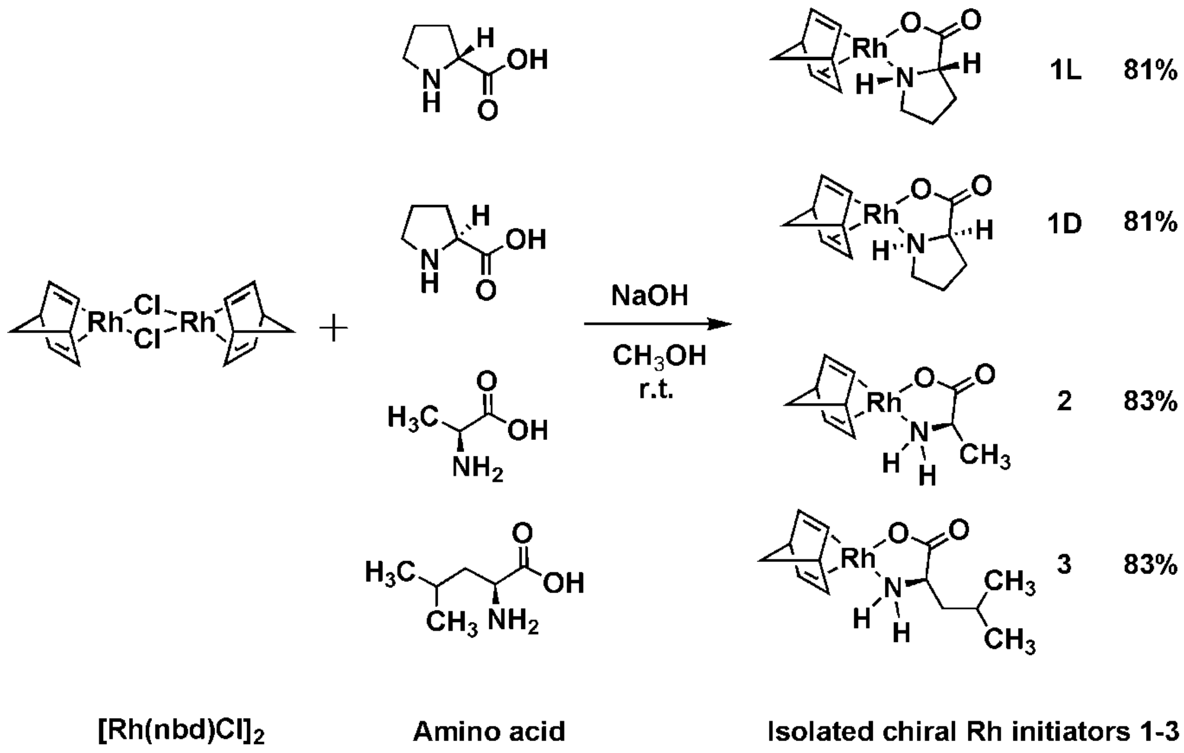
4.3.1 Materials

All the solvents used for synthesis and polymerization of the monomers were distilled as usual. The polymerization initiator, $[Rh(nbd)Cl]_2$ (nbd = 2,5 norbornadiene), purchased from Aldrich Chemical was used as received.

4.3.2 Measurements

^{1}H NMR (400MHz) spectra were recorded on a JEOL LEOLEX-400 spectrometer. The average molecular weights (M_n and M_w) were evaluated by gel permeation chromatography (GPC) by using JASCO liquid chromatography instruments with PU-2080, DG-2080-53, CO-2060, UV-2070, CD-2095, and two polystyrene gel columns (Shodex KF-807 L, THF eluent, polystyrene calibration). We recorded CD spectra by using a JASCO J-720WI spectropolarimeter with a Peltier controller for temperatures at 20℃ (a quartz cell of 1 mm path length; sample concentration: 0.100 to 2.00 mM based on the monomer unit). The infrared spectra were recorded on FT/IR-4200 (JASCO).

4.3.3 Synthesis of the isolated chiral Rh initiators 1-3 (Scheme 3)



Scheme 3. Synthesis of isolated chiral Rh initiators **1**-**3** in this study.

The isolated chiral Rh initiators **1-3** were synthesized facilely as shown in Scheme 3. A typical procedure was as follows [5]: A solution of L-proline (126 mg, 1.09 mmol) and sodium hydroxide (45.0 mg, 1.15 mmol) in methanol (5.00 mL) was added to a brown suspension of $[Rh(nbd)Cl]_2$ (247 mg, 0.500 mmol) in methanol (5.00 mL). The obtained clear-brown solution was stirred for 1h at room temperature. The solvent was removed *in vacuo*, and the crude product was dissolved in dichloromethane (15.0 mL). The mixture was filtrated, and subsequently the solvent was evaporated. The product was obtained as a yellow powder (200 mg, 81.0%). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 4.02, 3.98 (br s, 4H, nbd-C$\underline{H}$ olefinic), 3.90 (s, 2H, nbd-C$\underline{H}$), 3.70 (m, 1H, C$\underline{H}$-COO), 2.86-2.73 (m, 2H, C$\underline{H}_2$-NH), 2.19-2.12 (m, 1H, CH_2-C$\underline{H}$), 2.05-1.91 (m, 2H, CH_2-C$\underline{H}_2$-CH-COO), 1.69-1.61 (m, 1H, CH_2-CH_2-C$\underline{H}$-COO), 1.25 (s, 2H, nbd-C$\underline{H}_2$).^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ 184.99 (COO), 62.51 (COO-CH), 61.69 (nbd-CH_2), 51.02 (nbd-CH non-olefinic), 49.13 (NH-CH_2), 30.13 (COO-CH-CH_2), 25.72 (NH-CH_2-CH_2) [6].

4.3.4 Polymerization of the monomers RPA by isolated chiral Rh initiators 1-3 (Scheme 1)

The achiral monomers **RPA**s synthesized [3b] were polymerized by using the isolated chiral Rh initiators **1-3** as shown in Scheme 1. A typical polymerization procedure was as follows: A solution of **1** (2.47mg, 8.00 μmol) in dry toluene (1.00 mL) was added to a dry toluene (3.00 mL) solution of **OcPA** (116 mg, 400 μmol). The solution was stirred at room temperature for 6 h and then treated with 1M HCl. The crude polymer was purified by reprecipitation of the toluene solution into a large amount of methanol twice and the formed solid was dried *in vacuo* to give poly(**OcPA**) as an orange solid (yield, 60.0%).

4.4 Results and Discussion

The resulting polymers from the achiral **OcPA** prepared by using the isolated chiral Rh initiatores **1-3** were chiral because they had CD absorption bands (Table 1, nos.1-5). Since the CD bands observed around 450nm were assigned to the main chain, the polymers had the chirality in the main chain, that is, one-handed helical backbone. In addition, the sense of the helicity was controlled by the sign of the chirality of the isolated Rh initiator **1L** or **1D** as shown in Nos. 1 and 2 in Figure 1 and Table 1. Therefore, the HSSP of **OcPA** by using the isolated chiral Rh initiators, **1L** and **1D** has been successfully achieved. From the achiral monomer **DoPA**, a one-handed helical polymer was also obtained by the same initiators.

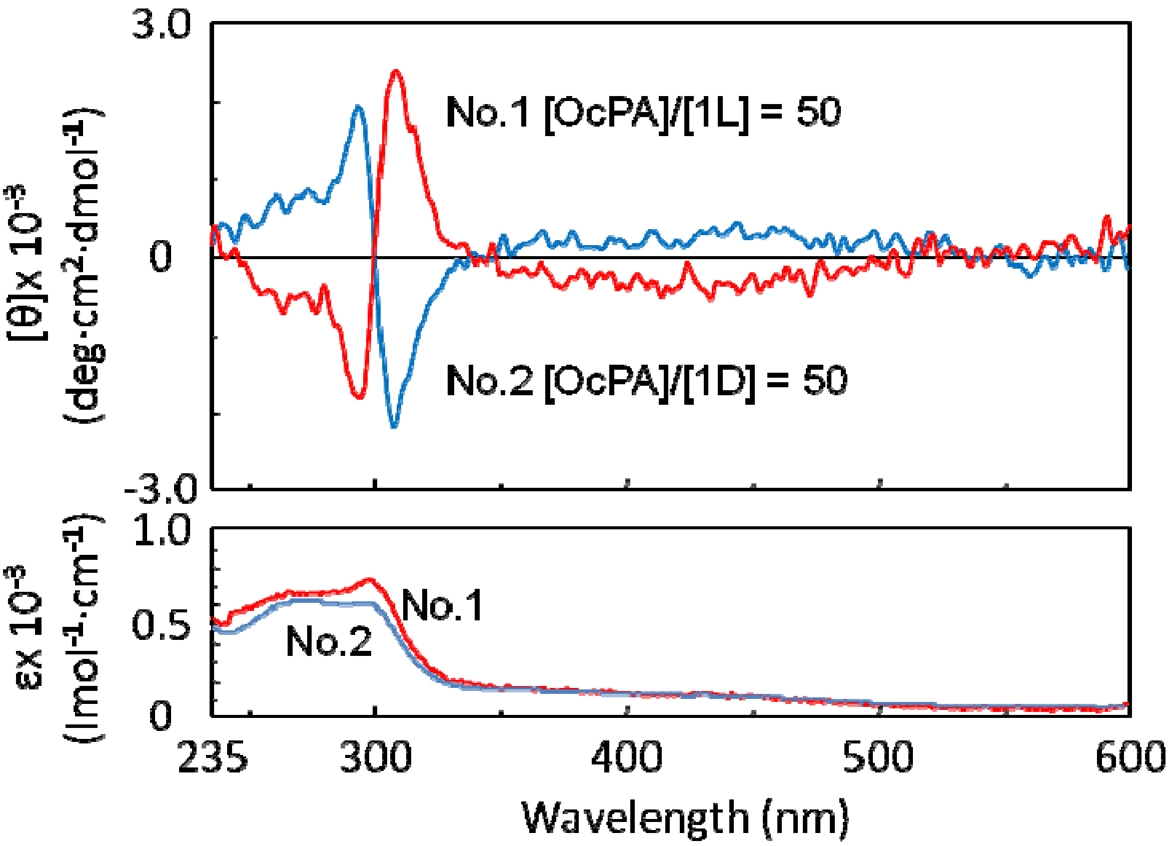


Figure 1. CD spectra of poly(**OcPA**) in $CHCl_3$ (Table 1, Nos. 1 and 2).

By using **1L** (Table 1, no. 8, [Chiral ligand]/[Monomer] = 0.02), an optically active polymer showing a higher relative optical purity (100%) was obtained.

On the other hand, although 12.5 times higher ratio of the chiral ligand in the case of $[Rh(nbd)Cl]_2$/(*R*)-PEA than that of **1L** was used ([Chiral ligand]/[Monomer] = 0.25), the resulting polymer showed a lower optical purity (Table1, no. 9, 9.63%). Therefore, the efficiency of the HSSP of **1L** was much higher than that of the $[Rh(nbd)Cl]_2$ /(*R*)-PEA.

When the same ratio and compound of the chiral source ([L-proline or L-prolinole]/[Monomer] = 0.020) were used, the polymer prepared by the isolated Rh initiator **1L** showed a higher relative optical purity (Table 1, no. 1, 100%) than the polymer by the two component chiral initiator systems, $[Rh(nbd)Cl]_2$/L-prolinole and $[Rh(nbd)Cl]_2$/L-proline. Actually the former gave no chirality of the polymer (Table 1, no. 6) and the latter gave no polymers (Table 1, no. 7).

All the isolated chiral Rh initiators **1-3** were suitable for HSSP. When we compared relative optical purities of the polymers prepared by **1-3** (nos, 3-5) in the same polymerization condition ([Chiral ligand]/[Monomer] = 0.010), the **1** gave a poly(**OcPA**) having the highest relative optical purity (Table 1, no. 3, 78.5%). The highest value may be caused by the planar structure consisting of the two condensed five membered rings of the **1** which can enhance the discriminating ability during HSSP.

The polymers synthesized by the isolated chiral Rh initiators **1-3** showed extremely high M_w (ca. 10^7). For example, M_w (1.59×10^7) of poly(**DoPA**) synthesized by **1L** (Table 1, no. 8) was 4.8 times higher than that by $[Rh(nbd)Cl]_2$/(*R*)-PEA (Table 1, no. 9). In general, the high M_w of polymers are needed for high processability. For example, poly(**DoPA**) whose M_w was lower than 10^5 had no self-supporting membrane forming ability. [7] Therefore, the isolated initiator easily prepared is very useful for practical use.

In our previous study, (*R*)-PEA/$[Rh(nbd)Cl]_2$ = 250 was used as the best condition for HSSP of DoPA. Since the catalytic system contained free chiral

Table 1. Helix-sense-selective polymerization of **RPA** with various chiral Rh initiators in toluene at room temperature.

No.	**Monomer** [a]	**Rh initiator** [a]	**[Chiral ligand] /[Rh]**	**[Chiral ligand] /[Monomer]**	**Yield (%)**	M_w [b] ($\times 10^6$)	**Cis%** [c]	**[θ]** [d] **$\times 10^{-3}$ (deg·cm^2·dmol^{-1})**		**Relative** [e] **optical purity (%)**
								308 nm	**430 nm**	
1	**OcPA**	**1L**	1.00	0.020	60	12.1	91	24.6	-4.92	100
2		**1D**	1.00	0.020	63	43.3	90	-21.9	3.01	89.0
3		**1D**	1.00	0.010	70	15.2	88	-19.3	3.09	78.5
4		**2**	1.00	0.010	62	31.6	94	2.53	-1.67	10.3
5		**3**	1.00	0.010	68	23.2	92	1.91	-0.883	7.76
6		[Rh(nbd)Cl]$_2$ / L-prolinole	1.00	0.020	88	33.4	93	0	0	0
7		[Rh(nbd)Cl]$_2$ / L-proline	1.00	0.020	0	—	—	—	—	—
8	**DoPA**	**1L**	1.00	0.020	27	15.9	91	9.22	-2.58	100
9 [f]		[Rh(nbd)Cl]$_2$ / (*R*)-PEA	12.5	0.25	67	3.30 [g]	—	0.888	-0.193	9.63

[a] For the codes, see Scheme 1. [b] Determined by GPC based on PSt standard (eluent:$CHCl_3$). [c] Determined by ^1H NMR in $CDCl_3$/DMSO-d_6 = 1/1 (v/v). [d] In $CHCl_3$. [e] Relative optical purity of the polymers based on the $[\theta]_{308}$ of No. 1 for poly(OcPA)s, and No.8 for poly(DoPA)s. [f] From ref. 3e). [g] Determined by GPC based on PSt standard (eluent:THF).

ligands (Scheme 2), the chiral amines and two hydroxyl groups of the monomer can interact. To clear the mechanism and enhance the efficiency, isolation of the real active species from the $[Rh(nbd)Cl]_2$/(*R*)-PEA was desired but it was difficult due to the low stability. In this study, since HSSP of **DoPA** was achieved by using the isolated chiral Rh initiators **1-3**, real and pure HSSP was proved.

4.5 Conclusions

In conclusion, the isolated chiral Rh initiators **1-3** were found to be suitable for the HSSP of achiral phenylacetylene monomers. The sense of the helix was controlled by the sign of the chirality of the isolated Rh initiator **1L** or **1D**. The relative optical purity ([θ] value) and the efficiency of the chiral induction ([chiral ligand]/[Monomer]) of the isolated Rh initiator **1** during the HSSP was much higher than that of the corresponding two component chiral initiator system $[Rh(nbd)Cl]_2$/L-prolinole. The polymers synthesized by the isolated chiral Rh initiators **1-3** showed extremely high M_w (ca. 10^7). In addition, the preparation and isolation of the initiators were easy and the possible mechanism became simple because the initiator was well-defined. Therefore, the isolated Rh initiators **1-3** are more valuable than the two component chiral initiator systems for the HSSP.

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Abe, Y. Kakihana, M. Teraguchi, T. Kaneko, *Chem. Commun.* **2012**, *48*, 4761. f) M. Teraguchi, T. Aoki, T. Kaneko, D. Tanioka, *ACS Macro Lett.* **2012**, *1*, 1258. g)) L. Liu, T. Namikoshi, Y. Zang, T. Aoki, S. Hadano, Y. Abe, I. Wasuzu, T. Tsutsuba, M. Teraguchi, T. Kaneko, *J. Am. Chem. Soc.* **2013**, *135*, 602.

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[6] A similar NMR was obtained for 1D. Similarly 2 and 3 were isolated as a brownish yellow solid in 83.0 and 83.0%, respectively.

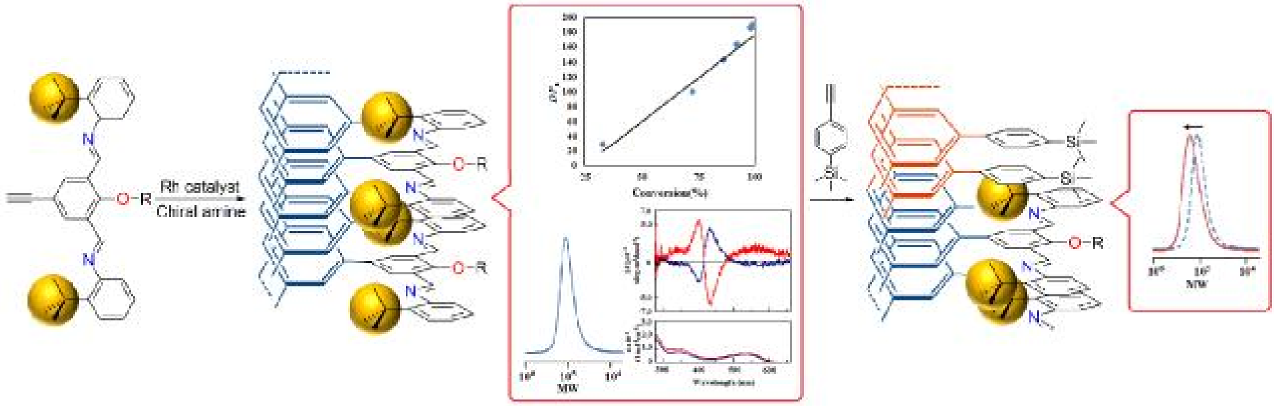
[7] Unpublished data in our lab.

Chapter 5

Living-Like Helix-Sense-Selective Polymerization of an Achiral Substituted Acetylene Having Bulky Substituents

5.1 Abstract

By using a new achiral phenylacetylene having bulky substituents as a monomer, living-like helix-sense-selective polymerization (**HSSP**) has been achieved. This is the first example of the **HSSP** of substituted acetylenes where the degree of polymerization was controlled. The resulting one-handed helical living polymer initiated polymerization of a second monomer to successfully yield a block copolymer.



5.2 Introduction

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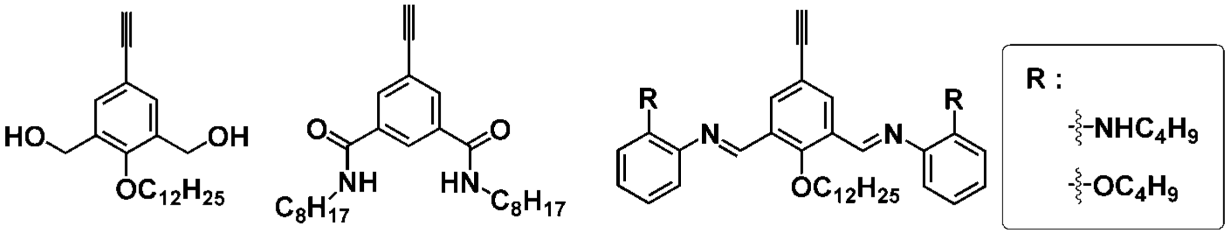


I II III

Chart 1. Examples of three kinds of achiral monomers suitable to the **HSSP** we reported before.

Living polymerization is a very useful method to obtain well-organized polymers and to prepare block copolymers. For substituted terminal acetylenes, some living polymerizations have been realized by using precisely designed initiators [16-22]. However, living polymers could not be obtained by polymerization of the monomers suitable to the **HSSP** when such initiators were used [23]. It was thought to be caused by very high polymerization rates. To realize living **HSSP** of substituted acetylenes, other strategy is needed.

In this chapter, we report our trial to find a new achiral monomer which produces a one-handed helical living polymer by using a binary catalytic system, *i.e.*, to cause living polymerization and **HSSP** in an identical polymer at the same time. To find such a monomer, we synthesized four new achiral phenylacetylens having bulky substituents such as *tert*-butyl groups as R groups in **III** (Chart 1) and polymerized them by using the catalytic system because bulky substituents can suppress polymerization rates.

5.3 Experimental

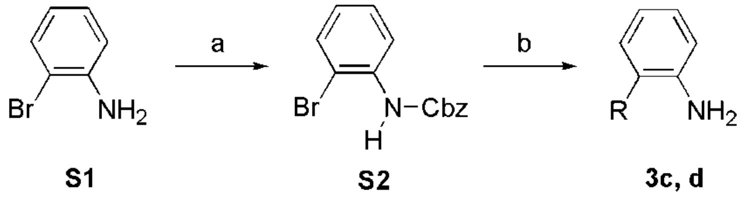
5.3.1 Materials

All the solvents used for monomer synthesis and polymerization were distilled as usual. Dry tetrahydrofuran (99.5% purity) and dry diethyl ether (99.5% purity) purchased from Kanto Chemical was used as received. The polymerization initiator, $[Rh(nbd)Cl]_2$ (nbd = 2,5-norbornadiene), purchased from Aldrich Chemical was used as received. *N*-(2-bromophenyl)-*O*-benzyl carbamate (**S2** in Scheme 1) was synthesized according to literature [24]. 4-dodecyloxy-3,5-bis(hydroxymethyl)phenylacetylene (**1**) [9] and 4-(trimethylsilyl)phenylacetylene (**SPA**) [25] were synthesized according to our report.

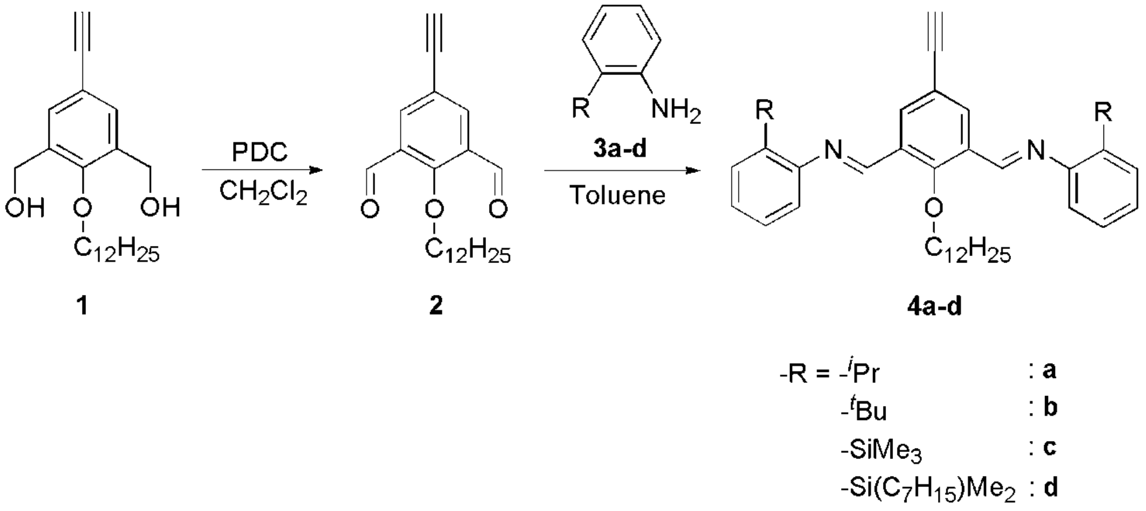
5.3.2 Measurements

Average molecular weight (M_n) was estimated by gel permeation chromatography (tetrahydrofuran as an eluent, polystyrene calibration) using JASCO Liquid Chromatography instruments with PU 2080, DG 2080 53, CO 2060, UV 2070, CD2095, and two polystyrene gel columns (Shodex KF 807L). NMR spectra were recorded on a JEOL GSX 270 at 400 MHz for ^{1}H. IR spectra were recorded on a JASCO FTIR 4200 spectrometer. CD spectra were measured with a JASCO J 720 spectropolarimeter.

5.3.3 Synthesis of the monomers (Schemes 1 and 2)



Scheme 1. A synthetic route to **3c** and **3d**. a: benzyl chloroformate/pyridine, ethyl acetate, Cbz = benzyloxycarbonyl, b: (1) *n*-BuLi, chlorotrimethylsilane or chloroheptyldimethylsilane/diethyl ether, (2) Pd/C, H_2.



Scheme 2. A synthetic route to **4a-d**. (PDC = pyridinium dichromate).

5.3.3.1 Synthesis of 4-dodecyloxy-3,5-diformyphenylacetylene (**2**) (Scheme 2) [13]

A solution of **1** (3.26 g, 9.41 mmol) in dichloromethane (200 mL) was added dropwise to a solution of pyridinium dichromate (17.7 g, 47.0 mmol) in dichloromethane (100 mL) at room temperature. The solution was stirred for 48 hours. The resulting solution was filtered through a bed of celite, and then the filtrate was concentrated by evaporation. The brown residue was purified by silica-gel column chromatography (eluent; hexane: ethyl acetate = 2:1) to give **2** as a white solid. Yield: 86.6% (2.79 g). Rf : 0.65 (hexane: ethyl acetate = 2:1). IR (KBr): 1692 (C=O) cm^{-1}; ^1H NMR(400 MHz, $CDCl_3$, ppm) δ: 10.4 (s, 2H, C*H*O), 8.17 (s, 2H, Ph*H*), 4.15 (t, 2H, O-CH_2CH_2), 3.14 (s, 1H, C≡C*H*), 2.03 (br, 2H, CH_2OH), 1.81 (tt, 2H, O-CH_2-CH_2-CH_2), 1.27-1.57 (m, 18H, CH_2-$(CH_2)_9$-CH_3), 0.88 (t, 3H, CH_2-$(CH_2)_9$-CH_3).

5.3.3.2 Synthesis of 2-trimethylsilylaniline (**3c**)(Scheme 1) [26, 27]

A hexane solution of *n*-BuLi (1.59M, 13.8 mL, 22.0 mmol) was added dropwise to **S2** (3.06 g, 10.0 mmol) in diethyl ether (45 mL) at -78°C. After the mixture was stirred for 1 hour at the same temperature, chlorotrimethylsilane was added dropwise to the reaction mixture. The resulting mixture was stirred at the same temperature for 6 hours and then at room temperature for 12 hours. The reaction mixture was quenched with 2N HCl aq. and stirred for 1 hour. After separation of the two layers, the aqueous layer was extracted with diethyl ether. The organic layer was dried over anhydrous $MgSO_4$ and concentrated to give crude product as yellow liquid. The product was used for synthesis of **3c** without further purification.

The mixture of the obtained product (1.23 g) and 10% Pd/C (10wt%, 123 mg) was stirred in H_2 at room temperature for 24 hours. The resulting mixture was diluted with diethyl ether (20.0 mL) and filtrated. After concentration, the crude product was purified by Al_2O_3 column chromatography (hexane: ethyl acetate = 20:1) to give **3c** as yellow liquid. Yield: 12.7% (210 mg). Rf : 0.20 (hexane: ethyl acetate = 20:1). ^1H NMR(400 MHz, $CDCl_3$, ppm) δ: 7.30 (dd, 1H, Ph*H*), 7.17 (dt, 1H, Ph*H*), 6.77 (dt, 1H, Ph*H*), 6.63 (d, 1H, Ph*H*), 3.77 (br, 2H, NH_2), 0.34 (s, 9H, $Si(CH_3)_3$)

5.3.3.3 Synthesis of 2-(heptyldimethylsilyl)aniline (**3d**) (Scheme 1) [26, 27]

A hexane solution of *n*-BuLi (1.59M, 8.18 mL, 13.0 mmol) was added dropwise to **S2** (1.53 g, 5.00 mmol) in diethyl ether (20.0 mL) at -78°C. After the mixture was stirred for 1 hour at the same temperature, chloroheptyldimethylsilane was added dropwise to the reaction mixture. The resulting mixture was stirred at the same temperature for 6 hours and then at room temperature for 12 hours. The reaction mixture was quenched with 2N HCl aq. and stirred for 1 hour. After separation of the two layers, the aqueous layer was extracted with diethyl ether. The organic layer was dried over anhydrous $MgSO_4$ and concentrated to give crude product as yellow liquid. The product was used for synthesis of **3d** without further purification.

The mixture of the obtained product (450 mg) and 10% Pd/C (10wt%, 45.0 mg) was stirred in H_2 at room temperature for 24 hours. The resulting mixture was diluted with diethyl ether (10.0 mL) and filtrated. After concentration, the crude product was purified by Al_2O_3 column chromatography (hexane: ethyl acetate = 20:1) to give **3d** as yellow liquid. Yield: 19.0% (250 mg). Rf : 0.30 (hexane: ethyl acetate = 20:1). ^{1}H NMR(400 MHz, $CDCl_3$, ppm) δ: 7.27 (dd, 1H, Ph*H*), 7.16 (dt, 1H, Ph*H*), 6.76 (dt, 1H, Ph*H*), 6.62 (d, 1H, Ph*H*), 3.77 (br, 2H, NH_2), 1.16-1.36 (m, 10H, $SiCH_2(CH_2)_5$), 0.87 (t, 3H, $Si(CH_2)_6CH_3$), 0.81 (t, 2H, $SiCH_2(CH_2)_5$) 0.31 (s, 6H, $Si(CH_3)_2$)

5.3.3.4 Synthesis of 4-dodecyloxy-3,5-bis(2-isopropyphenyliminomethyl)phenylacetylene (**4a**) (Scheme 2) [13]

A mixture of **2** (250 mg, 0.732 mmol), 2-isopropylaniline (0.223 mL, 1.61 mmol), and Al_2O_3 (502 mg) in toluene (20.0 mL) was stirred for 18 hours at room temperature. After the mixture was filtered, the solvent was removed. The crude product was purified by Al_2O_3 column chromatography (hexane: ethyl acetate = 19:1) to give **4a** as light yellow solid. Yield: 86.8% (363 mg). Rf : 0.47 (hexane: ethyl acetate = 19:1). IR (KBr): 1616 (C=N) cm^{-1}; ^{1}H NMR(400 MHz, $CDCl_3$, ppm) δ: 8.71 (s, 2H, C*H*=N), 8.43 (s, 2H, Ph*H*), 7.23~7.34 (m, 6H, N-Ph*H*), 6.90 (d, 2H, N-Ph*H*), 3.98 (t, 2H, $O\text{-}CH_2CH_2$), 3.56 (qq, 2H, $CH(CH_3)_2$), 3.14 (s, 1H, C≡C*H*), 1.84 (tt, 2H, $O\text{-}CH_2\text{-}CH_2\text{-}CH_2$), 1.23-1.56 (m, 30H, $CH_2\text{-}(CH_2)_9\text{-}CH_3$ and $CH(CH_3)_2$), 0.88 (t, 3H, $O\text{-}(CH_2)_{11}\text{-}CH_3$).

5.3.3.5 Synthesis of 4-dodecyloxy-3,5-bis(2-tert-butylphenyliminomethyl)phenylacetylene (**4b**) (Scheme 2) [13]

A mixture of **2** (1.50 g, 4.39 mmol), 2-*tert*-butylaniline (1.51 mL, 9.66 mmol), and Al_2O_3 (2.24 g) in toluene (20.0 mL) was stirred for 18 hours at room temperature. After the mixture was filtered, the solvent was removed. The crude product was purified by Al_2O_3 column chromatography (hexane: ethyl acetate = 5:1) to give **4b** as yellow solid. Yield: 88.7% (2.36 g). Rf : 0.47 (hexane: ethyl acetate = 5:1). IR (KBr): 1616 (C=N) cm^{-1}; ^1H NMR(400 MHz, $CDCl_3$, ppm) δ: 8.64 (s, 2H, C*H*=N), 8.39 (s, 2H, Ph*H*), 7.44 (dd, 2H, N-Ph*H*), 7.18~7.25 (m, 4H, N-Ph*H*), 6.83 (d, 2H, N-Ph*H*), 3.96 (t, 2H, O-CH_2CH$_2$), 3.14 (s, 1H, C≡C*H*), 1.84 (tt, 2H, O-CH$_2$-CH_2-CH$_2$), 1.47 (s, 18H, C(CH_3)$_3$), 1.21-1.26 (m, 18H, CH$_2$-(CH$_2$)$_9$-CH$_3$), 0.88 (t, 3H, O-(CH_2)$_{11}$-CH_3). Anal. Calcd for $C_{42}H_{56}N_2O$: C, 83.39; H, 9.33; N, 4.63. Found. C, 83.23; H, 9.47; N, 4.47.

5.3.3.6 Synthesis of 4-dodecyloxy-3,5-bis(2-trimethylsilylphenyliminomethyl)phenylacetylene (**4c**) [13]

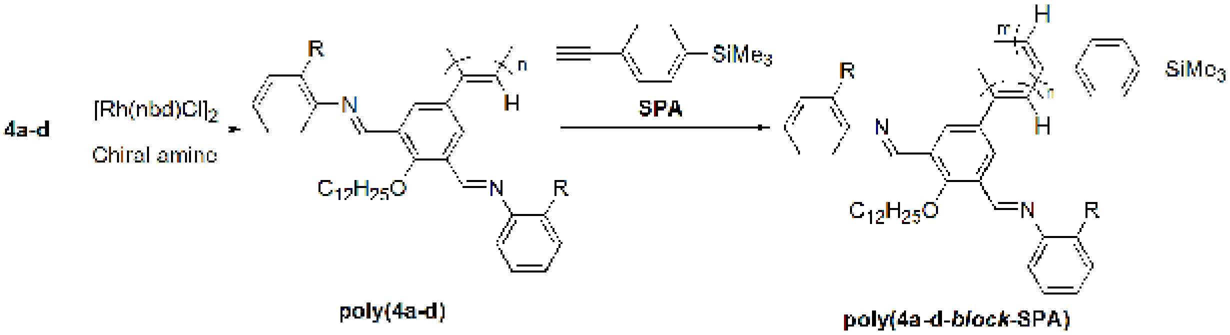
A mixture of **2** (173 mg, 0.508 mmol), **3c** (210 mg, 1.27 mmol), and Al_2O_3 (207 mg) in toluene (1.69 mL) was stirred for 3 days at room temperature. After the mixture was filtered, the solvent was removed. The crude product was purified by Al_2O_3 column chromatography (hexane: ethyl acetate: trietylamine = 60:2:1) to give **4c** as yellow viscous liquid. Yield: 46.3% (150 mg). Rf : 0.60 (hexane: ethyl acetate: triethylamine = 60:2:1). IR (KBr): 1614 (C=N) cm^{-1}; ^1H NMR(400 MHz, $CDCl_3$, ppm) δ: 8.71 (s, 2H, C*H*=N), 8.38 (s, 2H, Ph*H*), 7.56 (dd, 2H, N-Ph*H*), 7.42 (dt, 2H, N-Ph*H*), 7.25 (t, 2H,N-Ph*H*), 7.00 (d, 2H, N-Ph*H*), 3.96 (t, 2H, O-CH_2CH$_2$), 3.12 (s, 1H, C≡C*H*), 1.19-1.33 (m, 20H, O-CH$_2$-(CH_2)$_{10}$-CH$_3$), 0.88 (t, 3H, O-(CH$_2$)$_{11}$-CH_3), 0.34 (s, 18H, Si(CH_3)$_3$). Anal. Calcd for $C_{40}H_{56}N_2OSi_2$: C, 75.41; H, 8.86; N, 4.40. Found. C, 75.09; H, 9.00; N, 4.30.

5.3.3.7 Synthesis of 4-dodecyloxy-3,5-bis(2-heptyldimethylsilylphenyliminomethyl)phenylacetylene (**4d**) (Scheme 2) [13]

A mixture of **2** (148 mg, 0.431 mmol), **3d** (250 mg, 0.949 mmol), and Al_2O_3 (180 mg) in toluene (1.44 mL) was stirred for 24 hours at room temperature.

After the mixture was filtered, the solvent was removed. The crude product was purified by Al_2O_3 column chromatography (hexane: ethyl acetate: triethylamine = 40:2:1) to give **4d** as yellow viscous liquid. Yield: 30.6% (110 mg). Rf : 0.70 (hexane: ethyl acetate: trietylamine = 40:2:1). IR (KBr): 1619 (C=N) cm^{-1}; ^1H NMR(400 MHz, $CDCl_3$, ppm) δ: 8.70 (s, 2H, C*H*=N), 8.38 (s, 2H, Ph*H*), 7.55 (dd, 2H, Ph*H*), 7.42 (dt, 2H, N-Ph*H*), 7.25 (dt, 2H, N-Ph*H*), 6.99 (d, 2H, N-Ph*H*), 3.95 (t, 2H, O-CH_2CH_2), 3.10 (s, 1H, C≡C*H*), 1.77-1.86 (m, 2H, O-CH_2-CH_2-CH_2), 1.15-1.35 (m, 38H, CH_2-$(CH_2)_9$-CH_3 and Si-CH_2-$(CH_2)_5$-CH_3), 0.82-0.91 (m, 13H, O-$(CH_2)_{11}$-CH_3 and Si-CH_2-$(CH_2)_5$-CH_3), 0.30 (s, 12H, -$Si(CH_3)_2$). Anal. Calcd for $C_{52}H_{80}N_2OSi_2$: C, 77.55; H, 10.01; N, 3.48. Found. C, 76.71; H, 10.20; N, 2.95.

5.3.4 Polymerization (Scheme 3) [28]



Scheme 3. Polymerization of **4a-d** and synthesis of block copolymers poly(**4a-d**-*block*-**SPA**). (Chiral amine = (*R*)-*N,N*-dimethyl-1-phenylethylamine (DMPEA) or (*R*)- or (*S*)-phenylethylamine (PEA)).

All the procedures were performed under dry nitrogen. A typical polymerization procedure is as follows: A solution of $[Rh(nbd)Cl]_2$ (0.38 mg, 0.83 μmol) and (*R*)-*N,N*-dimethyl-1-phenylethylamine (DMPEA) (34 μL, 0.21 mmol) in toluene (0.33 mL) was added to a solution of **4b** (50 mg, 83 μmol) in toluene (0.50 mL). The reaction solution was stirred at room temperature for 3 hours. The crude polymer was purified by precipitation of the toluene solution into a large amount of methanol and dried *in vacuo* to give a red polymer.

Polymerizations of **4a**, **4c**, and **4d** were carried out similarly. The results are summarized in Table 1. Other amines were also used as a cocatalyst. The results are summarized in Table 3.

5.3.5 Synthesis of a block copolymer (poly(4b-block-SPA)) by polymerization of SPA initiated by living poly(4b) (Scheme 3)

SPA was added to the polymerization solution of monomer **4b** as described above. The resulting solution was stirred for 60 min (polymerization condition: in toluene, room temperature; [**4b**]$_0$ = 0.1 M, [**SPA**] = 0.67 M, [**4b**]$_0$/[[Rh(nbd)Cl]$_2$] = 100, [(*R*)-DMPEA]/[[Rh(nbd)Cl]$_2$] = 250). The polymerization solution was added to a large amount of acetone to precipitate the block copolymer. The precipitate was dried *in vacuo* to give a red polymer.

5.4 Results and Discussion

In general, polymerization rates of phenylacetylenes which were suitable to the helix-sense-selective polymerization (**HSSP**) we found and developed [9-15] were very high and therefore the control of their degree of polymerizations (DP_n) was impossible [23]. To suppress the polymerization rates, four new achiral monomers having bulky substituents (**4a-d** in Scheme 2) were designed and synthesized according to a synthetic route as shown in Scheme 2. These monomers (**4a-d**) have *i*-propyl(^{i}Pr) (**4a**), *t*-butyl(^{t}Bu) (**4b**), trimethylsilyl($SiMe_3$) (**4c**), and dimethylheptylsilyl($SiC_7H_{15}Me_2$) (**4d**) groups, respectively. The increasing order of bulkiness is ^{i}Pr- < ^{t}Bu- < -$SiMe_3$ < -$SiC_7H_{15}Me_2$.

They were polymerized by the chiral catalytic system, a binary catalyst consisting of (*R*)-*N,N*-dimethylphenylethylamine (DMPEA) and [Rh(nbd)Cl]$_2$ (nbd = 2,5-norbornadiene), for the **HSSP** we developed before [9-15]. Table 1 and Figure 1 list the results together with those of *p*-trimethylsilylphenylacetylene (**SPA**) having no bulky groups. The conversion of **4a** and **4b** reached almost

100%, while the others were low (Table 1 and Figure 1a). Only the degree of polymerization (DP_n) of **4b** could be controlled by changing conversion and polymerization time (Figures 1b, 2 and 3). The M_w/M_n value of poly(**4b**) was smallest among the three monomers (**4a-c**) that produced high-molecular-weight polymers. In addition, the polymerization of **4b** proceeded in first order indicating a bimolecular reaction (Figure 1c). Therefore, polymerization of **4b** was found to have more number of characteristics as living polymerization.

Table 1. Polymerization of phenylacetylene having bulky groups (**4a-d**)[a]

no.	monomer	conversion(%)[b]	$M_n(\times 10^5)$[b]	DP_n[b]	M_w/M_n[b]	$g(\times 10^{-5})$[c]
1	**4a**	91.7	2.38	413	2.85	0
2	**4b**	98.7	1.15	190	1.46	1.3
3	**4c**	43.1	0.118	18.5	1.60	0
4	**4d**	23.7	0.0277	3.4	1.10	0
5[d]	**SPA**	90.0	2.56	1470	1.96	0

[a] Polymerized at room temperature in toluene. $[\text{monomer}]_0$ = 0.10 mol/L, $[\text{monomer}]_0$ / $[[\text{Rh(nbd)Cl}]_2]$ = 100, [(*R*)-DMPEA] / $[[\text{Rh(nbd)Cl}]_2]$ = 250. Polymerization time: 3, 3, 48, 48, and 3 h, for nos. 1-5, respectively. [b] By GPC. [c] $g = ([\theta]/3300)/\varepsilon$. [d] **SPA**: *p*-trimethylsilylphenylacetylene. [TEA] / $[[\text{Rh(nbd)Cl}]_2]$ = 250.

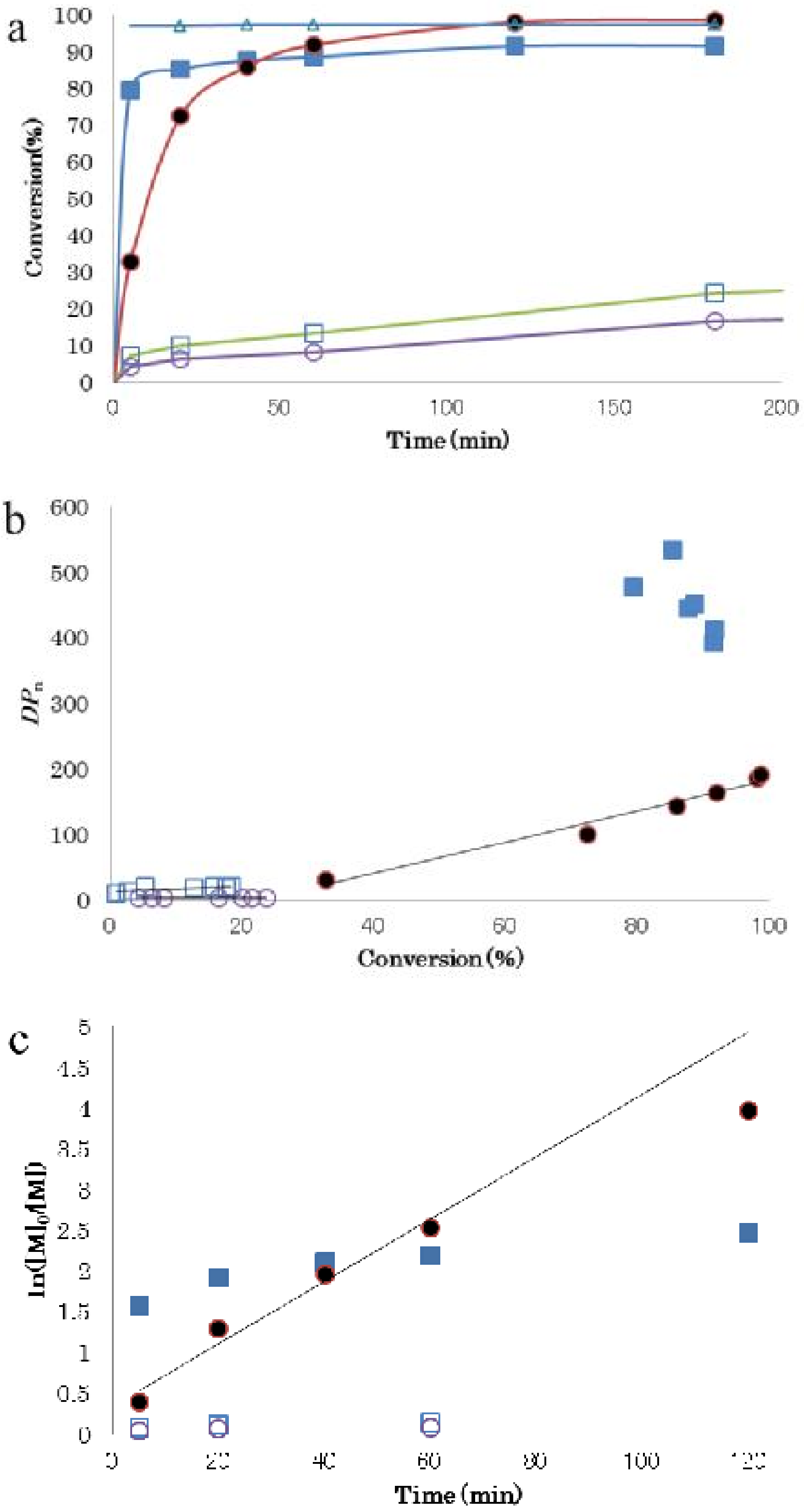


Figure 1. (a) Time-conversion curves, (b) conversion-DP_n plots, and (c) first-order plots for polymerization of **4a** (■), **4b** (●), **4c** (□), **4d** (○), and **SPA** (△).

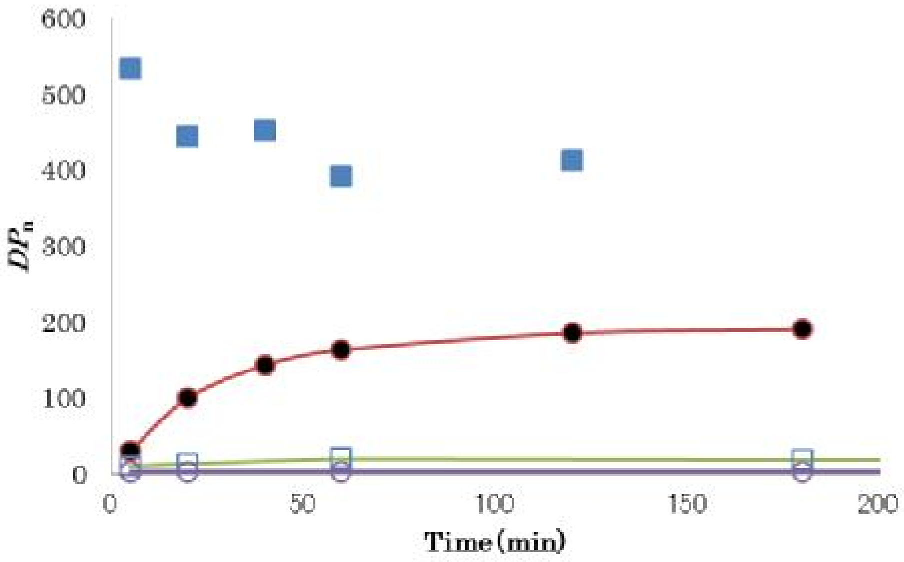


Figure 2. Time-DP_n curves for polymerization of **4a** (■), **4b** (●), **4c** (□), **4d** (○).

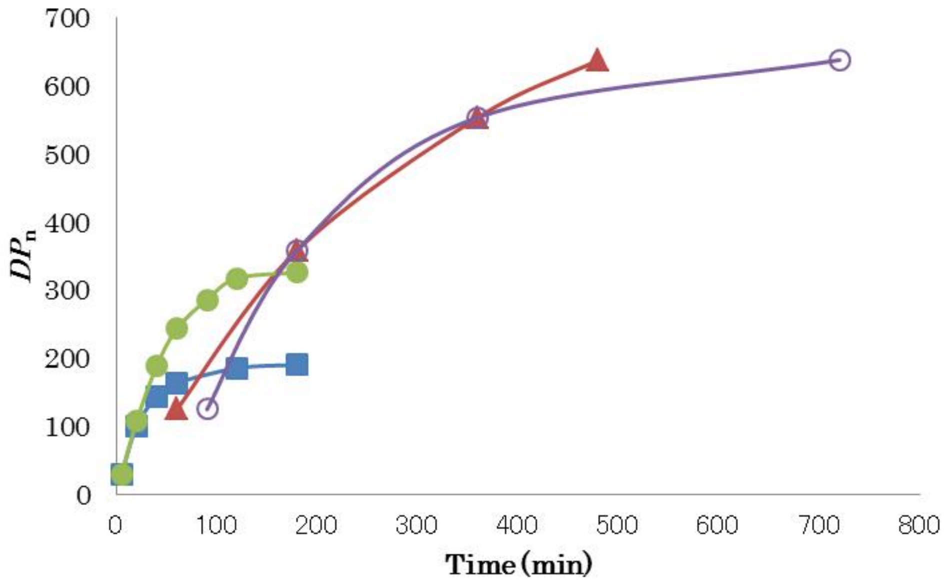


Figure 3. Time-DP_n curves for polymerization of **4b** by using (*R*)-DMPEA (■), TEA (●), (*S*)-PEA (▲), or (*S*)-PEA/TEA (○) as cocatalysts.

In order to confirm the living nature of the resulting polymer prepared by polymerization of **4b** by the binary catalyst, (*R*)-DMPEA / $[Rh(nbd)Cl]_2$, we tried to synthesize a block copolymer, poly(**4b**-*block*-**SPA**), prepared by polymerization of **SPA** by using the living poly(**4b**) as a polymer initiator (Scheme 3). As shown in Figure 4(A) and Table 2, one hour after **SPA** was added to the living poly(**4b**), **SPA** was completely consumed and the GPC peak of the original poly(**4b**)(Figure 4A(1)) moved to higher MW position(Figure 4A(2)) with maintaining the shape. Since the composition was the same as that in the feed (Table 2) and the product was soluble in ethyl acetate where poly**SPA** was insoluble, formation of poly (**4b**-*block*-**SPA**) was confirmed. Therefore, the living nature was confirmed.

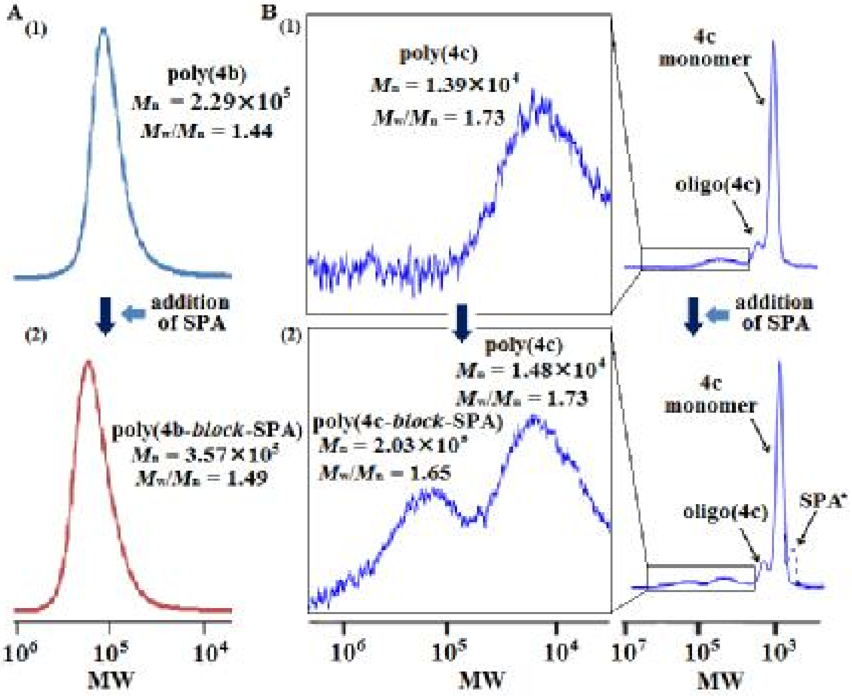


Figure 4. GPC charts of poly(**4b**) (A) and poly(**4c**) (B). (1) before addition of **SPA**; (2) 1 hour after addition of **SPA**. (**SPA***: Monomer peak appeared just after addition.)

In the case of poly (**4c**) prepared by polymerization for 48 hours in Figure 4B(1), at that time the conversion did not increase even if residual **4c** was present, *i.e.*, no further homopolymerization was initiated. Therefore, no active initiation system such as Rh(nbd)((*R*)-DMPEA)(**4c**) remained in the polymerization system. However, 1 hour after **SPA** monomer having no bulky groups was added to the polymerization system, the **SPA** monomer peak disappeared completely and a new peak at a higher MW appeared (Figure 4B(2)). Therefore, the new peak must be poly(**4c**-*block*-**SPA**). However, since original poly(**4c**) peak still remained, original poly(**4c**) was found to be partly active. Since the substituents were too bulky to yield polymers having high *DP*n, termination or chain transfer reaction partly happened more frequently than propagation.

Table 2. Preparation of block copolymer, poly(**4b**-*block*-**SPA**) prepared by polymerization of **SPA** initiated by living poly(**4b**)

no.	**4b** conv.[a] (%)	**SPA** conv.[a] (%)	**SPA**$_{\text{Feed}}$ (mol%)	**SPA**unit$_{\text{composition}}$[b] (mol%)
1[c]	89.0	-	0	0
2[d]	90.9	99.0	40	40

[a] By GPC. [b] By ^{1}H NMR. [c] Polymerized for 3 h at room temperature in toluene. [**4b**]$_0$ = 0.10 mol/L, [**4b**]$_0$/ [[Rh(nbd)Cl]$_2$] = 100 , [(*R*)-DMPEA] / [[Rh(nbd)Cl]$_2$] = 250. [d] **SPA** was added to the resulting solution of no.1, and copolymerized for 1 h.

To optimize the living polymerization condition, other amines such as triethylamine (TEA), phenylethylamine (PEA), and their mixture (PEA/TEA) were examined for the polymerization of **4b** as cocatalysts in the binary catalytic system. In all the amines used, their *M*n and *DP*n values could be controlled by changing time (Figure 5b) and 1st order relationships were observed (Figure 5c), although in the case of PEA, the conversion was low (Figure 5a) and *M*w/*M*n was large (Table 3) . Therefore, when DMPEA, TEA, or PEA/TEA was used, the polymerization included living nature. High conversions were observed in the presence of tertiary amines, DMPEA and TEA, while low conversion was observed in the presence of a primary amine, PEA. This may be because active species such as Rh(nbd)((*R*)-DMPEA)(**4b**) were more effectively produced by tertiary amines having stronger basicity than by the primary amine.

In addition, the resulting living poly(**4b**) prepared by using (*R*)-DMPEA and (*S*)-PEA/TEA as a cocatalyst showed CD signals and the signs were controlled by the chirality of the chiral amines as shown in Figure 6. Therefore, living-like **HSSP** of a substituted acetylene has been realized for the first time.

Table 3. Polymerization of phenylacetylene having *t*-butyl groups(**4b**) in the presence of different amines [a]

no.	amine	conversion(%)[b]	M_n(×10^6)[b]	DP_n[b]	M_w/M_n[b]	g(× 10^{-5})[c]
1	(*R*)-DMPEA	99.4	0.120	198	1.50	1.3
2	TEA	94.2	0.197	326	1.60	0
3	(*R*)-PEA	46.6	2.00	3310	2.12	4.7
4[d]	(*S*)-PEA/TEA	73.5	0.686	1130	1.84	- 1.7

[a] Polymerized at room temperature in toluene. $[\mathbf{4b}]_0$ = 0.10 mol/L, $[\mathbf{4b}]_0/[[\mathrm{Rh(nbd)Cl}]_2]$ = 100, $[\mathrm{amine}]/[[\mathrm{Rh(nbd)Cl}]_2]$ = 250. Polymerization time: 3, 3, 18, and 12 h, for nos. 1-4, respectively. [b] By GPC. [c] $g = ([\theta]/3300)/\varepsilon$. [d] [TEA]/[(*S*)-PEA] = 10.

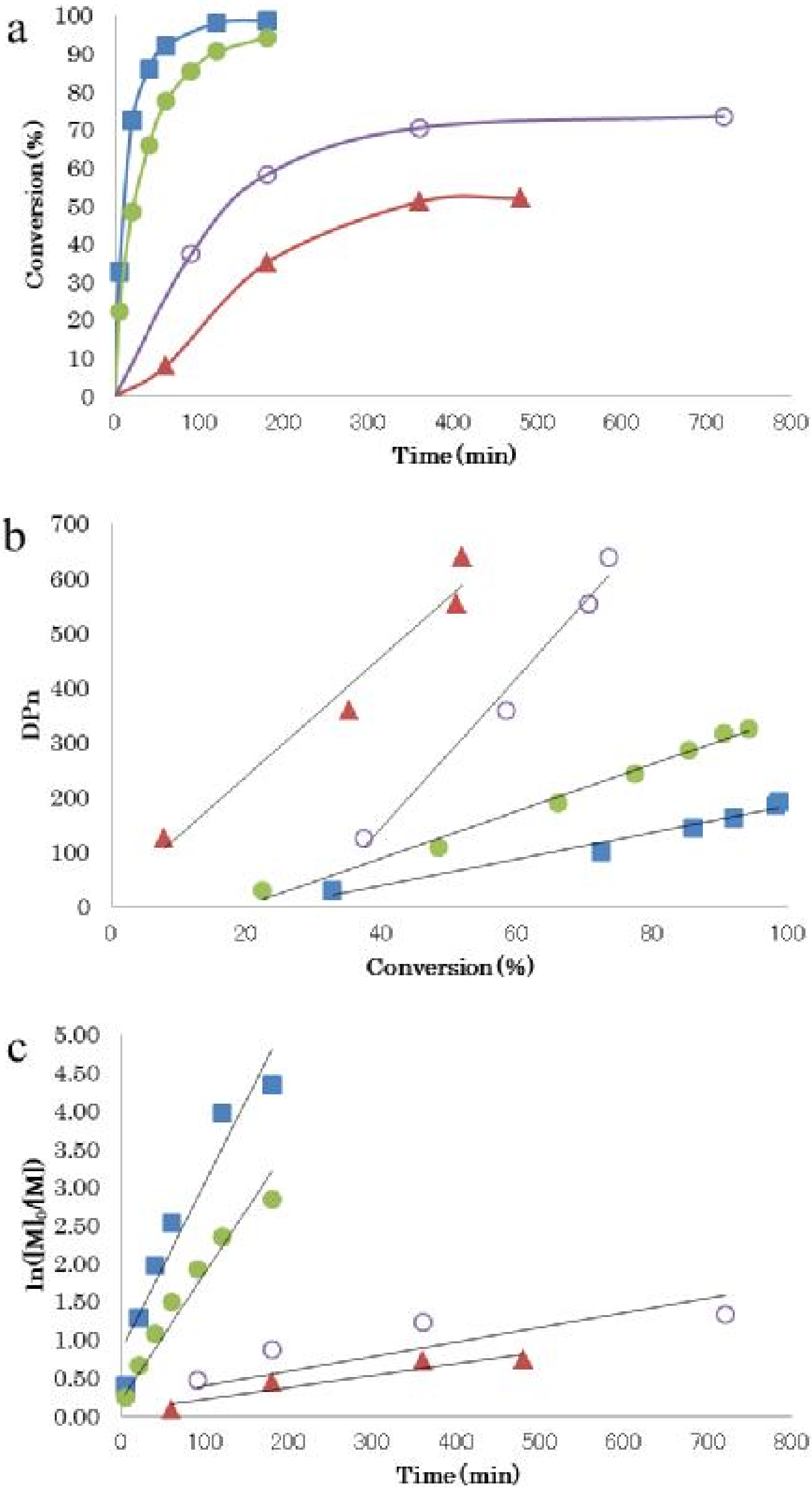


Figure 5. (a) Time-conversion curves, (b) conversion-DP_n plots, and (c) first-order plots for polymerization of **4b** with (*R*)-DMPEA (■), TEA (●), (*S*)-PEA (▲), or (*S*)-PEA/TEA (○).

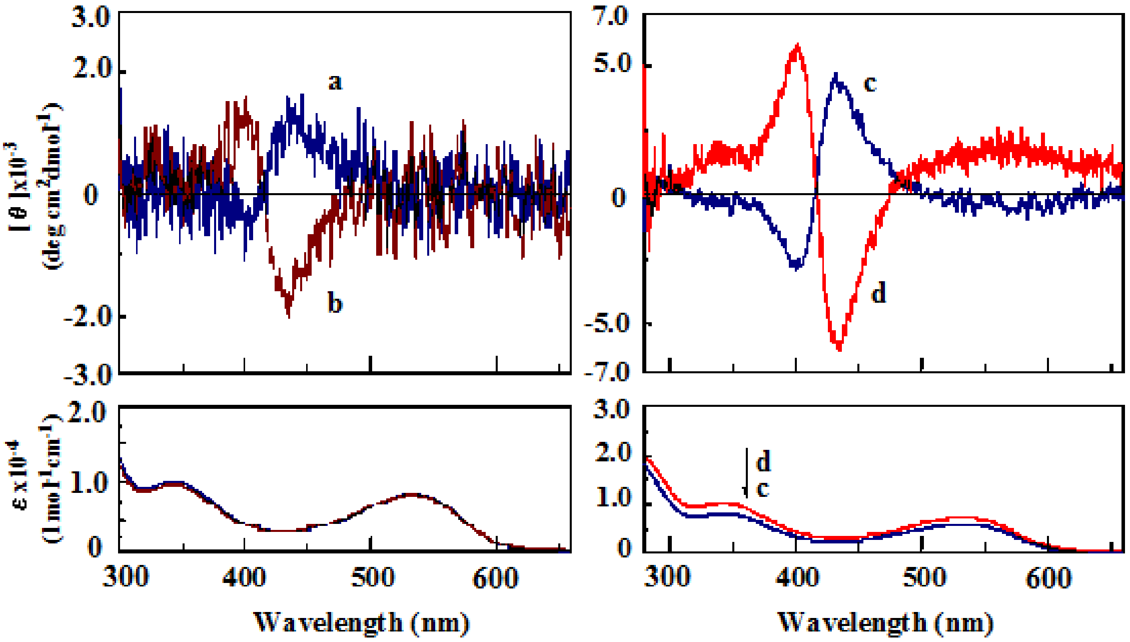


Figure 6. CD and UV-vis spectra of the poly(**4b**) polymerized by using (*R*)-DMPEA(a) (Table 3, no. 1), (*S*)-PEA/TEA (b) (Table 3, no. 4), (*R*)-PEA (c) (Table 3, no. 3), (*S*)-PEA (d), respectively as a cocatalyst.

5.5 Conclusions

In conclusion, by using a new achiral phenylacetylene having bulky *tert*-butyl substituents as a monomer, living-like helix-sense-selective polymerization (**HSSP**) has been achieved. This is the first example of **HSSP** of substituted acetylenes whose degree of polymerization was controlled. The one-handed helical living polymer could initiate polymerization of the second monomer, *p*-trimethylsilylphenylacetylene (**SPA**) to successfully yield a block copolymer. The polymerization rate of a monomer(**4a**) having less bulky substituents, *iso*-propyl groups was too high to control the molecular weight, while the polymerization rates of monomers(**4c**,**d**) having more bulky substituents such as trimethylsilyl or dimethylheptylsilyl groups were too low to maintain the activity of the propagation species during polymerization. In addition, polymerization of the monomer (**4b**) having *tert*-butyl substituents gave a one-handed helical polymer judging from their CD and UV. Therefore, the bulkiness of *tert*-butyl group was the best to produce polymers simultaneously having one-handed helix and controlled *DP*n, that is, to realize living **HSSP**.

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Supporting Information

Table S1. Polymerization of **4a** by (*R*)-DMPEA/$[Rh(nbd)Cl]_2$ [a]

no.	time(min)	conversion(%)[b]	M_n(×10^5)[b]	DP_n[b]	M_w/M_n[b]
1	5	79.4	2.76	478	2.74
2	20	85.2	3.08	534	2.43
3	40	87.7	2.57	446	2.79
4	60	88.7	2.61	452	2.70
5	120	91.6	2.26	392	3.12
6	180	91.7	2.38	413	2.85

[a] At room temperature in toluene. $[\mathbf{4a}]_0$ = 0.10 mol/L, $[\mathbf{4a}]_0/[[Rh(nbd)Cl]_2]$ = 100 , [(*R*)-DMPEA]/$[[Rh(nbd)Cl]_2]$ = 250. [b] By GPC.

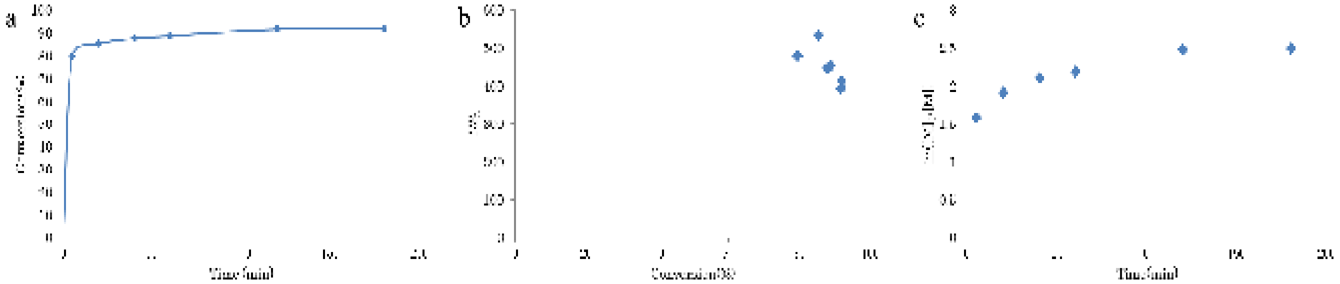


Figure S1. (a) A time-conversion curve, (b) a conversion-DP_n plot, and (c) a first-order plot for polymerization of **4a** with (*R*)-DMPEA.

Table S2. Polymerization of **4b** by (*R*)-DMPEA/$[Rh(nbd)Cl]_2$ [a]

no.	time (min)	conversion(%)[b]	$M_n(\times 10^4)$[b]	DP_n[b]	M_w/M_n[b]
1	5	32.7	1.78	29.4	1.23
2	20	72.4	6.05	100	1.33
3	40	86.0	8.65	143	1.34
4	60	92.0	9.86	163	1.35
5	120	98.1	11.2	185	1.43
6	180	98.7	11.5	190	1.46
7	360	99.4	12.0	198	1.50

[a] At room temperature in toluene. $[\mathbf{4b}]_0$ = 0.10 mol/L, $[\mathbf{4b}]_0/[[Rh(nbd)Cl]_2]$ = 100 , [(*R*)-DMPEA]/$[[Rh(nbd)Cl]_2]$ = 250. [b] By GPC.

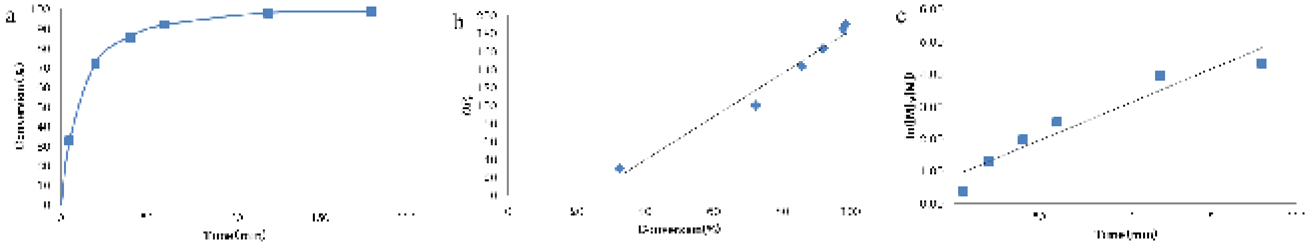


Figure S2. (a) A time-conversion curve, (b) a conversion-DP_n plot, and (c) a first-order plot for polymerization of **4b** with (*R*)-DMPEA.

Table S3. Polymerization of **4c** by (*R*)-DMPEA/$[Rh(nbd)Cl]_2$ [a]

no.	yime(min)	conversion(%)[b]	$M_n(\times 10^3)$[b]	DP_n[b]	M_w/M_n[b]
1	5	7.25	6.22	9.80	1.10
2	20	9.79	8.75	13.7	1.20
3	60	13.4	12.5	19.6	1.31
4	180	24.3	11.6	18.2	1.36
5	360	30.4	12.8	20.1	1.56
6	1440	39.7	12.3	19.3	1.62
7	2880	43.1	11.8	18.5	1.60

[a] At room temperature in toluene. $[\mathbf{4c}]_0$ = 0.10 mol/L, $[\mathbf{4c}]_0/[[Rh(nbd)Cl]_2]$ = 100 , $[(R)\text{-DMPEA}]/[[Rh(nbd)Cl]_2]$ = 250. [b] By GPC.

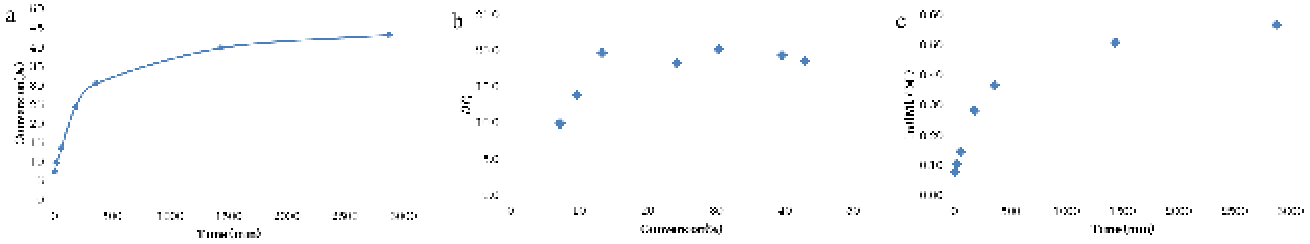


Figure S3. (a) A time-conversion curve, (b) a conversion-DP_n plot, and (c) a first-order plot for polymerization of **4c** with (*R*)-DMPEA.

Table S4. Polymerization of **4d** by (*R*)-DMPEA/[Rh(nbd)Cl]$_2$ [a]

no.	time(min)	conversion(%)[b]	M_n(×10^3)[b]	DP_n[b]	M_w/M_n[b]
1	5	4.26	2.52	3.1	1.08
2	20	6.24	2.66	3.3	1.10
3	60	8.10	2.74	3.4	1.11
4	180	16.5	2.83	3.5	1.12
5	360	20.0	2.80	3.5	1.11
6	1440	21.6	2.79	3.5	1.11
7	2880	23.7	2.77	3.4	1.10

[a] At room temperature in toluene. [**4d**]$_0$ = 0.10 mol/L, [**4d**]$_0$/[[Rh(nbd)Cl]$_2$] = 100 , [(*R*)-DMPEA]/[[Rh(nbd)Cl]$_2$] = 250. [b] By GPC.

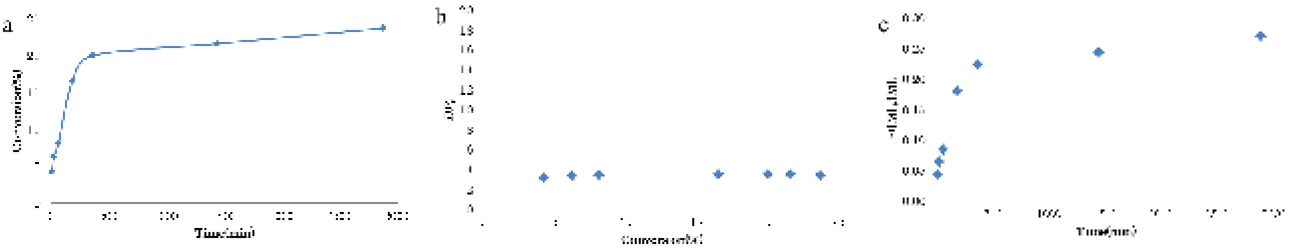


Figure S4. (a) A time-conversion curve, (b) a conversion-DP_n plot, and (c) a first-order plot for polymerization of **4d** with (*R*)-DMPEA.

Table S5. Preparation of block copolymer of poly(**4c**-*block*-**SPA)** prepared by polymerization of **SPA** initiated by living poly(**4c**)

no.	**4c** conv.[a] (%)	**SPA** conv.[a] (%)	**SPA**$_{\text{Feed}}$ (mol%)	**SPA** unit$_{\text{composition}}$[a] (mol%)
1[b]	22.8	-	0	0
2[c]	0	99.1	50	88

[a] By GPC. [b] Polymerized for 48 h at room temperature in toluene. [**4c**]$_0$ = 0.10 mol/L, [**4c**]$_0$/[[Rh(nbd)Cl]$_2$] = 100 , [(*R*)-DMPEA]/[[Rh(nbd)Cl]$_2$] = 250. [c] **SPA** was added to the resulting solution of no.1, and copolymerized for 1 h.

Table S6. Polymerization of **4b** by TEA/[Rh(nbd)Cl]$_2$ [a]

no.	time(min)	conversion(%)[b]	M_n(×10^4)[b]	DP_n[b]	M_w/M_n[b]
1	5	22.3	1.75	28.9	1.17
2	20	48.4	6.50	107	1.19
3	40	66.0	11.4	188	1.26
4	60	77.4	14.7	243	1.31
5	90	85.4	17.3	286	1.39
6	120	90.5	19.2	317	1.45
7	180	94.2	19.7	326	1.60

[a] At room temperature in toluene. [**4b**]$_0$ = 0.10 mol/L, [**4b**]$_0$/[[Rh(nbd)Cl]$_2$] = 100 , [TEA]/[[Rh(nbd)Cl]$_2$] = 250. [b] By GPC.

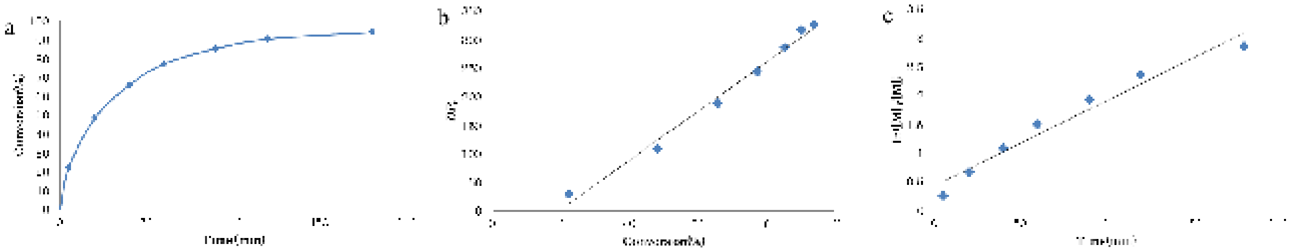


Figure S5. (a) A time-conversion curve, (b) a conversion-DP_n plot, and (c) a first-order plot for polymerization of **4b** with TEA.

Table S7. Polymerization of **4b** by (*S*)-PEA/$[Rh(nbd)Cl]_2$ [a]

no.	time(hour)	conversion(%)[b]	M_n($\times10^5$)[b]	DP_n[b]	M_w/M_n[b]
1	1	7.84	0.753	124	1.27
2	3	35.1	2.17	359	1.67
3	6	51.0	3.35	554	1.95
4	8	51.9	3.86	638	1.84

[a] At room temperature in toluene. $[\mathbf{4b}]_0$ = 0.10 mol/L, $[\mathbf{4b}]_0/[[Rh(nbd)Cl]_2]$ = 100 , [(*S*)- PEA]/$[[Rh(nbd)Cl]_2]$ = 250. [b] By GPC.

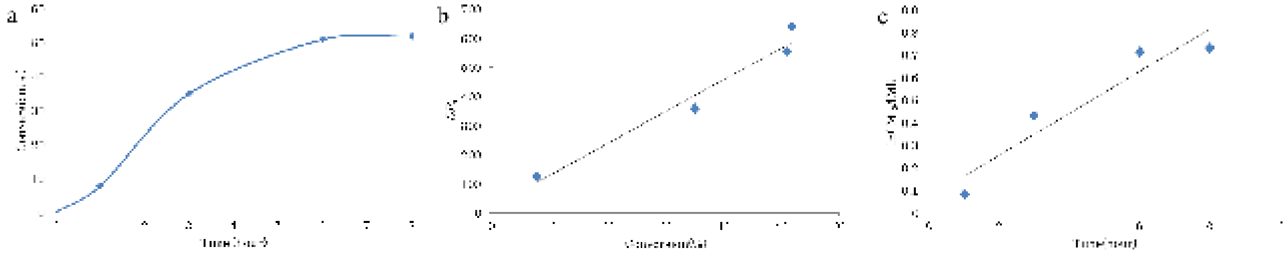


Figure S6. (a) A time-conversion curve, (b) a conversion-DP_n plot, and (c) a first-order plot for polymerization of **4b** with (*S*)-PEA.

Table S8. Polymerization of **4b** by TEA/(*S*)-PEA/[Rh(nbd)Cl]$_2$ [a]

no.	time(hour)	conversion(%)[b]	$M_n(\times 10^5)$[b]	DP_n[b]	M_w/M_n[b]
1	1.5	37.3	2.39	124	1.21
2	3	58.3	4.78	359	1.38
3	6	70.5	6.66	554	1.66
4	12	73.5	6.86	638	1.84

[a] At room temperature in toluene. $[\mathbf{4b}]_0$ = 0.10 mol/L, $[\mathbf{4b}]_0/[[\text{Rh(nbd)Cl}]_2]$ = 100 , $[\text{TEA}]/[[\text{Rh(nbd)Cl}]_2]$ = 250, [TEA]/[(*S*)-PEA] = 10. [b] By GPC.

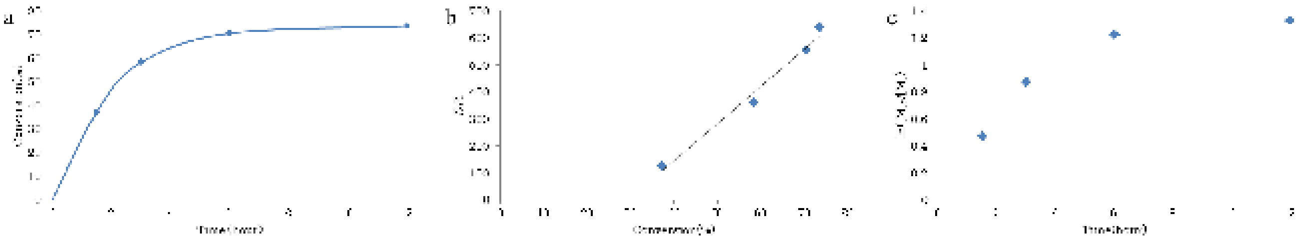
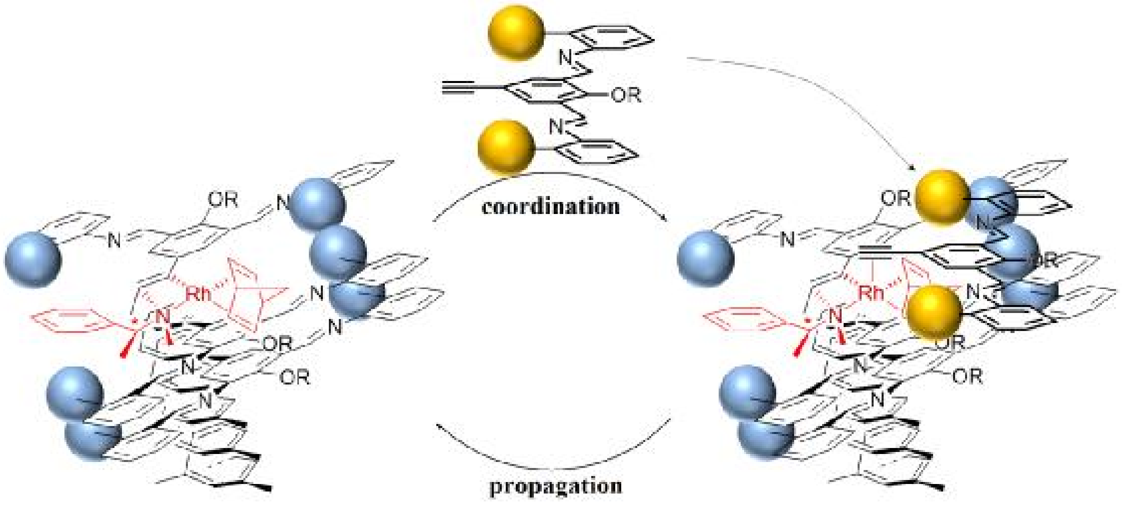


Figure S7. (a) A time-conversion curve, (b) a conversion-DP_n plot, and (c) a first-order plot for polymerization of **4b** with TEA/(*S*)-PEA.



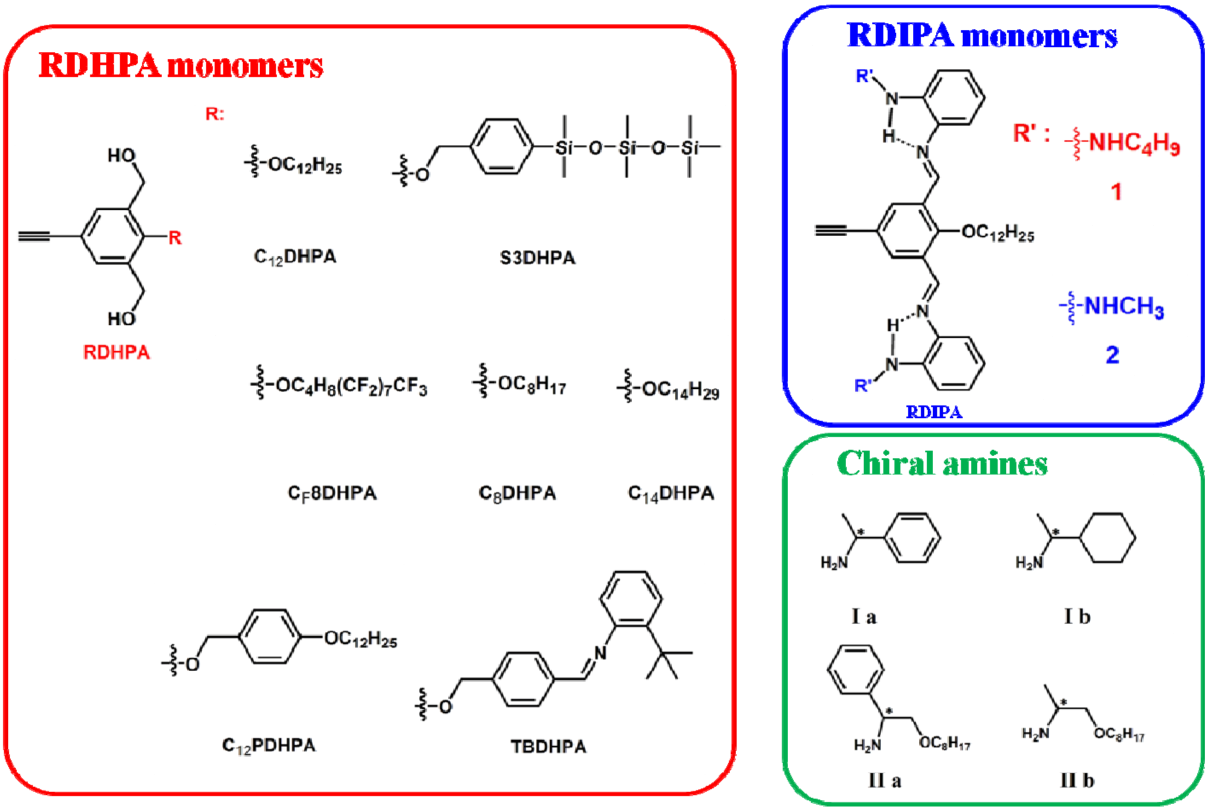
Scheme S1. Polymerization mechanism of the living **HSSP**.

Chapter 6

Optimization of Helix-Sense-Selective Polymerization of Various Achiral Phenylacetylenes

6.1 Abstract

The monomer structures suitable to the helix-sense-selective polymerization (HSSP) and the suitable combination of chiral amines and monomers were discussed. For the HSSP of RDHPA the most suitable chiral amine was IIa. For TBDHPA, Ib was the best cocatalyst. For RDIPA type monomers, Ia was the best cocatalyst. The combination of monomer C_{12}DHPA and chiral amine IIa was the best to synthesize one-handed helical polymers with the highest optical purity.

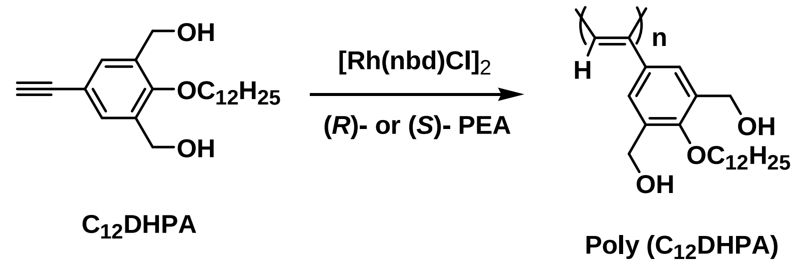


6.2 Introduction

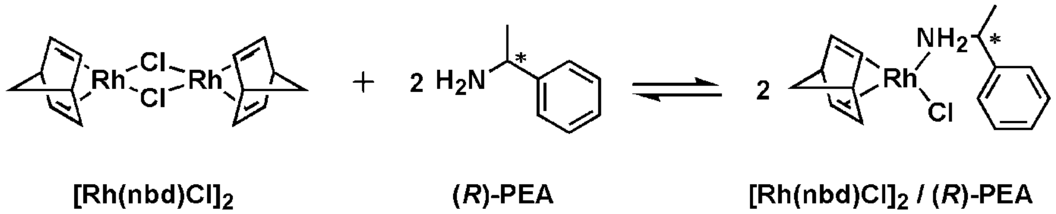
Several kinds of asymmetric polymerizations of achiral monomers to obtain chiral polymers having their chiral structures in their main chains have been reported. [1] Among them, a direct synthetic method of *soluble* chiral π-conjugated polymers whose chiral structures arise solely from the one-handed helical conformation of the conjugated main chains (therefore, they have no asymmetric carbons) and are stable alone *in solution* was so far only the helix-sense-selective polymerization (HSSP) of an achiral phenylacetylene monomer such as C_{12}DHPA (Scheme 1) by using a chiral catalytic system [Rh(nbd)Cl]$_2$ / (*R*)-phenylethylamine ((*R*)-PEA)(Scheme 2) developed in our laboratory. [2]

In addition, the role of chiral amine cocatalysts in the HSSP had been reported by our group.[3] Several chiral amines were effective for the polymerisation reaction and their effectiveness depended on their bulkiness and coordination ability to rhodium. However, the optical purity of the resulting polymers was low and the best condition for HSSP hadn't been discussed.

In this study, the HSSP conditions such as suitable combination of chiral amines, and monomers to obtain polymers with higher optical purity (*i. e.* higher *g* value) were optimized (Chart 1).



Scheme 1. Helix-sense-selective polymerization (HSSP) of C_{12}DHPA.



Scheme 2. Two component chiral initiator system in our previous study.

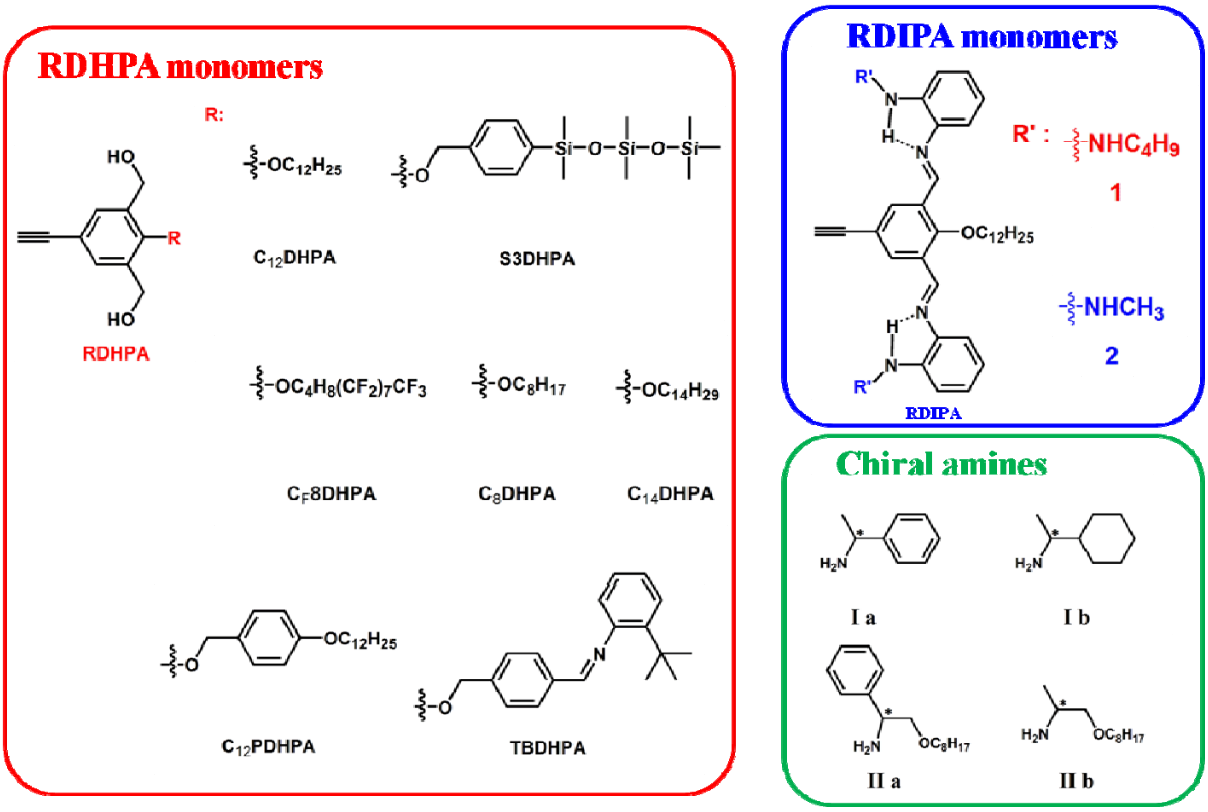


Chart 1. Chemical structures of monomers and chiral amines.

6.3 Experimental

6.3.1 Materials

All the solvents used for monomer synthesis and polymerization were distilled as usual. The polymerization initiator, $[Rh(nbd)Cl]_2$ (nbd = 2,5-norbornadiene), purchased from Aldrich Chemical was used as received. Monomers C_{12}DHPA [2a], C_8DHPA [2b], C_{14}DHPA [2b], S3DHPA [2d] and C_{12}PDHPA [2d], were synthesized according to our previous reports. The synthetic methods of monomers TBDHPA, RDIPA, and C_F8DHPA were described in Chapter 1, Chapter 2 and Chapter 3, respectively. Chiral amines IIa and IIb were synthesized according to the ref. [2c].

6.3.2 Measurements

Average molecular weight (M_n) was estimated by gel permeation chromatography (tetrahydrofuran as an eluent, polystyrene calibration) using

JASCO Liquid Chromatography instruments with PU 2080, DG 2080 53, CO 2060, UV 2070, CD2095, and two polystyrene gel columns (Shodex KF 807L). NMR spectra were recorded on a JEOL GSX 270 at 400 MHz for ^{1}H. IR spectra were recorded on a JASCO FTIR 4200 spectrometer. CD spectra were measured with a JASCO J 720 spectropolarimeter.

6.3.3 helix-sense-selective polymerization (HSSP) of the monomers

A typical polymerization procedure for C_{12}DHPA was as follows: A solution of $[Rh(nbd)Cl]_2$ (1.06 mg, 2.30 μmol) and IIa (114 mg, 460 μmol) in dry toluene (0.575 mL) was added to a dry toluene (0.575 mL) solution of C_{12}DHPA (40.0 mg, 115 μmol). The reaction solution was stirred at room temperature for 4 h. The crude polymer was purified by reprecipitation of the toluene solution into a large amount of methanol and the formed solid was dried in *vacuo* to give an orange solid. Poly(C_{12}DHPA):Yield: 4.70% (2.00 mg). M_w $=0.8\times10^6$. $M_w/M_n = 2.7$ (Table 1, no. 3).

The other polymerizations of the monomers were also carried out similarly.

6.4 Results and discussion

We used nine achiral monomers and four chiral amines as cocatalysts (Chart 1), *i.e.*, chiral amines Ia-b and chiral alkoxyamines IIa-b with different bulkiness and basicity. The results of the polymerization reactions are listed in Table 1. The CD and UV spectra were shown in Figures 1 and 2. Cotton effects were observed for the polymers obtained by using different chiral amines as cocatalysts. These findings indicated the presence of an excess of one-handed helical polyacetylene backbone. It was clear that HSSP by using chiral amines Ia-b and chiral alkoxyamines IIa-b were successful.

Among the CD intensity (*g* value) of the poly(C_{12}DIPA)s polymerized by Ia-b and IIa-b , the values obtained using bulky chiral amine IIa (Table 1, nos.1 $g =$ -5) was the highest. For other DHPA type monomers such as S3DHPA and

C_F8DHPA, polymers synthesized byIIa showed high g values as well (Chart 2). However, the yield was too low and above 90% monomer was remained. I tried

Table 1. HSSP of different monomers at room temperature.

No.	Monomer [a] (solvent)	Chiral amine [a]	[Monomer]/ [[Rh(nbd)Cl]$_2$]	Yield (%)	M_w [b] ($\times 10^6$)	M_w/M_n [b]	g_{307} [c] ($\times 10^{-5}$)
1	C_{12}DHPA	Ia	50.0	92	2.5	29	0.22
2	(toluene)	Ib	50.0	83	4.9	5.3	-1.0
3		IIa	50.0	4.7	0.80	2.7	-5.0
4		IIb	50.0	58	1.1	5.2	1.2
5	S3DHPA	Ia	50.0	73	4.0	8.8	-0.94
6	(toluene)	Ib	50.0	75	0.23	3.3	-0.59
7		IIa	50.0	5.0	0.060	1.9	-0.85
8		IIb	50.0	65	0.37	3.5	0.33
9	C_F8DHPA [d]	Ia	50.0	83	---- [d]	---- [d]	-0.70
10	(C_6F_6)	Ib	50.0	84	---- [d]	---- [d]	-0.32
11		IIa	50.0	19	---- [d]	---- [d]	0.72
12		IIb	50.0	67	---- [d]	---- [d]	1.1
13	C_8DHPA	Ia	500	25	1.0	5.0	0.16
14	C_{14}DHPA	Ia	500	28	6.7	4.7	0.056
15	C_{12}PDHPA	Ia	50.0	93	7.9	4.0	0.019
16	TBDHPA	Ia	10.0	84	2.4	13	-2.7
17	(THF)	Ib	10.0	51	26	6.9	-3.7
18		IIa	10.0	8.0	20	10	-0.067
19		IIb	10.0	59	29	8.0	3.3
20	1	Ia	100	89	4.5	2.3	2.4 [e]
21	(toluene)	Ib	100	91	3.1	6.6	1.2 [e]
22		IIa	100	57	3.7	11	-2.4 [e]
23		IIb	100	87	1.3	5.7	-0.81 [e]
24	2	Ia	100	83	0.36	4.0	2.2 [e]
25	(toluene)	Ib	100	44	0.13	5.7	0.041 [e]
26		IIa	100	58	0.56	5.6	0.54 [e]
27		IIb	100	85	0.28	3.8	-0.30 [e]

[a] [Monomer] = 0.1mol/L, [Chiral amine]/[[Rh(nbd)Cl]$_2$] = 200~250, 4h, for the codes, see Chart 1; [b] By GPC correlating with polystyrene standard (eluent: THF); [c] g value at 307nm, $g = ([\theta]/3300/\varepsilon) \times 0.001$; [d] No data because of insolubility in THF; [e] g_{297}.

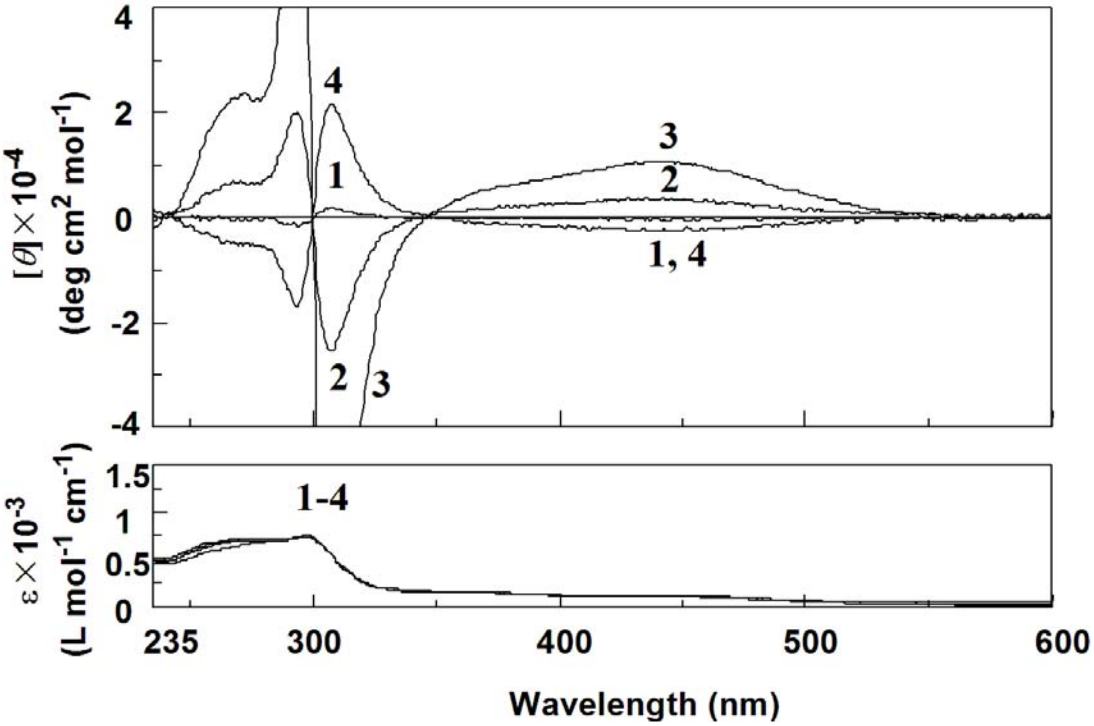


Figure 1. CD and UV spectra of poly(C_{12}DHPA) (Table 1, Nos. 1-4) in $CHCl_3$.

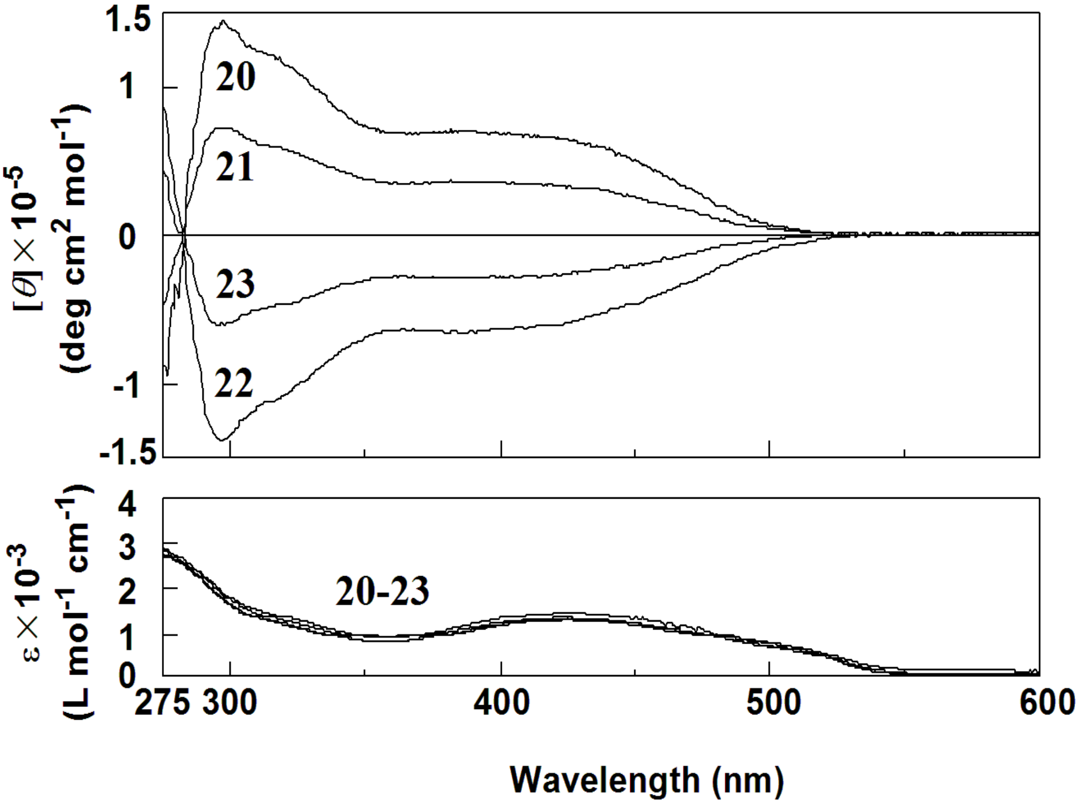


Figure 2. CD and UV spectra of poly(**1**) (Table 1, Nos. 20-23) in $CHCl_3$.

Table 2. HSSP of C_{12}DHPA at room temperature.

No.	Chiral amine	Time (h)	Yield (%)	M_w [b] ($\times 10^5$)	M_w/M_n [b]	g_{307} [c] ($\times 10^{-5}$)
1	IIa	4	4.7	8.0	2.7	-5.0
2	IIa	20	4.8	7.2	4.3	-5.3
3	IIa	30	4.8	7.1	3.6	-5.8
4	IIa	44	4.9	7.2	3.7	-5.8
5	IIa	95	4.9	7.0	4.2	-5.6
6	IIa	120	5.0	8.1	4.3	-4.8

[a] [M]=0.1mol/L, [M]/[Rh(nbd)Cl]$_2$=50, chiral amine]/[Rh(nbd)Cl]$_2$=200, in toluene. [b] By GPC correlating with polystyrene standard (eluent:THF). [c] *g* value at 307nm, *g*=([θ]/3300/ε)×0.001.

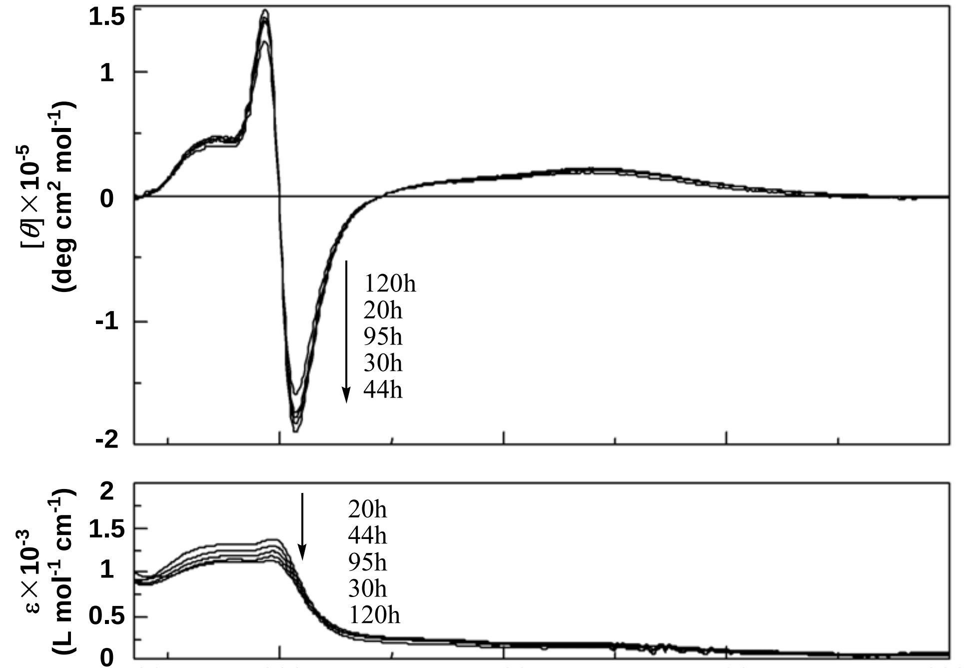


Figure 3. CD and UV spectra of poly(C_{12}DHPA) by using chiral amines IIa as cocatalysts (Table 2, nos. 1-6).

to prolong the polymerization time from 4h to 120h (Table 2, nos. 1-6), the M_w and CD strength almost no change (Figure 3). It indicated that the polymerization finished before 4h. Moreover, the polymerization speed was pretty low, the color and viscosity of polymerization system changed slowly.

The HSSP of monomer TBDHPA showed different tendency on g value by using Ia-b and IIa-b. Ib showed the best performance. This result may be caused by the effect of polymerization solvent. HSSP of other monomers were carried out in toluene except TBDHPA because the insolubility of TBDHPA in toluene. As a result, the polymerization solvent has large effect on the HSSP.

In the case of RDIPA type monomers **1** and **2**, the best achiral amine for HSSP was unbulky chiral amineIa, the poly(**1**) and poly(**2**) showed the highest g values 2.4 and 2.2, respectively by using unbulky chiral amineIa as cocatalyst. (Chart 2). This finding suggests that chiral amine having large substituents have a low coordination ability, while chiral amines having small substituents have a low selectivity in the polymerization after they have coordinated to the metal. Therefore, the combination between monomers and chiral amine cocatalysts is important for synthesizing polymers with higher optical purity.

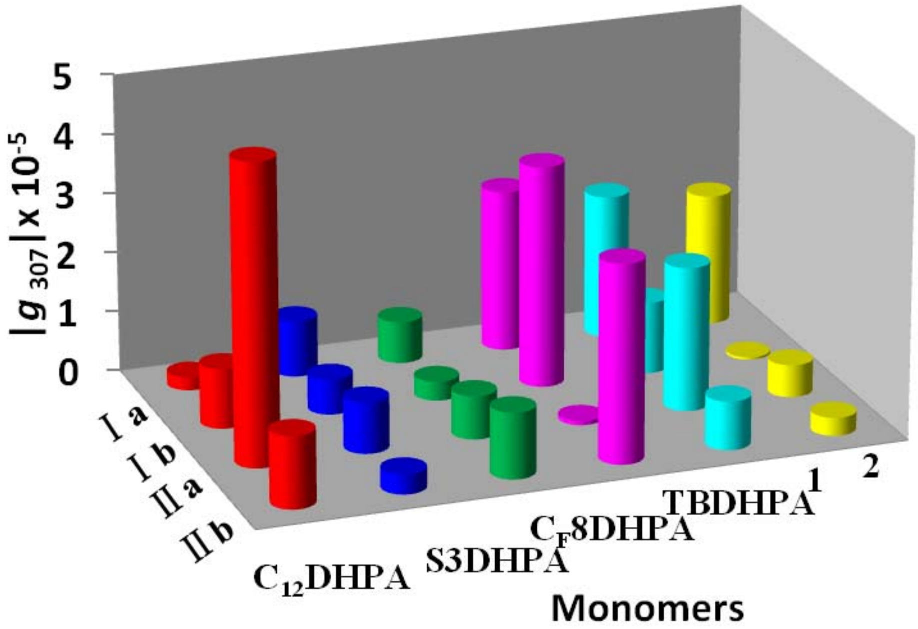


Chart 2. The relationship of g_{307} value between different monomers and chiral amines.

6.5 Conclusions

For the HSSP of unbulky monomers RDHPA, the most suitable chiral amine was bulky amine IIa. For TBDHPA, Ib was the best cocatalyst. For the bulky monomers RDIPA, unbulky amineIa was the best cocatalyst. The combination of monomer C_{12}DHPA and chiral amine IIa was the best to synthesize one-handed helical polymers with the highest optical purity.

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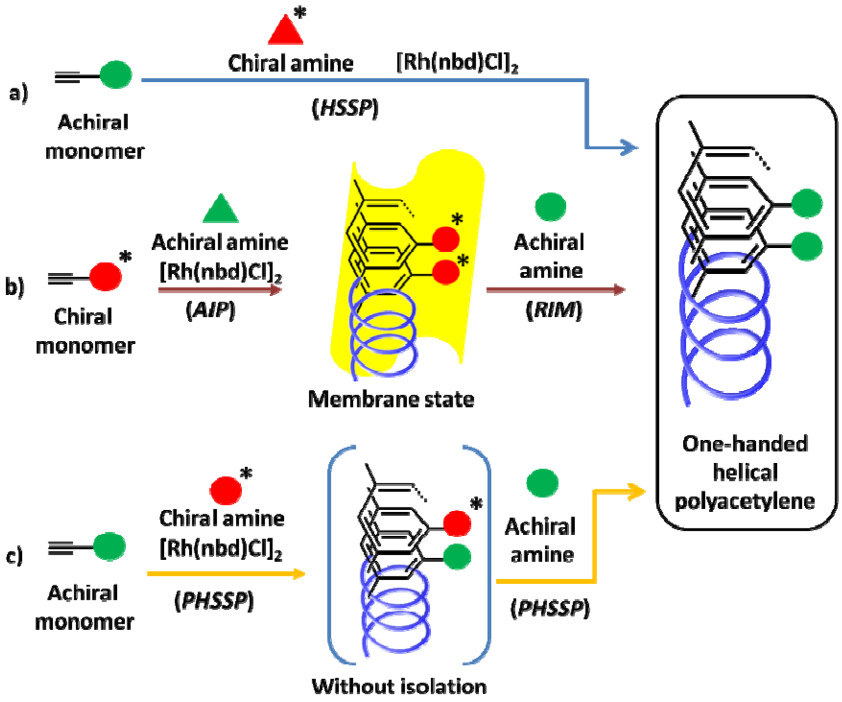
Conclusions of Part I

Imine containing RDIPA monomer **1** was the best one to synthesize one-handed helical polymers with the highest optical purity. For the bulky monomers RDIPA, unbulky amine Ia was the best cocatalyst. By introducing perfluorinated alkanes side group to RDHPA type monomer, the efficiency and ability of the chiral induction were improved. For HSSP of unbulky monomers RDHPA, the most suitable chiral amine was bulky amine IIa.

The best asymmetric polymerization method to obtain polymers with the highest optical purity and chiral induction efficiency ([chiral source]/[monomer]) among pseudo helix-sense-selective polymerization (PHSSP), helix-sense-selective polymerization (HSSP) and asymmetric induced polymerization followed by polymer reaction in membrane (AIP-RIM) was pseudo helix-sense-selective polymerization (PHSSP) because of the introduction of dynamic covalent imino bond.



PART II

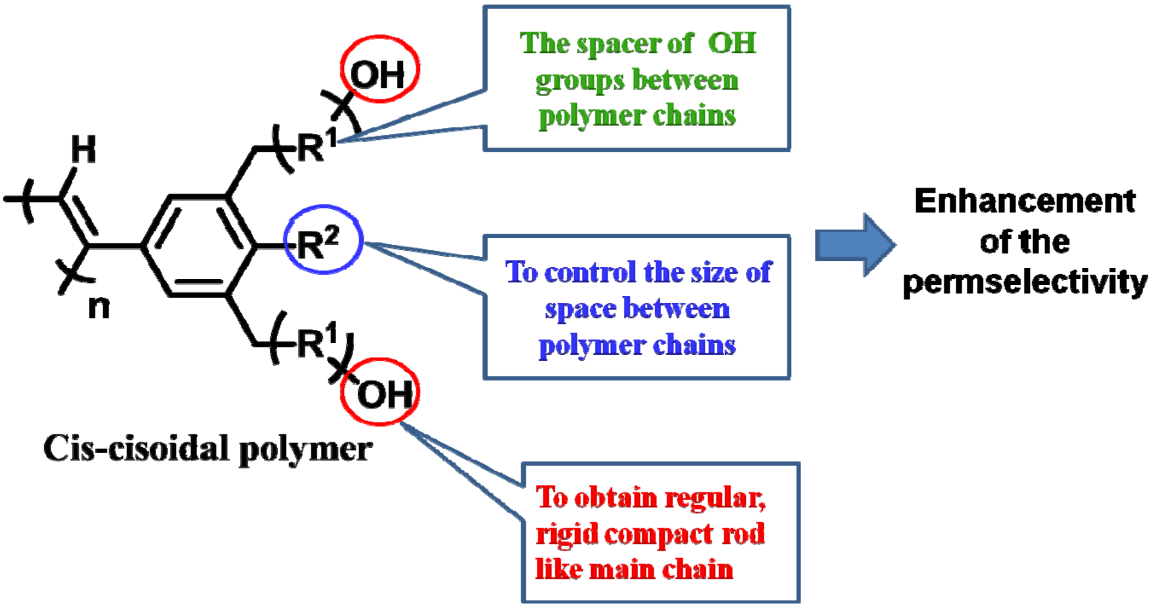
Application of the Helical Polymers Prepared by the HSSP for Membranes

Chapter 7

Application of the One-Handed Helical Polymers Prepared by the HSSP to Polymer Membranes for Gas Separation

7.1 Abstract

The new phenylacetylenes having two hydroxyl groups were synthesized and polymerized. The polymeric dense membranes were expected to enhance gas permselectivity because of the high regularity of the polymer structure. Gas permselectivities of the resulting membranes were determined and the membrane forming ability was optimized by selecting a better casting solvent. The effects of the two hydroxyl groups and the conformation of the main chain on the gas permselectivity were discussed.



7.2 Introduction

The first and higher order structures of polymers play an important role for the gas permselectivity of nonporous membranes. Separation of gases like O_2 and CO_2 through permselective membranes is a very promising method to solve the energy or environmental problems.[1] Our group has reported many polyphenylacetylene membranes having siloxanyl groups showed good self-membrane forming ability and high gas permeabilities (poly(**A**), poly(**B**)). [2] The poly(**A**) showed relativily high permselectivity. Because of the glass transition temperatures (Tg) and free volumes increased owing the bulkiness of the trimethylsilyl group, however, the permearbility was low. In addition, siloxane containing polymer(**B**) showed good self-membrane forming ability and high permeability due to the flexible of siloxane (Si-O-Si) bond in the polymer, however, the permselectivity was low. Moreover, one-handed helical polyphenylacetylenes were synthesized by our group successfully. [3]

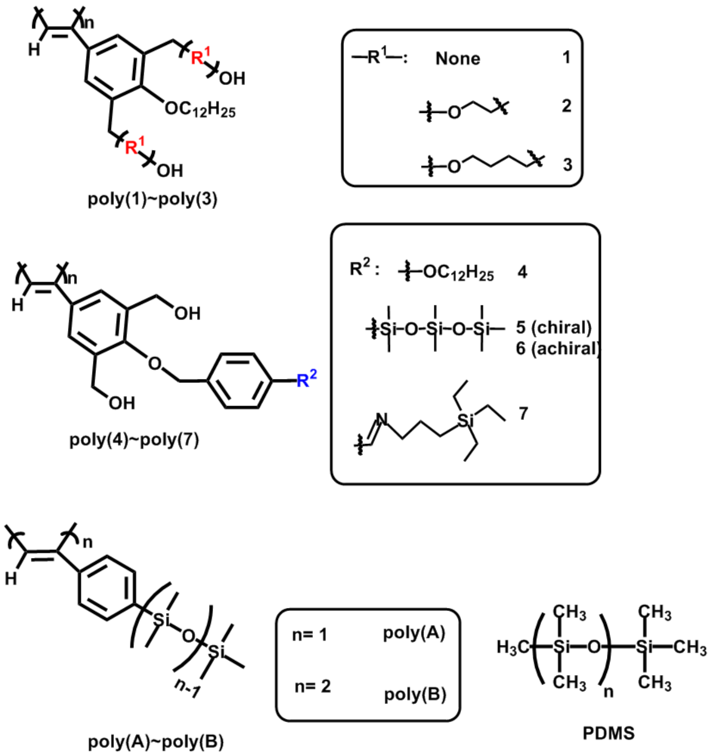


Chart 1. Chemical structures of polyphenylacetylenes used as membrane material in this chapter.

This kinds

of polymers containing compact rod like cis-cisoidal main chain as a pseudo-hexagonal columnar structure, the membranes showed high regularity structures.

In this chapter, the new phenylacetylenes having two hydroxyl groups were synthesized and polymerized. The polymeric dense membranes (poly(**1**)-poly(**7**)) were expected to enhance gas permselectivity because of the high regularity of the polymer structure. Gas perm-selectivities of the resulting membranes were determined and the membrane forming ability of poly(**1**) was optimized by selecting a better casting solvent. The effects of the two hydroxyl groups and the conformation of the main chain on the gas permselectivity were discussed.

7.3 Experimental

7.3.1 Materials

All the solvents used for synthesis and polymerization of the monomers were distilled as usual. The polymerization initiator, $[Rh(nbd)Cl]_2$ (nbd = 2,5 norbornadiene), purchased from Aldrich Chemical was used as received. Poly(**1**), poly(**4**) - poly(**6**), poly(**A**), and poly(**B**) was synthesized according to our previous report.[4] Poly(**7**) was synthesized according Chapter 1.

7.3.2 Measurements

7.3.2.1 Measurement of oxygen and nitrogen permeability

Oxygen and nitrogen permeability coefficients (P_{O_2} and P_{N_2}: $cm^3 \cdot$ (STP) $\cdot$ cm $cm^{-2} \cdot s^{-1} \cdot cmHg^{-1}$) and the oxygen separation factor ($\alpha = P_{O_2} / P_{N_2}$) were measured by a gas chromatographic method using YANACO GTR-10 according to Ref. [5]. The gas permeability coefficient and can be

$$P = \frac{L}{\Delta p \cdot A \cdot t} q \qquad D = \frac{L^2}{6\theta}$$

$$S = \frac{P}{D} \qquad \alpha = \frac{P_{O_2}}{P_{N_2}}$$

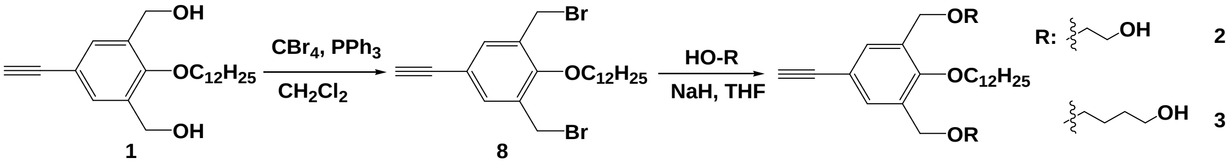
L(cm): thickness; q (cm^3): quantity;
p(cmHg): pressure; A(cm^2): area;
t(s): permeation time; θ(s): time lag;

explained on the basis of the solution-diffusion mechanism ($P = DS$), where D is the diffusion coefficient and S is the solubility coefficient. The diffusion coefficient was calculated by the time-lag method represented by $D = L^2 / 6\theta$, where L is the thickness of the membrane and θ is the time-lag.

7.3.2.2 Other measurements

^{1}H NMR (400MHz) spectra were recorded on a JEOL LEOLEX-400 spectrometer. The average molecular weights (M_n and M_w) were evaluated by gel permeation chromatography (GPC) by using JASCO liquid chromatography instruments with PU-2080, DG-2080-53, CO-2060, UV-2070, CD-2095, and two polystyrene gel columns (Shodex KF-807 L, THF eluent, polystyrene calibration). We recorded CD spectra by using a JASCO J-720WI spectropolarimeter with a Peltier controller for temperatures at 20°C (a quartz cell of 1 mm path length; sample concentration: 0.100 to 2.00 mM based on the monomer unit). The infrared spectra were recorded on FT/IR-4200 (JASCO).

7.3.3 Synthesis of the monomers 2 and 3 (Scheme 1)



Scheme 1. Synthetic route of monomers **2** and **3**.

7.3.3.1 4-Dodecyloxy-3,5-bis(bromomethyl)phenylacetylene (**8**)

Monomer **1** (1.00g, 2.89mmol), CBr_4 (3.23g, 9.73mmol), PPh_3 (2.27g, 8.67mmol), CH_2Cl_2 (40ml) were add to the flask. The solution was stirred for 4h in ice bath. It was purified by silica-gel column chromatography (Hexane, Rf: 0.14) to gave compound **8** as a white solid. The yield was 88.5%. ^{1}H-NMR(400MH$_Z$, $CDCl_3$, TMS, δ): 7.50 (s, 2H, Ph*H*), 4.48(d, 4H, PhCH_2Br), 4.09(t, 2H, $\mathrm{PhOC}H_2$), 3.06(s, $\mathrm{1H{\equiv}C}H$), 1.89(p, 2H, $\mathrm{OCH_2C}H_2\mathrm{CH_2}$), 1.54-1.27(m,18H,$(\mathrm{C}H_2)_9\mathrm{CH_3}$), 0.88(t,3H, $(\mathrm{CH_2})_9\mathrm{C}H_3$).

7.3.3.2 4-Dodecyloxy-3,5-bis(2-hydroxyethyloxymethyl)phenylacetylene (**2**)

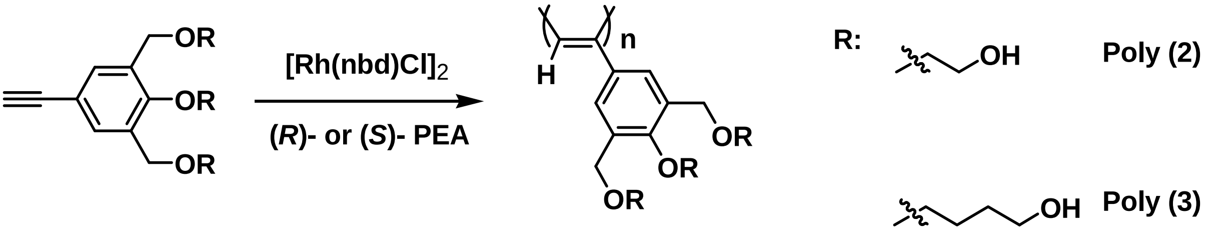
Sodium hydride (144mg, 3.00mmol) was added to a solution of compound **8** (300mg, 0.600mmol) and ethylene glycol (0.330mL, 6.00mmol) in THF (60.0mL). The mixture was refluxed for 3 days, and water was added. The resulting mixture was extracted with ethyl acetate, dried over $MgSO_4$, and evaporated to dryness. The product was purified with silica gel chromatography (hexane/AcOEt= 2/1; Rf: 0.23). A white solid was obtained in a 68.6% yield.

^{1}H-NMR(400MH$_Z$, $CDCl_3$, TMS, δ): 7.43(s, 2H, $\mathrm{Ph}H$), 4.50(d, 4H, $\mathrm{PhC}H_2\mathrm{O}$), 3.76(t, 2H, $\mathrm{PhOC}H_2$), 3.70(t, 4H, $\mathrm{CH_2C}H_2\mathrm{OH}$), 3.55(t, 4H, $\mathrm{C}H_2\mathrm{CH_2OH}$), 2.96(s, 1H, $\mathrm{C{\equiv}C}H$), 1.93(t, 2H, $\mathrm{CH_2CH_2O}H$), 1.72(p, 2H, $\mathrm{OCH_2C}H_2\mathrm{CH_2}$), 1.45-1.19(m, 18H, $(\mathrm{C}H_2)_9\mathrm{CH_3}$)，0.81(t, 3H, $(\mathrm{CH_2})_9\mathrm{C}H_3$).

7.3.3.2 4-Dodecyloxy-3,5-bis(4-hydroxybutyloxymethyl)phenylacetylene (**3**)

Sodium hydride (150mg, 3.20mmol) was added to a solution of compound **8** (300mg, 0.640mmol) and 1,4-butane diol (0.560mL, 6.35mmol) in THF (60.0mL). The mixture was refluxed for 3 days, and water was added. The resulting mixture was extracted with ethyl acetate, dried over $MgSO_4$, and evaporated to dryness. The product was purified with silica gel chromatography (hexane/AcOEt= 2/1; Rf: 0.12). A colorless liquid was obtained in a 47.6% yield. ^{1}H-NMR(400MH$_Z$, $CDCl_3$, TMS, δ), 7.48(s, 2H, $\mathrm{Ph}H$), 4.50(s, 4H, $\mathrm{PhC}H_2\mathrm{O}$), 3.81(t, 2H, $\mathrm{PhOC}H_2$), 3.64(t, 4H, $\mathrm{CH_2(CH_2)_2C}H_2\mathrm{OH}$), 3.53(t, 4H, $\mathrm{C}H_2\mathrm{(CH_2)_2CH_2OH}$), 3.01(s, 1H, $\mathrm{C{\equiv}C}H$), 1.93(t, 2H, $\mathrm{CH_2CH_2O}H$), 1.78(p, 2H, $\mathrm{OCH_2C}H_2\mathrm{CH_2}$), 1.65(m, 8H, $\mathrm{CH_2(C}H_2)_2\mathrm{CH_2OH}$), 1.45-1.26(m, 18H, $(\mathrm{C}H_2)_9\mathrm{CH_3}$), 0.88(t, 3H, $(\mathrm{CH_2})_9\mathrm{C}H_3$).

7.3.4 Polymerization of the monomers 2 and 3 (Scheme 2)



2 and 3 **Poly (2) and poly(3)**

Scheme 2. Helix-sense-selective polymerization (HSSP) of **2** and **3**.

A typical procedure for monomer (**2**) was as follows: A solution of $[Rh(nbd)Cl]_2$ (2.12mg, 4.6μmol) and (*S*)- or (*R*)-phenylethylamine (PEA) (118μl, 0.920mmol) in dry toluene (1.44mL) was added to a dry toluene (1.44mL) solution of **2** (100mg, 230μmol). The reaction solution was stirred at room temperature for 4h. The crude polymer was purified by reprecipitation of the THF solution into a large amount of methanol and the formed solid was dried *in vacuo* to give a red solid.

Other helix-sense-selective polymerisation (HSSP) of the monomers **1-7**, **A** and **B** were carried out similarly.

7.3.5 Membrane preparation

A typical membrane fabrication method for poly(**2**) was as follows: A solution of the poly(**2**) (0.0600-10.0 wt%) in dry toluene (40.0 mg/mL) was cast on a poly(tetrafluoroethylene) sheet (4 cm^2). After evaporating of the solvent for 12h at 25°C, the membranes were detached from the sheet and dried in *vacuo* for 24 h. Thickness (L) of the membranes was 50.0-80.0 μm.

7.4 Results and Discussion

7.4.1 The effect of membrane preparation method on O_2/N_2 selective permeation

Oxygen permselectivities of polymer membranes prepared from solutions in a different solvent (Chart 1, poly(**1**)) were shown in Figure. 2 and Tables 2.

Poly(**1-b**) which was cast from a solution of toluene and $CHCl_3$ (two component solvent) showed the highest permselectivity among the membranes prepared by the other solvents (poly(**1-a**), poly(**1-c**), and poly(**1-d**)). This may be caused by the difference of the amount of defects. The structures of membranes fabricated by different solvent and conditions were analyzed by X-ray diffraction. The results were shown in Figure. 1 and Table 1. The membranes prepared by $CHCl_3$ give highest columnar content. The membranes fabricated by polar solvents showed low columnar content. The higher the columnar content is the lower selectivity it will be. Poly(**1-b**) having appropriate columnar content show the best performance.

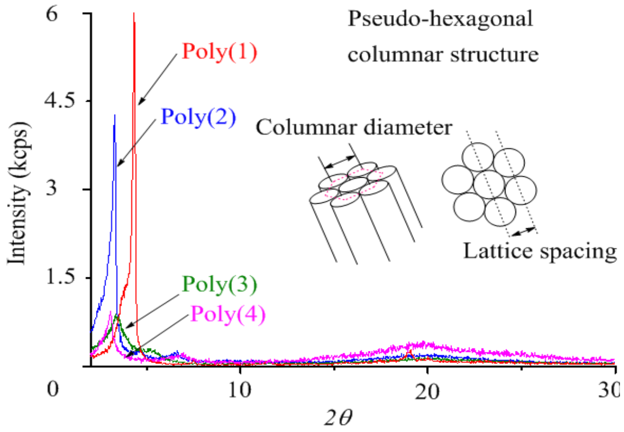


Figure 1. X-Ray diffraction diagrams of poly(**1**) - poly(**4**) membranes; scanning rate = 2 deg/min, λ=1.54 Å.

Table 1 . Structure of poly(1) membranes [a)]

Membrane	Solvent	Condition	Lattice [b)] spacing Å	Columnar [c)] diameter Å	Columnar [d)] content %	Membrane [e)] forming ability	d [f)]	Color
1-a	toluene	25°C / 101KPa	20.53	23.71	69.3	+	--- [g]	orange
1-b	toluene/$CHCl_3$	25°C / 101KPa	20.53	23.71	67.8	++	--- [g)]	orange
1-c	$CHCl_3$	25°C / 101KPa	20.42	23.58	85.9	++	0.906	orange
1-d	pyridine	45°C / 61KPa	20.62	23.81	29.0	++	--- [g)]	red
1-e	$CHCl_3$/DMSO	60°C / 31KPa	31.30	35.33	27.0	–	--- [g)]	orange

a) By solvent casting; b) Determined by XRD, calculated from the following equations: 2d sin θ =n λ, where n=1 and λ =1.54 Å; c) d/sin 60; d) The ratio of the area of columnar region to the area of the entire region; e) ++ :Excellent; + : good; – : poor; f) Density determined by densimeter (g/cm^3); g) No determined.

Table 2. Oxygen permselectivity of polymer membranes.

	Solvent	Membrane forming ability a)	P_{O_2} b)	P_{O_2}/P_{N_2}	D_{O_2} c)	D_{O_2}/D_{N_2}	S_{O_2} d)	S_{O_2}/S_{N_2}	d e)
poly(**1-a**)	toluene	±	1.28	2.17	1.70	1.87	7.53	1.16	------
poly(**1-b**)	toluene/$CHCl_3$ (1/1)	+	1.41	2.61	1.80	1.19	7.83	2.19	------
poly(**1-c**)	$CHCl_3$	±	1.39	2.19	1.16	1.04	11.98	2.10	0.906
poly(**1-d**)	pyridine	±	1.46	2.07	1.37	1.19	10.65	1.74	------
poly(**2**)	THF	+	0.13	2.60	0.41	1.45	3.20	1.79	------
poly(**3**)	THF	+	0.16	2.67	0.50	1.34	3.20	1.99	------
poly(**4**)	toluene/$CHCl_3$ (1/1)	–	0.17	2.50	0.40	1.20	4.00	2.10	------
poly(**5**)	toluene/$CHCl_3$ (1/1)	+	2.14	2.00	------	-----	------	-----	------
poly(**6**)	toluene/$CHCl_3$ (1/1)	+	2.67	1.90	------	-----	------	-----	------
Poly(**7**)	toluene/$CHCl_3$ (1/1)	±	0.11	2.32	5.09	2.00	2.21	1.16	------
Poly(**A**) f)	$CHCl_3$	±	1.71	2.70	2.26	1.34	7.57	2.01	0.976
Poly(**B**) f)	$CHCl_3$	+	3.97	2.20	1.24	1.30	32.00	1.70	0.988
PDMS g)	------	------	3.50	1.90	19.00	1.40	1.90	1.50	------

a) +: Best; ±: good; –: poor; b) In 10^{-8}cm^3(STP)·cm·cm^{-2}·s^{-1}·cmHg^{-1}; c) In 10^{-6}cm^2·s^{-1}; d) In 10^{-3}cm^3(STP)·cm^{-3}·cmHg^{-1}; e) Density determined by densimeter (g/cm^3); f) From ref. 2); g) From ref. 6).

From the values of D_{O2}/D_{N2} and S_{O2}/S_{N2} in Table 2, increases in P_{O2}/P_{N2} values of poly(**1-b**) were caused by mainly increases in S_{O2}/S_{N2} values similarly to poly(**A**).

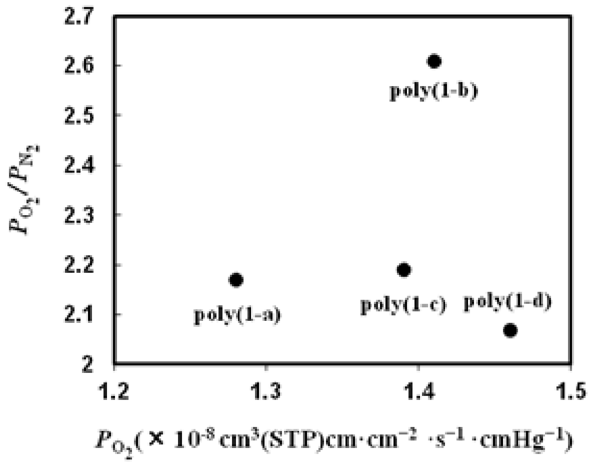


Figure 2. The relationship between permeablility and permselectivity for O_2 through the poly(**1**) membranes prepared from the solution of (**1-a**) toluene; (**1-b**) toluene/$CHCl_3$=1/1; (**1-c**) $CHCl_3$; and (**1-d**) pyridine.

7.4.2 The effect of Si% content on O_2/N_2 selective permeation

In order to increase the permeability and discuss the effect of Si% content on gas permselectivity, I synthesized the polymers containing siloxane groups poly(**5**), poly(**6**) and copolymerized monomer **5** with monomer **1**. The results were shown in Figure 3. The permeability was enhanced by increasing the amount of Si%. The soft Si-O made gas molecules permeate membranes readily.

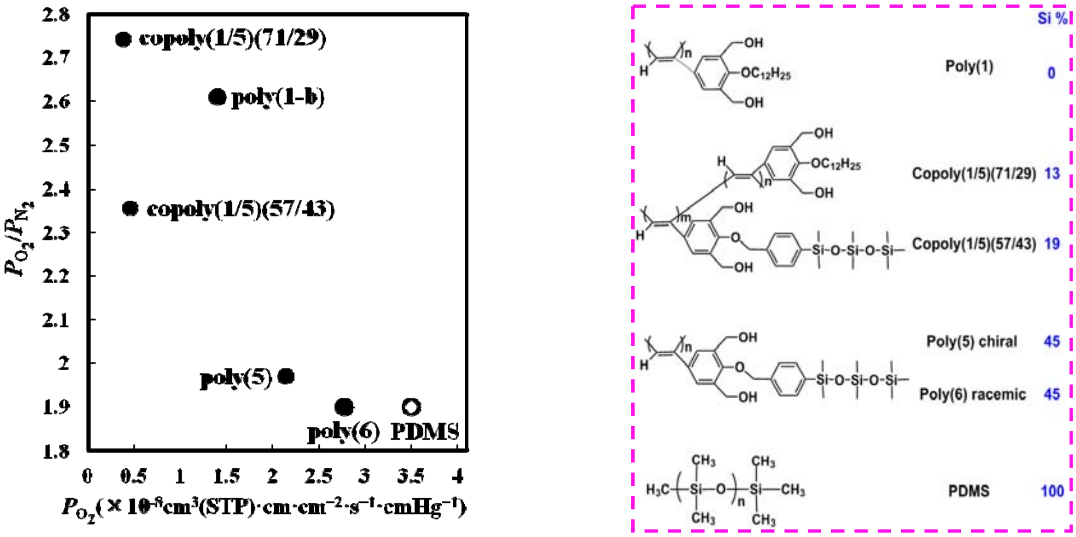


Figure 3. The relationship between permeablility and permselectivity for O_2 through the copoly(**1/5**), poly(**5**), poly(**6**) and PDMA membranes .

7.4.3 The effect of spacers on O_2/N_2 selective permeation

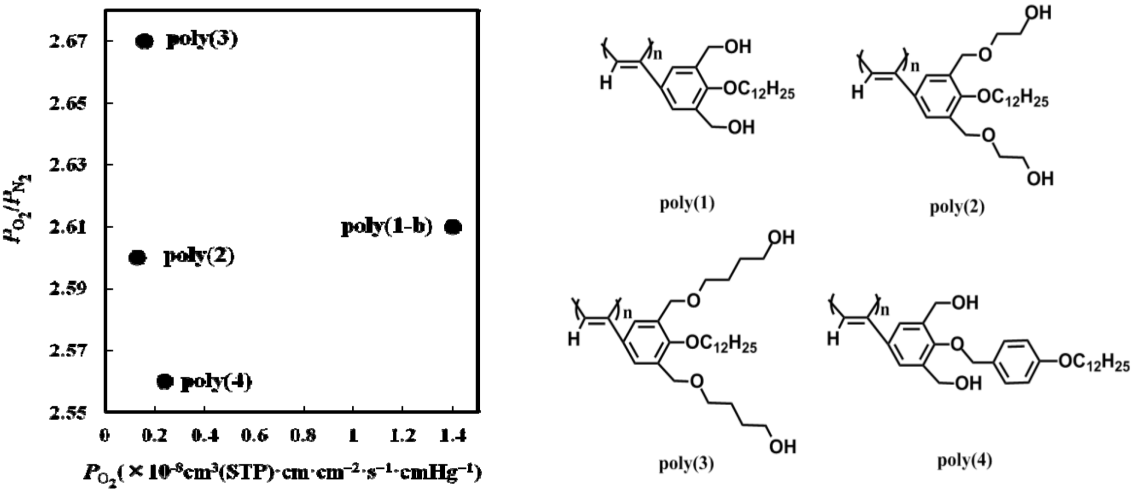


Figure 4. The relationship between permeablility and permselectivity for O_2 through the poly(**1-b**)-poly(**4**) membranes.

The effects of spacers on O_2/N_2 selective permeation were discussed. The polymers having different spacers were measured and the results were shown in Figure 4. By increasing the length of spacers of two hydroxyl groups, the permeability decreased. Moreover, to compare with poly(**1**) the spacer of benzyl group of poly(**4**) lead to negative effect on the permselectivity.

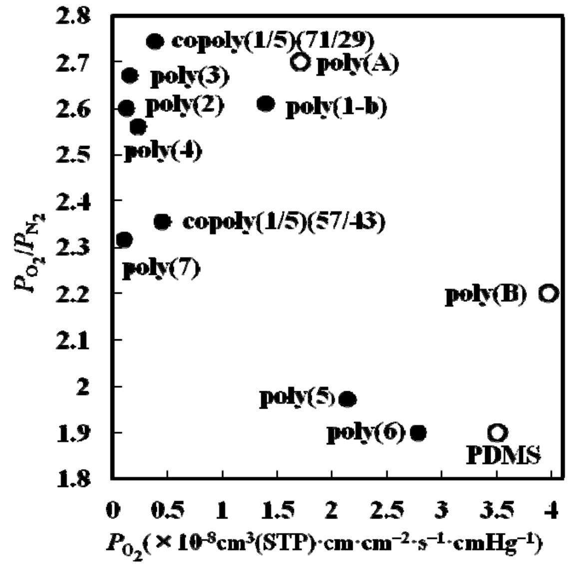


Figure 5. The relationship between permeablility and permselectivity for O_2 through the poly(**1-b**)-poly(**4**) membranes.

Higher P_{O2}/P_{N2} of poly(**1-b**) and copoly(**1**/**5**) membranes than other membranes in this study caused by 1) molecular level: higher regularity of the polymer main chain and uniform size of free volumes; 2) higher ordered level: the membranes forming ability was optimized by using better casting solvent as a result, the optimized membranes contain low ratio of defects.

7.5 Conclusions

To obtain membranes having the best performance, selection of solvent and condition in membrane preparation was important. The more rigid backbone of the polymers having the same oligosiloxane content decreased the permselectivity. The longer spacer increased flexibility and decreased the permeability.

References and Notes

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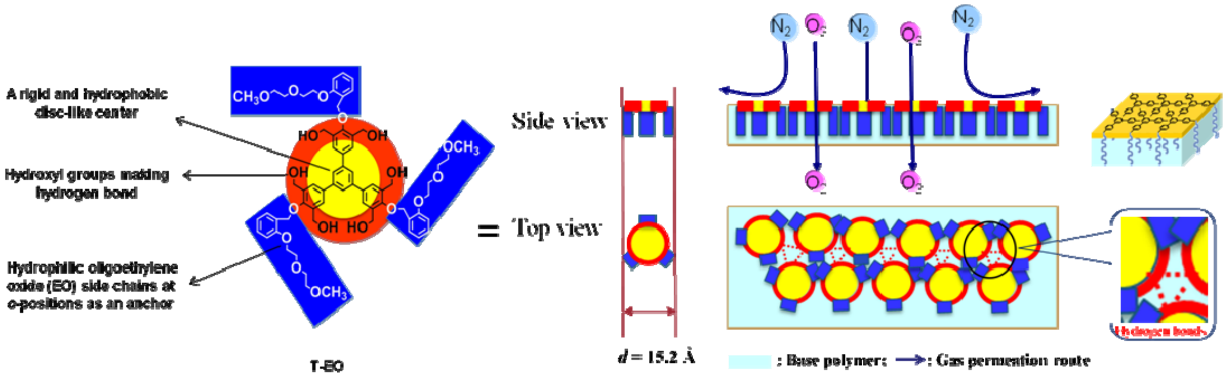
Chapter 8

Facile Synthesis of Amphiphilic 1,3,5-Trisubstituted Benzene Derivatives Having Six Hydroxyl Groups and Three Hydrophilic Groups as Novel 2D Surface Modifiers for Efficient Improvement of Oxygen Permselectivity of Polymer Membranes

8.1 Abstract

Facile synthesis of amphiphilic molecules 1,3,5-trisubstituted benzene derivatives having six hydroxyl groups and three hydrophilic groups as novel 2D surface modifiers were achieved. Surface modifications by 0.06~10 wt% of amphiphilic molecules T-EO, T-(EO-*co*-Do), on substrates PVA, PVAc and PDPS were achieved by a simple method, because the contact angles for blend membranes were increased. A supromolecular structure of the amphiphilic molecules T-EO having 2D regular size pores and thinner thickness in molecular level on the PVA membrane surface was formed. The oxygen permselectivity of substrate polymer membranes were improved highly from 1.71 to 4.11 without drop in P_{O_2}.

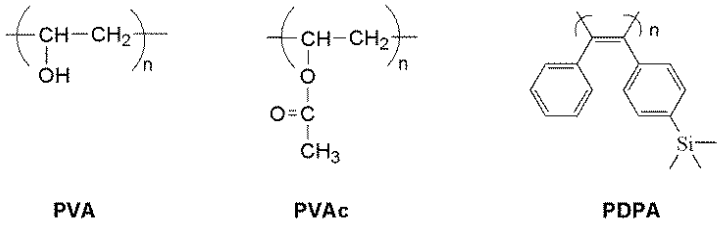


8.2 Introduction

Gas-permselective membranes are very important and valuable because the necessity to remove impurities or purify mixtures of gases whose molecular sizes are very similar is increasing because solving the recent environmental problems has been focused on. [1] Carbon molecular sieve membranes showed good gas permselectivity have been reported. [2] Tsuru group reported silica membranes with high gas-separation performance. [3] The silica membranes showed molecular sieving properties. However the inorganic membranes show no self-supporting membrane forming ability.

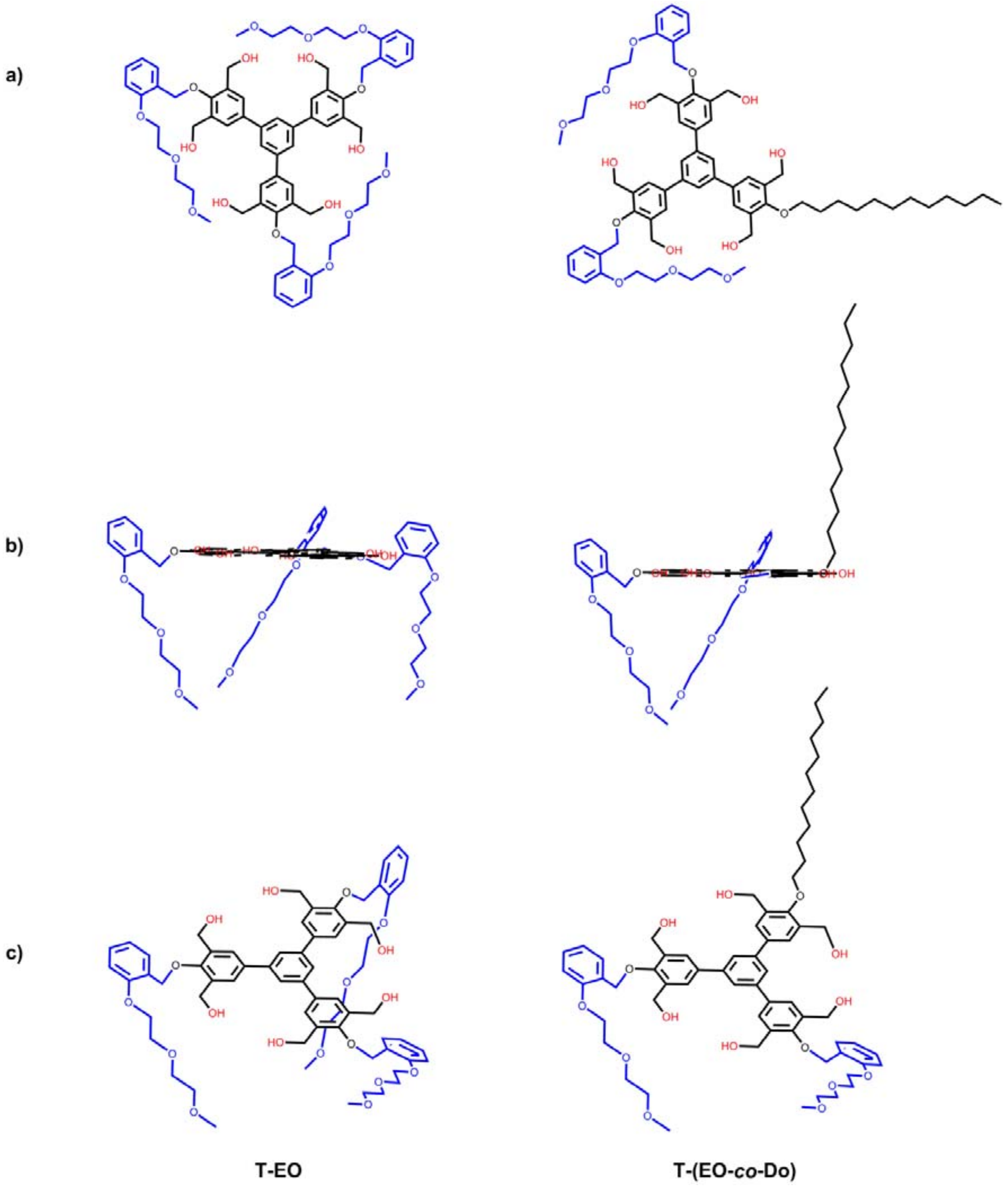
The formation of functionalized surfaces with periodicities on the nanometer scale attracts a lot of interest. [4] Molecules are ideal building blocks for the formation of such well-organized and functional surfaces via self-assembley. Two-dimensional (2D) pattern formation might turn out to be crucial to the design and properties of functional surfaces. [5] Noncovalent interactions are attractive tools to control the ordering of molecules on a surface. Hydrogen bonds are highly selective and directional, though moderately strong, and they have been extensively applied to direct the molecular ordering on surfaces. [6] Amphiphilic molecules were used as an ideal modifier for the formation of well-organized and functional surfaces via self-assembly. [7]

In this chapter, in order to enhance the O_2/N_2 permselectivity through the substrate membranes of poly(vinyl alcohol) (PVA) and poly(vinyl acetate) (PVAc) (Chart 1), an amphiphilic molecule **T-EO** having six hydroxyl groups and three hydrophilic groups (Figure 2) was used for the modification of the substrate members. The amphiphilic molecule **T-EO** was prepared by a facile method - highly selective photocyclic aromatization of cis-cisoid helical polymer (SCAT). [8] The O_2/N_2 permselectivity of the substrate polymer membranes were expected to be enhanced since the formation of 2D structure on the surface of substrate membranes. The membranes are expected to show molecular sieving properties.



PVA PVAc PDPA

Chart 1. Chemical structures of substrate polymers.



T-EO T-(EO-*co*-Do)

Figure 1. Chemical structures of **T-EO** and **T-(EO-*co*-Do)**, a) 2D chemical structure, b) 3D side view, c) 3D bird's-eye view.

8.3 Experimental

8.3.1 Materials

All the solvents used for monomer synthesis and polymerization were distilled as usual. The polymerization initiator, $[Rh(nbd)Cl]_2$ (nbd=2,5 norbornadiene), purchased from Aldrich Chemical Co., Inc., was used as received. 4-(Dodecyloxy)-3,5-bis(hydroxymethyl)phenylacetylene was synthesized from 4-bromophenol according to our previous report. [9] Poly(vinyl alcohol) (PVA) (M_w = 1500, degree of hydrolysis = 86.0~90.0 mol%) and poly(vinyl acetate) (PVAc) (M_w = 1500) purchased from Wako Pure Chemical Industries, LTD., were used as received. Poly(1-phenyl-2-[*p*-(trimethylsilyl)phenyl]acetylene) (PDPA) ($M_w = 8.72\times10^6$) was synthesized according to Masuda's report [10].

8.3.2 Measurements

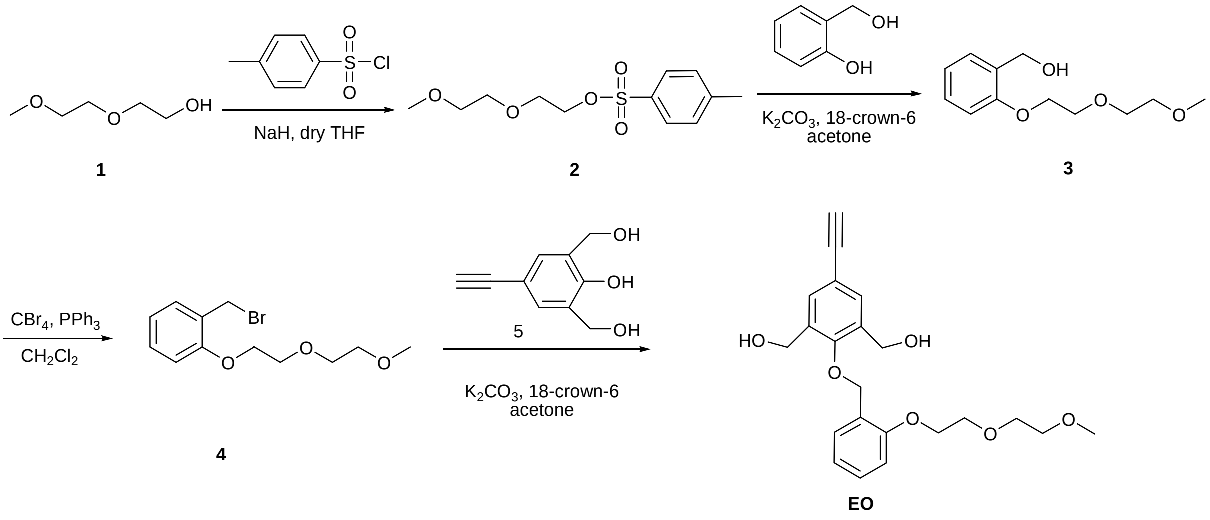
8.3.2.1 Measurement of oxygen and nitrogen permeability

Oxygen and nitrogen permeability coefficients (P_{O_2} and P_{N_2}: $cm^3\cdot(STP)\cdot cm\ cm^{-2}\cdot s^{-1}\cdot cm\cdot Hg^{-1}$) and the oxygen separation factor ($\alpha = P_{O_2}/P_{N_2}$) were measured by a gas chromatographic method using YANACO GTR-10 according to Ref. [11]. The gas permeability coefficient and can be explained on the basis of the solution-diffusion mechanism ($P = DS$), where D is the diffusion coefficient and S is the solubility coefficient. The diffusion coefficient was calculated by the time-lag method represented by $D = L^2 / 6\theta$, where L is the thickness of the membrane and θ is the time-lag.

8.3.2.2 Other measurements

^{1}H NMR (400MHz) spectra were recorded on a JEOL LEOLEX-400 spectrometer. The average molecular weights (M_n and M_w) were evaluated by gel permeation chromatography (GPC) by using JASCO liquid chromatography instruments with PU-2080, DG-2080-53, CO-2060, UV-2070, CD-2095, and two polystyrene gel columns (Shodex KF-807 L, THF eluent, polystyrene calibration). CD spectra were recorded by using a JASCO J-720WI spectropolarimeter with a Peltier controller for temperatures at 20°C (a quartz cell of 1 mm path length; sample concentration: 0.100 to 2.00 mM based on the monomer unit). The infrared spectra were recorded on FT/IR-4200 (JASCO). MALDI-TOF-MS spectra were recorded using a Bruker Reflex II mass spectrometer (Bruker Daltonics). Contact angles of distilled water droplets on the membranes were measured with a DM-301， Kyowa Interface Science Co., LTD. All molecular calculations were performed using Spartan’10.

8.3.3 Synthesis of the monomer EO (Scheme 1)



Scheme 1. Synthetic route to monomer **EO**.

8.3.3.1 2-(2-Methoxyethoxy)ethyl-4-methylbenzenesulfonate (**2**)

To a dry tetrahydrofuran (THF) solution (50.0 mL) of NaH (40% oil) (3.50 g, 87.6 mmol), diethyleneglycol monomethyl ether (7.80 mL, 65.7 mmol) and a dry THF solution of 4-toluenesulfonyl chloride (TsCl: 10.4 g, 54.8 mmol) were added dropwise at 0°C, respectively. After stirring for 9h at room temperature, the reaction mixture was treated with 4N HCl aq. and filtered, THF was removed by evaporation. The yellow solution was extracted by dichloromethane.

The organic layer was dried over anhydrous $MgSO_4$ and concentrated. The crude product was purified by silica-gel column chromatography to give **2** as a colorless liquid. Yield: 64.3% (9.66 g). $R_f = 0.36$ (ethyl acetate / hexane = 1 / 1). ^1H NMR ($CDCl_3$, TMS, ppm): $\delta = 7.80$ (d, 2H, Ph*H*), 7.34 (d, 2H, Ph*H*), 4.17 (t, 2H, $S(=O)_2OCH_2CH_2$), 3.69 (t, 2H, $S(=O)_2OCH_2CH_2O$), 3.58~3.48 (m, 4H, $OCH_2CH_2OCH_3$), 3.35 (s, 3H, OCH_3), 2.45 (s, 3H, $PhCH_3$) .

8.3.3.2 1-(1, 4, 7-Trioxaoctyl)-2-hydroxymethylbenzene (**3**)

To an acetone solution (200 mL) of K_2CO_3 (11.1 g, 80.6 mmol), 18-crown-6 (5.35 g, 20.1 mmol) and 2-hydroxybenzyl alcohol (5.00 g, 40.3 mmol), **2** (12.2 g, 44.3 mmol) was added dropwise at 0°C. After 48h at reflux, the reaction mixture was extracted with ethyl acetate. The organic layer was dried over $MgSO_4$ and concentrated. The crude product was purified by silica-gel column chromatography to give aim product **3**. Yield: 66.2% (6.03 g). $R_f = 0.31$ (ethyl acetate / hexane = 1 / 1). ^1H NMR ($CDCl_3$, TMS, ppm): $\delta = 7.23$ (m, 2H, Ph*H*), 6.90 (m, 2H, Ph*H*), 4.65 (d, 2H, $PhCH_2OH$), 4.18 (t, 2H, $PhOCH_2CH_2$), 3.83~3.54 (m, 6H, $CH_2CH_2OCH_2CH_2OCH_3$), 3.36 (s, 3H, OCH_3), 3.33 (t, 1H, CH_2OH).

8.3.3.3 1-(1, 4, 7-Trioxaoctyl)-2-bromomethylbenzene (**4**)

To a dichloromethane solution (200 mL) of **3** (5.71 g, 25.2 mmol) and tetrabromomethane (14.2 g, 42.9 mmol), triphenylphosphine (10.0 g, 38.2 mmol) was added dropwise at 0°C and then stirred for 1h. The saturated sodium bicarbonate solution was added to the mixture to stop the reaction. The reaction mixture was extracted with dichloromethane and the organic layer was dried over $MgSO_4$ and concentrated. The resulting yellow oil liquid was purified by silica-gel column chromatography to give aim product **4**. Yield: 86.5% (6.31 g). $R_f = 0.50$ (ethyl acetate / hexane = 1 / 3). ^1H NMR ($CDCl_3$, TMS, ppm): $\delta = 7.28$ (m, 2H, Ph*H*), 6.88 (m, 2H, Ph*H*), 4.57 (s, 2H, $PhCH_2Br$), 4.19 (t, 2H, $PhOCH_2CH_2$), 3.90~3.55 (m, 6H, $CH_2CH_2OCH_2CH_2OCH_3$), 3.37 (s, 3H, OCH_3).

8.3.3.4 2, 6-Bis(hydroxymethyl)-4-ethynylphenol (**5**) [9]

According to the literature procedure, **5** was prepared as a white solid. Yield: 29.9% (4.95 g). R_f = 0.27 (ethyl acetate / hexane = 1 / 1). ^{1}H NMR (DMSO-d_6, ppm): δ = 8.98 (s, 1H, PhO*H*), 7.27 (s, 2H, Ph*H*), 5.29 (s, 2H, Ph(CH_2O*H*$)_2$), 4.52 (s, 4H, Ph(C*H*$_2$OH$)_2$), 3.91 (s, 1H, *H*C≡C).

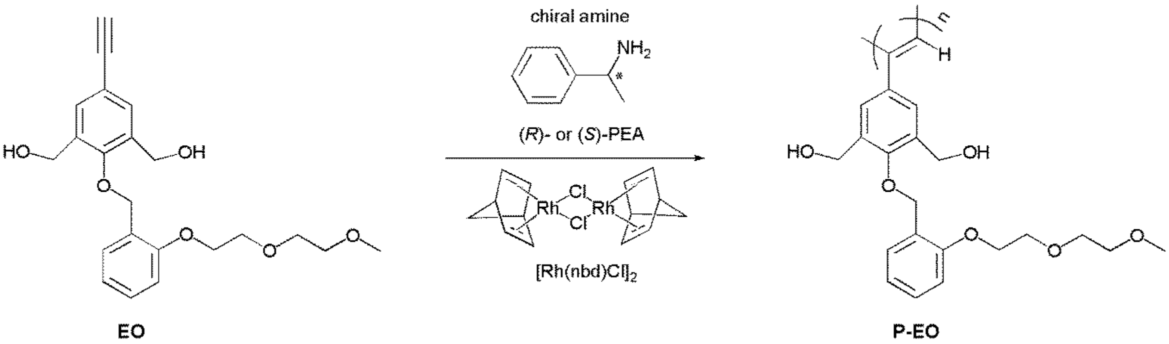
8.3.3.5 4-[4'-(1,4,7-Trioxaoctyl)benzyloxy]-3,5-bis(hydroxymethyl)phenylacetylene (**EO**)

A mixture of **4** (1.96 g, 6.79 mmol), **5** (1.10 g, 6.17 mmol), 18-crown-6 (1.79 g, 6.79 mmol) and K_2CO_3 (1.71 g, 12.3 mmol) in acetone (33.0 mL) was stirred for 50h at reflux. Then the mixture was filtered, the solvent was removed. The residue was washed with water and extracted with dichloromethane. The organic layer was dried over $MgSO_4$ and concentrated. The crude product was purified by silica-gel column chromatography to give aim product **EO**. Yield: 65.0% (1.55 g). R_f = 0.25 (ethyl acetate/hexane = 1/2). ^{1}H NMR ($CDCl_3$, TMS, ppm): δ = 7.53 (s, 2H, HC≡CPh*H*), 7.45~7.30 (m, 2H, Ph*H*OCH_2CH_2), 7.03~6.90(m, 2H, PhOCH_2Ph*H*), 5.01 (s, 2H, PhOC*H*$_2$Ph), 4.75 (d, 4H, Ph(C*H*$_2$OH$)_2$), 4.19 (t, 2H, PhOC*H*$_2$$CH_2$), 3.88~3.57 (m, 6H, CH_2C*H*$_2$OC*H*$_2$C*H*$_2$OCH_3), 3.36 (s, 3H, OC*H*$_3$), 3.03 (s, 1H, *H*C≡C), 2.82 (t, 2H, Ph(CH_2O*H*$)_2$). ^{13}C NMR ($CDCl_3$, TMS, ppm): δ = 159.11, 154.90, 134.85, 132.47, 130.08, 128.88, 118.45, 114,86 (aromatic), 83.31 (HC≡C), 77.16 (PhCH_2O), 76.71 (HC≡C), 60.36 (CH_2OH), 72.00, 70.80, 69.79, 67.49, 59.16 ($OCH_2CH_2OCH_2CH_2OCH_3$). Anal. Cacld for $C_{22}H_{26}O_6$: C, 68.38; H, 6.78; O, 24.84. Found: C, 68.25; H, 6.81; O, 24.94.

8.3.4 Synthesis of P-EO by polymerization of EO

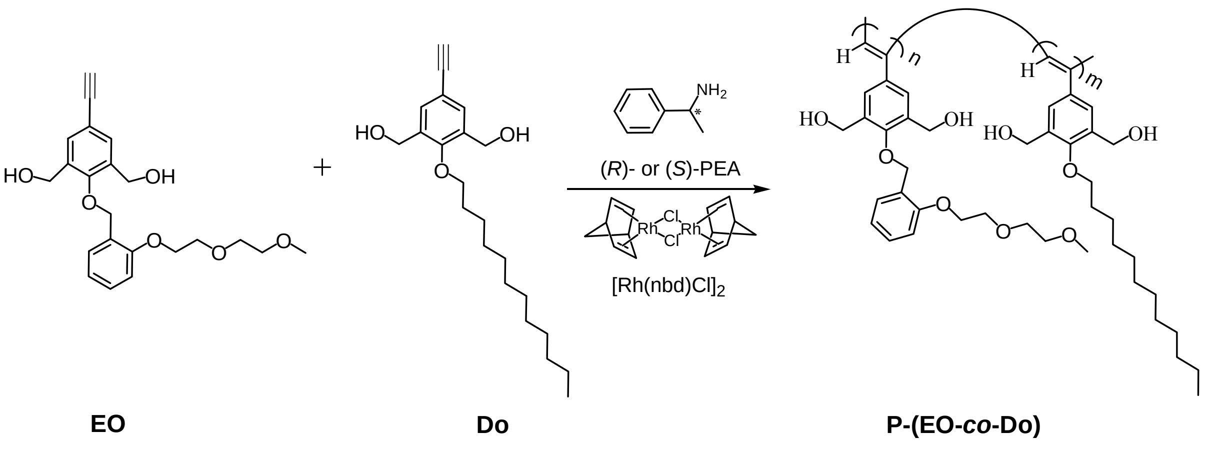
8.3.4.1 Polymerization of 4-[4'-(1,4,7-Trioxaoctyl)benzyloxy]-3,5-bis(hydroxymethyl)phenylacetylene (**EO**) (Scheme 2)

A solution of [Rh(nbd)Cl$]_2$ (3.58 mg, 7.77 μmol) and (*R*)-phenylethylamine (PEA) (0.398 mL, 3.10 mmol) in dry chloroform (2.60 mL) was added to a dry chloroform (1.59 mL) solution of **EO** (100 mg, 0.259 mmol). The reaction solution was stirred at room temperature for 12h. The crude polymer was purified by reprecipitation of the chloroform solution into a large amount of ethyl acetate / hexane = 3 / 2, and the formed solid was dried in *vacuo* to give a deep red solid. **P-EO**: Yield: 54.9% (54.9 mg). M_w =2.62×10^5, M_w/M_n = 7.40. ^{1}H NMR ($CDCl_3/DMSO\text{-}d_6$ = 60/40 (v/v), TMS, ppm): δ = 7.28 (d, 1H, Ph*H*OCH_2CH_2), 7.16 (t, 1H, Ph*H*OCH_2CH_2), 6.81 (m, 4H, HC=CPh*H* and Ph*H*OCH_2CH_2), 4.57~4.37 (m, 6H, $PhOCH_2Ph$ and $Ph(CH_2OH)_2$), 3.97~3.49 (m, 10H, $OCH_2CH_2OCH_2CH_2OCH_3$ and $Ph(CH_2OH)_2$)), 3.36 (s, 3H, OCH_3). Cis% = 94.4%.



Scheme 2. HSSP of **EO** by using [Rh(nbd)Cl_2] as a catalyst and (*R*)- or (*S*)-PEA as a cocatalyst.

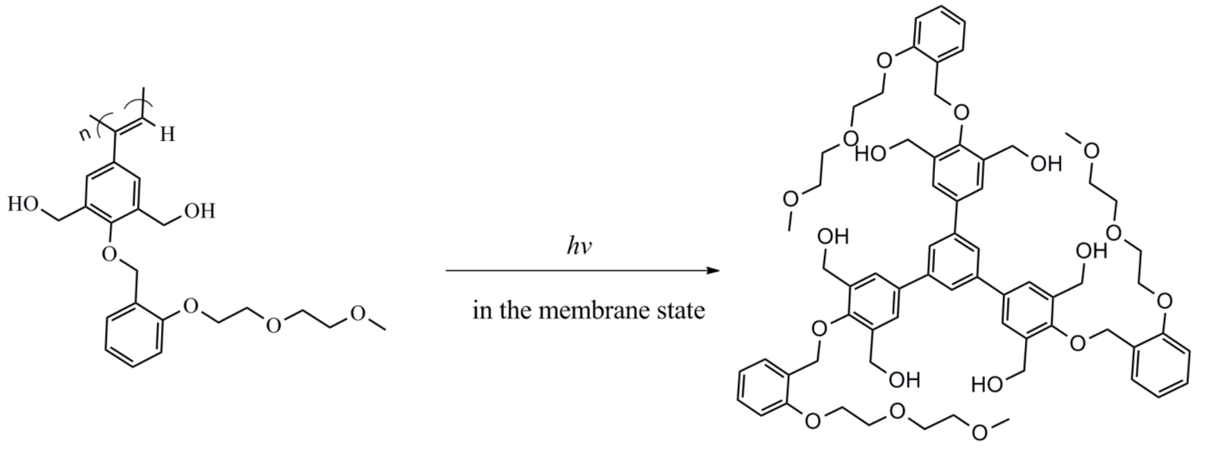
8.3.4.2 Copolymerization of 4-[4’-(1,4,7-trioxaoctyl)benzyloxy]-3,5-bis(hydroxymethyl)phenylacetylene (**EO**) and 4-(dodecyloxy)-3,5-bis(hydroxymethyl)phenylacetylene (**Do**) (Scheme 3)



Scheme 3. HSSP of **EO** with **Do** by using [Rh(nbd)Cl$_2$] as a catalyst and (*R*)- or (*S*)-PEA as a cocatalyst.

A solution of [Rh(nbd)Cl]$_2$ (3.58 mg, 7.77 μmol) and (*R*)-phenylethylamine (PEA) (0.398 mL, 3.10 mmol) in dry chloroform (2.60 mL) was added to a dry chloroform (1.59 mL) solution of **EO** (50.0 mg, 0.130 mmol) and **Do** (45.0 mg, 0.130 mmol). The reaction solution was stirred at room temperature for 12h. The crude polymer was purified by reprecipitation of the chloroform solution into a large amount of ethyl acetate / hexane = 3 / 2) and the formed solid was dried in *vacuo* to give a deep red solid. **P-(EO-*co*-Do)**: Yield: 74.5% (70.8 mg). $M_w = 1.41\times10^7$, $M_w/M_n = 2.57$, **Do** in copolymer = 37.5 mol%.

8.3.5 Preparation of T-EO and T-(EO-*co*-Do) (Scheme 4) [8]



P-EO **T-EO**

Scheme 4. One-pot synthesis of **T-EO** by SCAT of **P-EO**.

A typical procedure for **T-EO** was as follows: A solution of **P-EO** in chloroform (13 mg/mL) was cast on a poly(tetrafluoroethylene) sheet (100 cm^2), and the solvent was evaporated for 24 h at room temperature. The membrane (thickness 20.0 μm) was irradiated under nitrogen by visible light (400-500 nm, 2.54 mW/ cm^2) for 2 weeks. The reaction was monitored by GPC detected by UV and CD. Visible light (400-500 nm) irradiation was carried out by using a 300 W of Xe lamp (Asahi Spectra, MAX-302 with vis mirror module) through a cutoff filter (Asahi Spectra, LUX400 (λ > 400 nm), XF541 (λ < 510 nm), and XF546 (λ < 610 nm). All the resulting products were totally soluble and no insoluble parts were obtained. The crude product was purified by silica-gel column chromatography to give aim product **T-EO**. $R_f = 0.25$ (ethyl acetate / acetone = 4 / 1). Yield: 78.4%. ^{1}H NMR ($CDCl_3$, TMS, ppm): δ = 7.45~6.88 (m, 21H, $PhHOCH_2CH_2$, PhPh*H* and $PhH(CH_2OH)_2$)), 5.14 (s, 6H, $PhOCH_2Ph$), 4.86 (t, 6H, $Ph(CH_2OH)_2$), 4.62 (d, 12H, $Ph(CH_2OH)_2$), 4.13~3.43 (m, 24H, $OCH_2CH_2OCH_2CH_2OCH_3$), 3.24 (s, 9H, OCH_3). IR (film): 3700-3100(OH), 3000-2800(CH). TOF-MS m/z ($M + Na^+$): Calcd. 1181.52, Found. 1181.50.

The **T-(EO-*co*-Do)** was also prepared similarly from **P-(EO-*co*-Do)**. TOF-MS m/z ($M + Na^+$): Calcd. 1101.67, 1141.59, 1181.51, Found. 1101.70, 1141.64, 1181.57.

8.3.6 Membrane preparation

A typical blend membrane fabrication method for **T-EO**/PVA was as follows: A solution of the **T-EO** (0.0600~10.0 wt%) and the base polymer PVA (M_w = 1500, degree of hydrolysis = 86.0~90.0 mol%) in dry DMSO (40.0 mg/mL) was cast on a poly(tetrafluoroethylene) sheet (4 cm^2). After evaporating of the solvent for 12 h at 50°C, 1.33×10^{-3} MPa and annealing for another 24h, the membranes were detached from the sheet and dried in *vacuo* for 24 h. Thickness (L) of the membranes was 50.0~55.0 μm.

The blend membranes **P-EO**/PVA, **T-(EO-*co*-Do)**/PVA and **T-EO**/PVAc were also carried out similarly. Thickness (L) of the membranes was 52.0~55.0 μm.

The blend membrane **T-EO**/PDPA was fabricated as follows: A solution of the **T-EO** in $CHCl_3$ and a solution of the base polymer PDPA in toluene were blended together, and then the resulting blend solution was cast on a poly(tetrafluoroethylene) sheet. After evaporating the solvent for 24 h at room temperature, the membranes were detached from the sheet and dried in *vacuo* for 24 h. Thickness (*L*) of the membranes was 7.00~12.0 μm.

8.4 Results and Discussion

8.4.1 Design of the amphiphilic molecule T-EO and T-(EO-*co*-Do)

Amphiphilic molecules **T-EO** and **T-(EO-*co*-Do)** were designed, the chemical structures were shown in Figure 1. T-EO contain three parts: (1) a rigid and hydrophobic disc-like 2D center; (2) three hydrophilic oligoethylene oxid (**EO**) side chains at *o*-positions as an anchor; (3) six hydroxyl groups making intermolecular hydrogen bonds. The hydrophilic oligoethylene oxid (**EO**) side chains anchored to the hydrophilic substrate polymer, the rigid and hydrophobic disc-like 2D center appeared on the surface of the substrate polymer and then the resulting 2D structures were fixed by intermolecular hydrogen bonds.

In the case of **T-(EO-*co*-Do)**, hydrophobic alkyl chains were partly introduced to the *o*-positions, therefore, as an amphiphilic molecule, the hydrophilic oligoethylene oxid (**EO**) side chains anchored to the hydrophilic substrate polymers and the hydrophobic alkyl chains arranged to the air side. As a result, a 2D surface was formed.

The amphiphilic molecules **T-EO** assembled to forming 2D molecular on the substrate membranes. The possible closest packing structure of 2D molecular assembly of six **T-EO** molecules were shown in Figure 2, the rigid and hydrophobic disc-like 2D center showed lower surface energy and the hydrogen bonds were highly selective and directional for the formation of the 2D surface of the blend membranes.

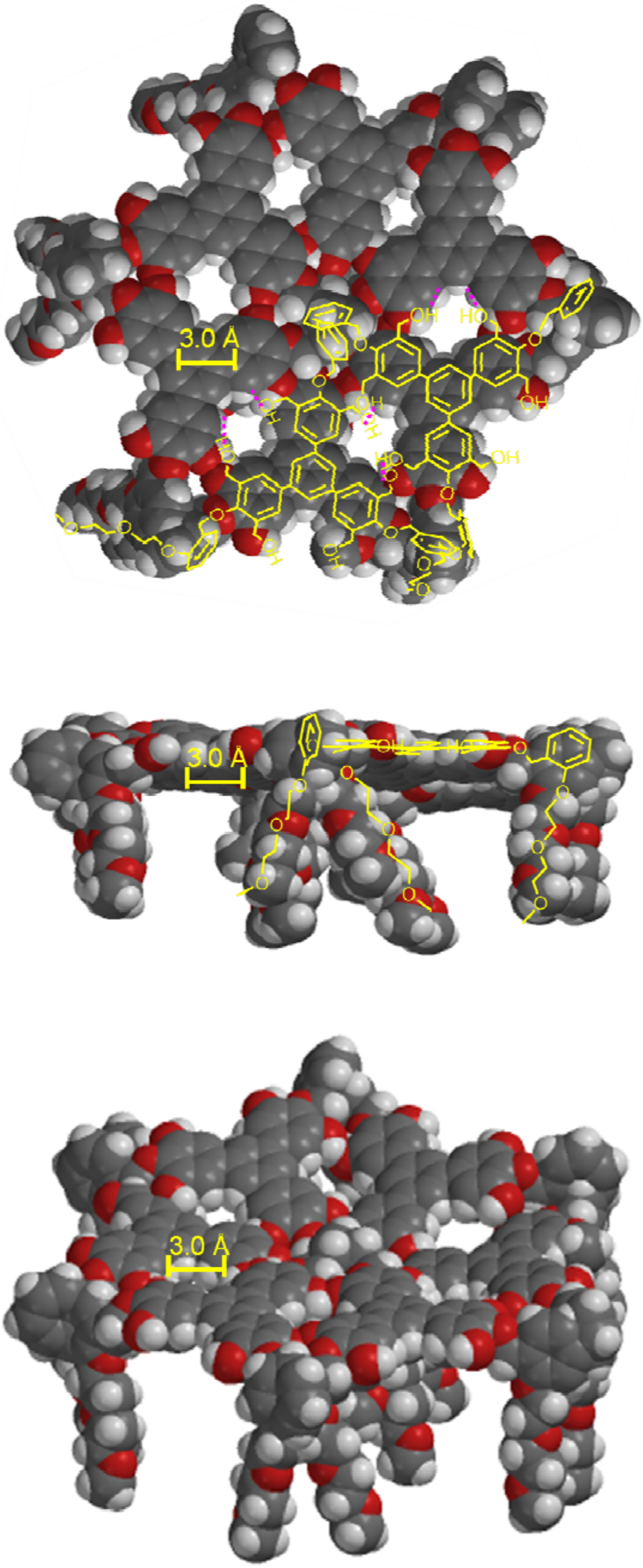


Figure 2. Possible closest packing structure of 2D molecular assembly of six **T-EO** molecules (┈┈ : hydrogen bond).

8.4.2 Surface modification and determination of surface structure

The surface modifications of hydrophilic PVA substrate polymer membranes were achieved by using 0.06-10 wt% of amphiphilic molecule **T-EO** and **T-(EO-*co*-Do)**, respectively. The contact angles of water on additives/substrate blend membranes were shown in Tables 1, 2 and Figure 3. The contact angles of the additives/PVA blend membranes increased notably by increasing the content of additives in membranes.

Figure 3 is the relationship between additives in membranes (wt%) and contact angles of **T-EO**/PVA and **P-EO**/PVA blend membranes, when only 0.06-10wt% of **T-EO** was used as a modifier, the contact angles of the blend membranes increased from 39.1°(Table 2, no. 4), to 53.1° (Table 1, no. 5), which is close to the pure **T-EO** (69.5°) (Table 2, no 1). However, by using the **P-EO** as a modifier, almost no increasing in the contact angle before and after modification of PVA can be observed. This finding indicated that the surface modifications of PVA membranes by amphiphilic molecules **T-EO** were achieved. The amphiphilic 2D structure of **T-EO** was the point for the successful of surface modification of PVA membranes. The imaginative 2D surface of **T-EO** on the PVA bird's–eye and top view of **T-EO**/PVA blend membranes with different amount of the **T-EO** were shown in Figure 4. The hydrophilic oligoethylene oxid (**EO**) side chains anchored to the hydrophilic substrate polymer, the rigid and hydrophobic disc-like 2D center appeared on the surface of the substrate polymer and then the resulting 2D structures were fixed by intermolecular hydrogen bonds. By calculation of minimum amount of **T-EO** required to covering the all surface, only 6.0×10^{-3} wt% of PVA was needed. When 0.06-10wt% of T-EO were added, multiple layers generated.

In addition, **T-(EO-co-Do)**/PVA blend membrane (Table 1, no. 6) showed higher contact angle than **T-EO**/PVA blend membrane (Table 1, no. 3). This result was caused by the existence of hydrophobic alkyl chain in the **T-(EO-co-Do)**. The surface modification of PVA with **T-(EO-co-Do)** was achieved as well, since the increasing in the contact angles. Moreover, **T-EO** was also used for modifying PVAc and PDPA membranes. No obviously increasing in contact angles of **T-EO**/PVAc and **T-EO**/PDPA can be found.

FTIR and ATR-IR of **T-EO**/PVA blend membranes were measured to confirm the surface structures. Unfortunately, no obviously change before and after modification on OH absorption, due to the strong OH absorption of PVA itself. Therefore, a OH free poly(SPA) was chosen as substrate and the ATR-IR spectra of **T-EO** (wt%)/poly(SPA) blend membranes were shown in Figure 5 (I). The poly(SPA) showed no OH absorption around 3300. The pure **T-EO** showed stronger OH absorption around 3377 cm^{-1}. By increasing the amount of **T-EO** (wt%), the OH absorption 3300 cm^{-1} can be observed clearly. This finding confirmed that the surface modification by using **T-EO** was achieved.

Table 1. Contact angles of water on additives/substrate blend membranes.

No.	Substrate [a]	Additives [a]	Content of additives in membranes (wt %)	Contact angle (deg) [b]
1	PVA	**T-EO**	0.06	40.4 ± 2.1
2			0.5	40.1 ± 2.6
3			1	40.4 ± 2.4
4			5	51.5 ± 1.4
5			10	53.1 ± 1.3
6	PVA	**T-(EO-co-Do)**	1	72.9 ± 2.6
7	PVA	**P-EO**	1	42.2 ± 2.1
8			5	30.2 ± 1.4
9			10	34.2 ± 1.3
10	PVAc	**T-EO**	0.06	90.0 ± 2.2
11			0.5	91.1 ± 1.1
12			1	91.9 ± 2.0
13	PDPA	**T-EO**	5	100 ± 1.0

[a] See Chart 1; [b] Contact angles for water droplets.

Table 2. Contact angles of water and oxygen permeation of polymer or supramolecular polymer membranes of additives or substrates.

No.	Membrane [a]	Contact angle (deg) [b]	P_{O_2} [c] × 10^2 (barrer)	α [d]
1	**T-EO**	69.5 ± 0.5	—	—
2	**T-(EO-co-Do)**	85.0 ± 2.3	—	—
3	**P-EO**	89.9 ± 0.5	—	—
4	PVA	39.1 ± 1.9	1.37	1.71
5	PVAc	90.2 ± 1.5	99.0	3.20
6	PDPA	110.0 ± 1.3	151,000	1.96

[a] See Chart 1; [b] Contact angles for water droplets; [c] In $10^{-10}\mathrm{cm}^3\cdot(\mathrm{STP})\cdot\mathrm{cm}\cdot\mathrm{cm}^{-2}\,\mathrm{s}^{-1}\cdot\mathrm{cmHg}^{-1}$ (= 1 barrer); [d] $\alpha = P_{O_2}/P_{N_2}$.

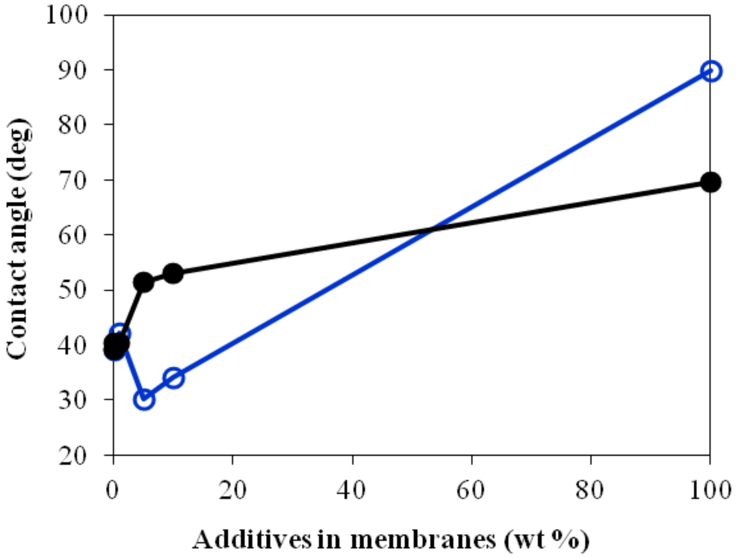


Figure 3. The relationship between additives in membranes (wt%) and contact angles of ●: **T-EO**/PVA; ○: **P-EO** / PVA blend membranes.

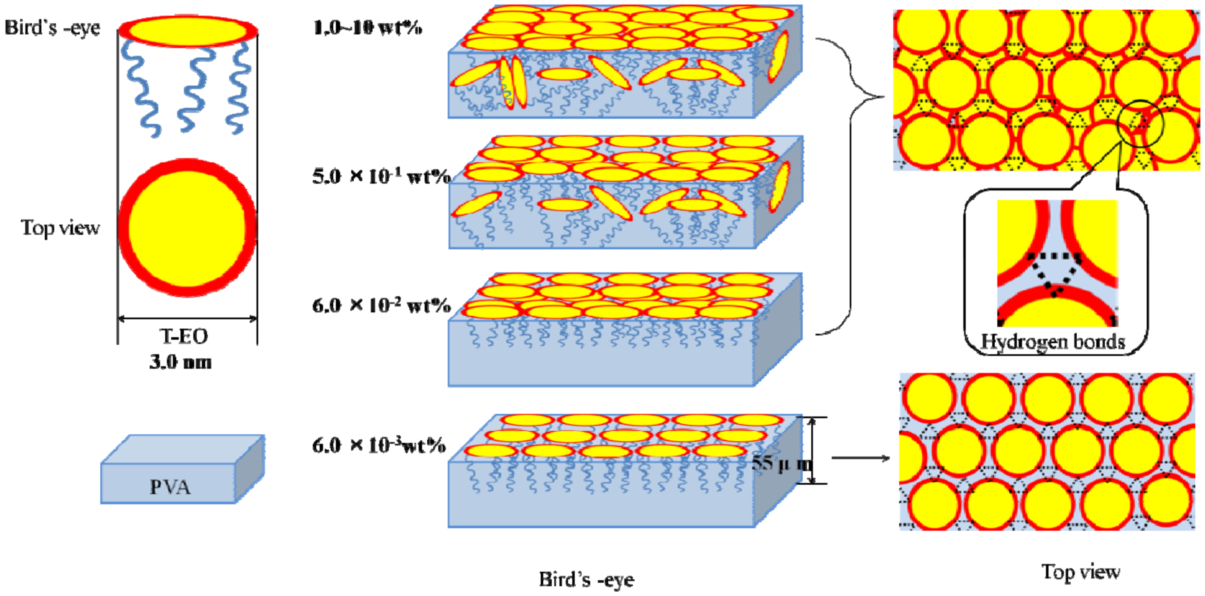


Figure 4. Imaginative 2D surface of **T-EO** on the PVA bird's–eye and top view of **T-EO**/PVA blend membranes with different amount of the **T-EO**.

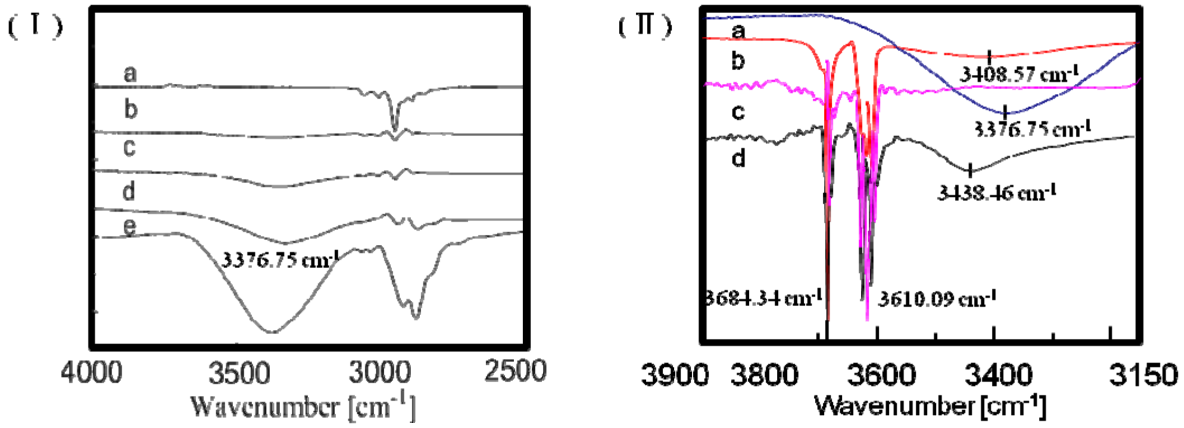


Figure 5. FTIR spectra of (I) ATR in membrane state of **T-EO** (wt%)/poly(SPA) a) 0 wt%, b) 0.5 wt%, c) 1.0 wt%, d) 5.0 wt%, e) 100 wt%, (II) a) **T-EO** membrane, b) 0.3 mmol/L in $CHCl_3$, c) 0.03 mmol/L in $CHCl_3$, d) 0.003 mmol/L in $CHCl_3$,

8.4.3 O_2/N_2 permselectivity of the modified blend membranes

8.4.3.1 O_2/N_2 permselectivity of the modified PVA blend membranes

O_2/N_2 permselectivity of the modified PVA blend membranes were measured and the results were listes in the Table 3 and Figure 6. By the surface modification of the **T-EO**, **T-(EO-co-Do)** and **P-EO** (Table 3, nos. 1-9), the O_2/N_2 permselectivity - α values of substrate PVA membranes increased largely from 1.71 (Table 2, no. 4) to 4.11(Table 3, no. 5). In the case of **T-EO**/PVA blend membranes, when the content of **T-EO** increased from 0.06 wt% to 1 wt%, the α value increased obviously from 1.80 to 3.88 with almost no drop in P_{O_2}. It may be caused by formation of a supromolecular structure of the amphiphilic molecules **T-EO** having 2D regular size pores and thinner thickness in molecular level on the PVA membrane surface. When the content of **T-EO** increased to 10 wt%, the highest α value was obtained, however, a large drop in P_{O_2} was happened simultaneously (Figure 6). This phenomenon may be caused by the excess amount of **T-EO** which formed not single 2D layer but multiple layers on the surface of PVA membrane as shown in Figure 4. The multiple layers and free **T-EO** decreased the permeability of oxygen.

To investigate the importance of formation of 2D surface on the PVA, **P-EO** which has no possibility to assemble to 2D structure was used as a modifier. The results were shown in Table 3 (nos. 7-9) and Figure 6. By using the same amount of additives, **T-EO**/PVA blend membranes showed better performance on pemselectivity and permeability. This result indicated that the O_2/N_2 permselectivity of the substrate polymer membranes were enhanced since the formation of 2D structure on the surface of substrate membranes. The membranes showed molecular sieving properties.

The amphiphilic molecules **T-(EO-co-Do)** having hydrophobic alkyl chains and the hydrophilic oligoethylene oxid (**EO**) side chains in the *o*-positions as surface modification reagent were prepared. The O_2/N_2 permselectivity of **T-(EO-co-Do)**/PVA membrane was measured. The similar tendency was obtained.

The oxygen permselectivity increased from 1.71 (Table 2, no. 4) to 2.35 (Table 3, no. 6) with a small drop in P_{O_2}.

8.4.3.1 O_2/N_2 permselectivity of the modified PVAc and PDPA blend membranes

The surface modification of PVAc and PDPA by amphiphilic molecules **T-EO** were carried out, results were shown in Table 3 and Figure 7. The oxygen permselectivity of **T-EO**/PVAc increased from 3.2 (Table 2, no. 5) to 3.95 (Table 3, no. 12) with a small drop in P_{O_2}. However, the **T-EO**/PDPA showed both increasing in α value and P_{O_2} which was locating near Robeson's upper boundary line (1991) (Figure 8). This result indicated that the formation of 2D structure on the surface of PDPA substrate membranes was much more ideal than that on the surface of PVAc of substrate membranes.

Table 3. Oxygen permeation of additives/substrate blend membranes.

No.[a]	Substrate[b]	Additives[b]	Content of additives in membranes (wt %)	$P_{O_2}{}^{c} \times 10^2$ (barrer)	α^{d}
1	PVA	**T-EO**	0.06	1.35	1.80
2			0.5	1.37	2.68
3			1	1.27	3.88
4			5	0.885	3.73
5			10	0.512	4.11
6	PVA	**T-(EO-co-Do)**	1	1.23	2.35
7	PVA	**P-EO**	1	1.29	2.15
8			5	0.883	2.25
9			10	0.488	3.82
10	PVAc	**T-EO**	0.06	95.6	3.11
11			0.5	70.2	3.76
12			1	56.7	3.95
13	PDPA	**T-EO**	5	305,000	2.34

[a] The numbers correspond to those in Table 1; [b] See Chart 1.
[c] In $10^{-10} cm^3 \cdot (STP) \cdot cm \cdot cm^{-2} \cdot s^{-1} \cdot cmHg^{-1}$ (= 1 barrer); [d] $\alpha = P_{O_2}/P_{N_2}$.

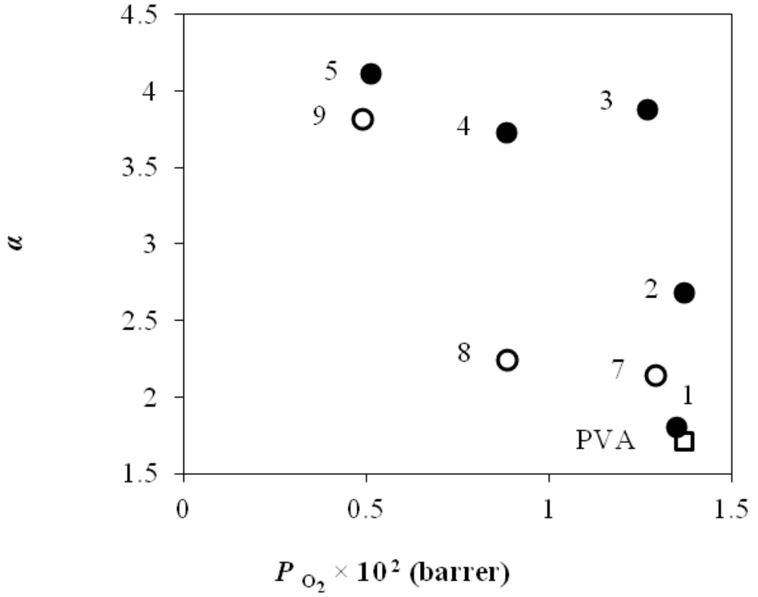


Figure 6. Oxygen permeation through membranes of ●: **T-EO**/PVA; ○: **P-EO** / PVA blend membranes (the numbers in the figure correspond to those in Table 3).

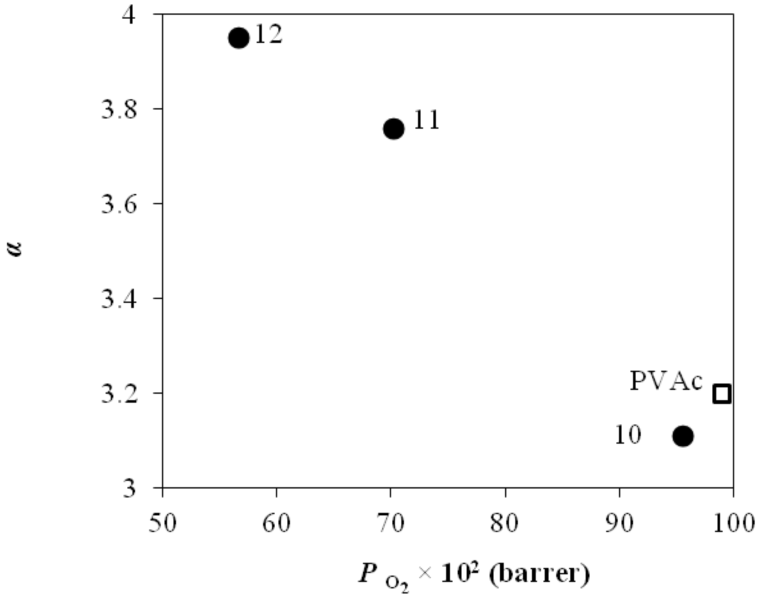


Figure 7. Oxygen permeation through membranes of **T-EO**/PVAc blend membranes (the numbers in the figure correspond to those in Table 3).

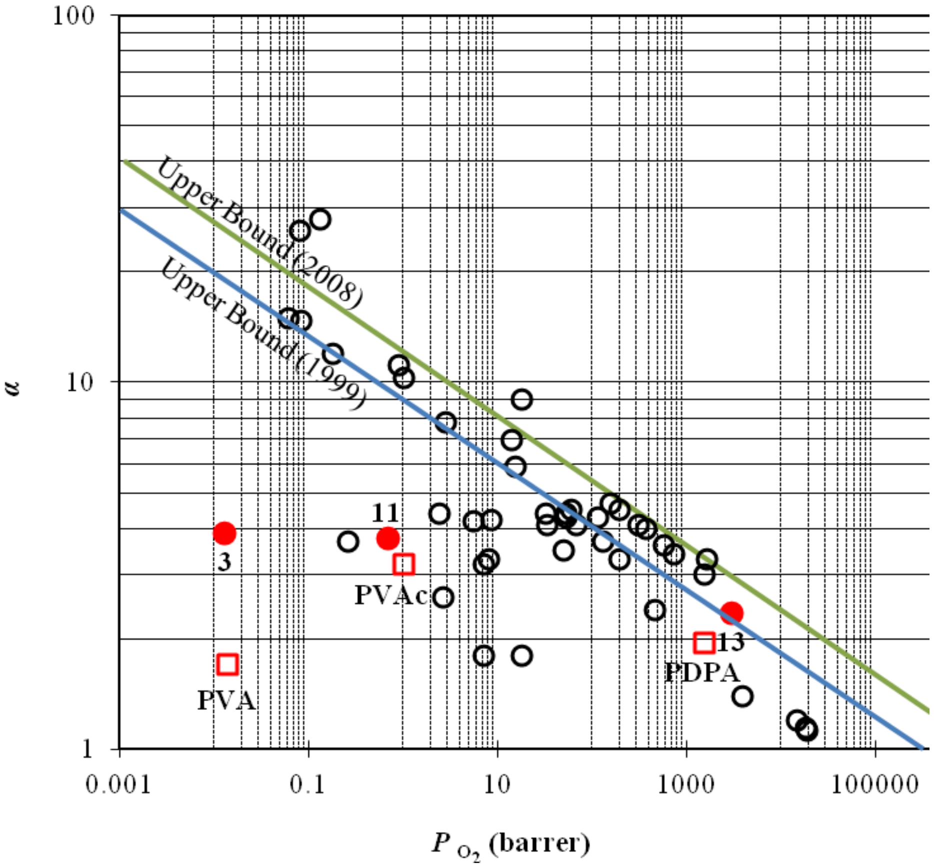


Figure 8. The relationship between P_{O_2} and α of the blend membranes ●: the numbers in the figure correspond to those in Tables 3; ○: Robeson's report (ref. 1e).

8.5 Conclusions

Facile synthesis of amphiphilic molecules 1,3,5-trisubstituted benzene derivatives having six hydroxyl groups and three hydrophilic groups as novel 2D surface modifiers were achieved. Surface modifications by 0.06-10 wt% of amphiphilic molecules **T-EO**, **T-(EO-co-Do)**, on substrates PVA, PVAc and PDPS were achieved by a simple method, because the contact angles for blend membranes were increased. A supromolecular structure of the amphiphilic molecules **T-EO** having 2D regular size pores and thinner thickness in molecular level on the PVA membrane surface was formed. The oxygen permselectivity of substrate polymer membranes were improved highly from 1.71 to 4.11 without drop in P_{O_2}.

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Supporting Information (SI)

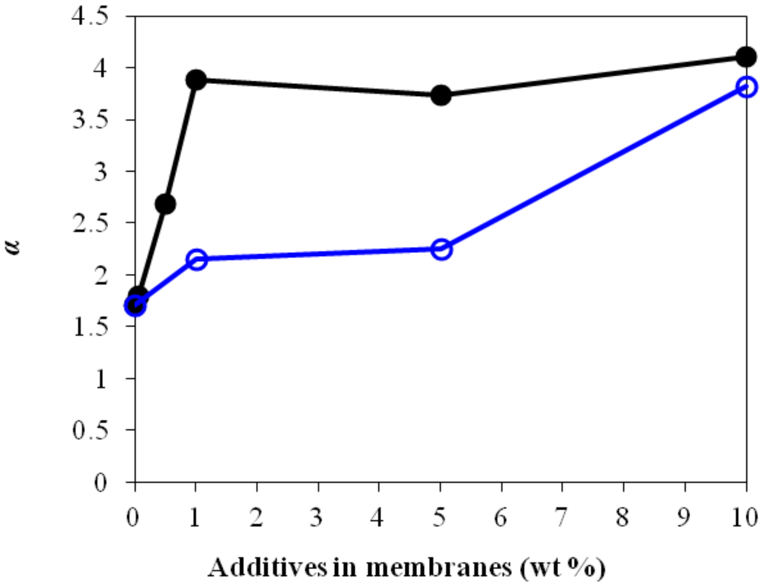


Figure S1. The relationship between additives in membranes (wt%) and *α* of ●: **T-EO**/PVA; ○: **P-EO**/PVA blend membranes.

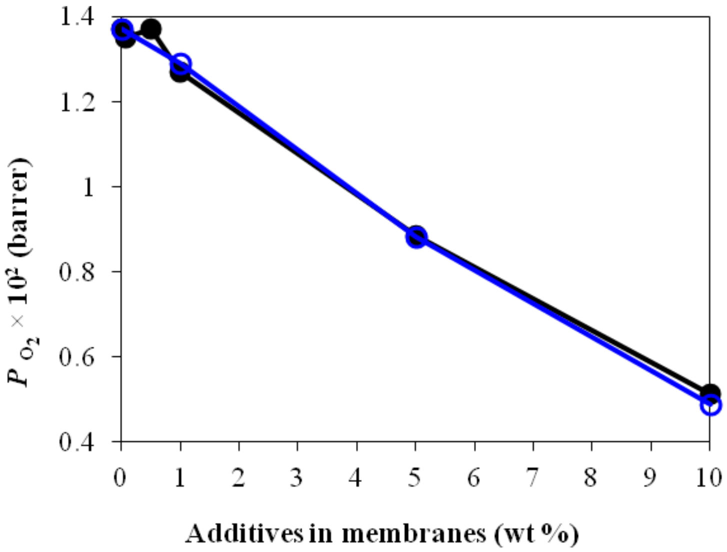


Figure S2. The relationship between additives in membranes (wt%) and P_{O_2} of ●: **T-EO**/PVA; ○: **P-EO**/PVA blend membranes.

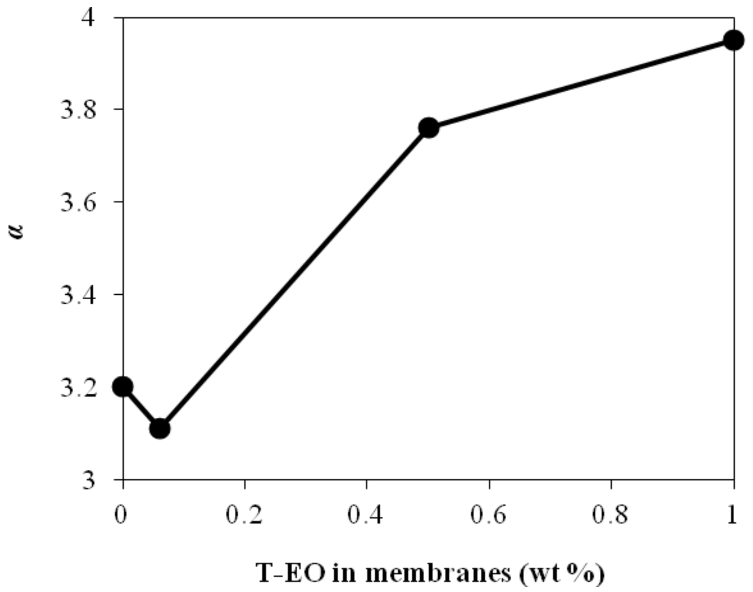


Figure S3. The relationship between **T-EO** in membranes (wt%) and α of **T-EO**/PVAc blend membranes.

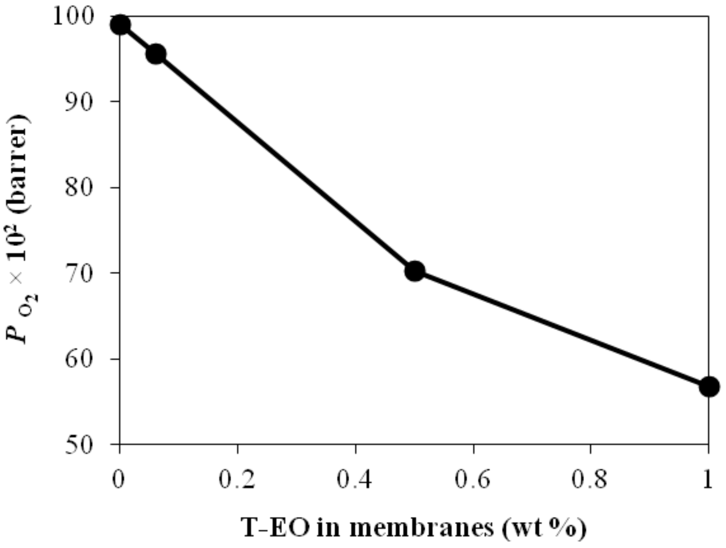


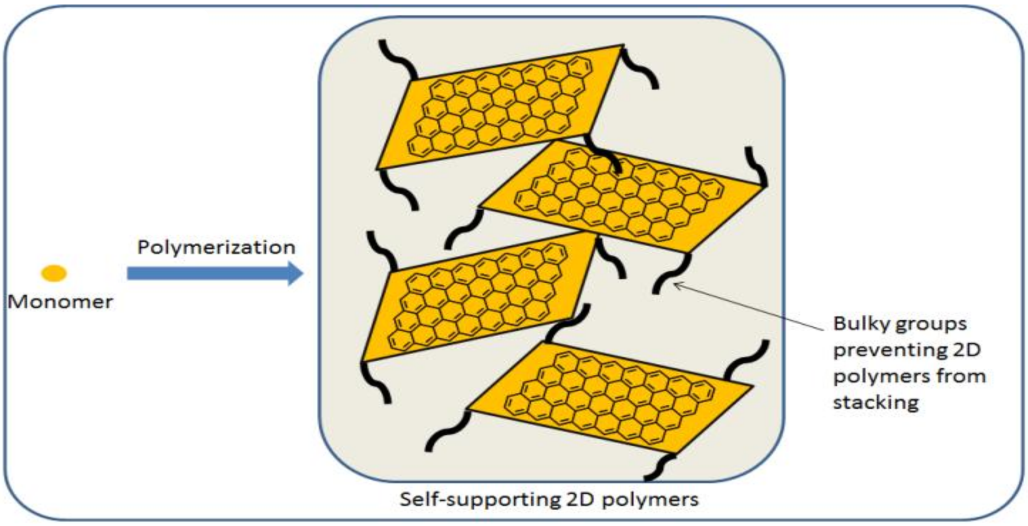
Figure S4. The relationship between **T-EO** (wt%) and P_{O_2} of **T-EO**/PVAc blend membranes.

Chapter 9

Synthesis of “2D polymer” membrane

9.1 Abstract

There are many kinds of polymers in the world, almost all the polymers were one-dimensional (linear or branched) or three-dimensional (cross-linking) structures. Actually, to my knowledge, no report can be found for the organic, soluble, and self-supporting two dimensional organic polymer ("2D polymer") having high molecular weight which structure can be characterized clearly. Since there is no report on the "2D polymer" described above, to review the reports of "2D polymer" is impossible. Therefore, in this review, a traditional "2D polymer" or a part of that will be reported.



9.2 Introduction

— Approaches toward the synthesis of self-supporting two dimensional organic polymer (= “2D polymer”)

There are many kinds of polymers in the world, almost all the polymers were one-dimensional (linear or branched) or three-dimensional (cross-linking) structures. Actually, to my knowledge, no report can be found for the organic, soluble, and self-supporting two dimensional organic polymer (“2D polymer”) having high molecular weight which structure can be characterized clearly. There are following three reasons for difficulty in synthesis of “2D polymer”: (1) Three-dimensional cross-linking (= insolubility) is difficult to be avoid when three functional groups containing monomer was used for synthesis of “2D polymer”; (2) Although the “2D polymer” was obtained, due to the intermolecular stacking of the planar structure (that is, the molecule itself has no “self-supporting” ability), the resulting polymer became insoluble. The characterization of the polymer structure was impossible; (3) The molecular weight couldn”t be increase because of the insolubility of the intermediate during the polymerization caused by the intermolecular stacking of the planar structure. Although there are such problems above, the paradigm shift from “the conventional “1D polymer” “ to “the unknown “2D polymer” “ is a challenge and a contribution to the academic and industrial.

Since there is no report on the “2D polymer” described above, to review the reports of “2D polymer” is impossible. Therefore, in this review, a traditional “2D polymer” or a part of that will be reported. The Part 9.3 will introduce the examples of reports from this view point.

9.3 The present development summarized from the previous reports

— Synthesis of the “2D polymer” molecular assembly as a precursor of “2D polymer” and the separation of a “2D polymer” by exfoliation

Graphene sheets (perhaps a natural “2D polymer”) which were prepared by mechanical exfoliation (repeated peeling) of small mesas of highly oriented pyrolytic graphite (equal to the “2D polymer” molecular assembly in this review) had been reported by the Nobel laureates in physics in 2010, Novoselov and Geim. [1-3] From this momentum, the interest in the two-dimensional polymer is increasing. The term two-dimensional polymers have been used in a variety of works or papers, however, the definition of clear description is very rare and the general definition has not been established. Sakamoto and co-workers, [4-5] defined the 2D polymer as “individual molecular sheets and not on layered systems which would then have to be taken apart in a separate step”. That is, a planar polymer can be formed without aggregation in solution and maintained into the single molecule, in other words, it is “self-supporting” two-dimensional polymer. In this review, we defined the “2D polymer” as a kind of “self-supporting two-dimensional polymer” having high molecular weight and high solubility which molecular structures can be characterized easily”.

There is almost no report on achieving the synthesis of such self-supporting two-dimensional polymer (=“2D polymer”) [6] On the other hand, several reports were found on the synthesis of “non-self-supporting” two-dimensional polymers (≠“2D polymer”). The “non-self-supporting” two-dimensional polymer can be classified in to two types: (1) “self-assembly” type which contain self-stacked molecular structure due to the intermolecular stacking; (2) “substrate support” type which was formed on graphite or a metal substrate, such as copper and gold (Figure 1). In this review, “self-supporting” two-dimensional polymer was defined as a “2D polymer”, and the “non-self-supporting” two-dimensional polymer was defined as precursor of “2D polymer”.

On the other hand, many researches on covalent organic frameworks (COF) have been reported. [7-12] Jiang and co-workers [7] defined the COF as “covalent porous crystalline polymers (composed of light-weight elements) that enable the elaborate integration of organic building blocks into an ordered structure with atomic precision". In this definition, the molecular aggregates were interested rather than a molecule. These molecules having this configuration were often used for synthesis of two-dimensional polymers. Depending on the building

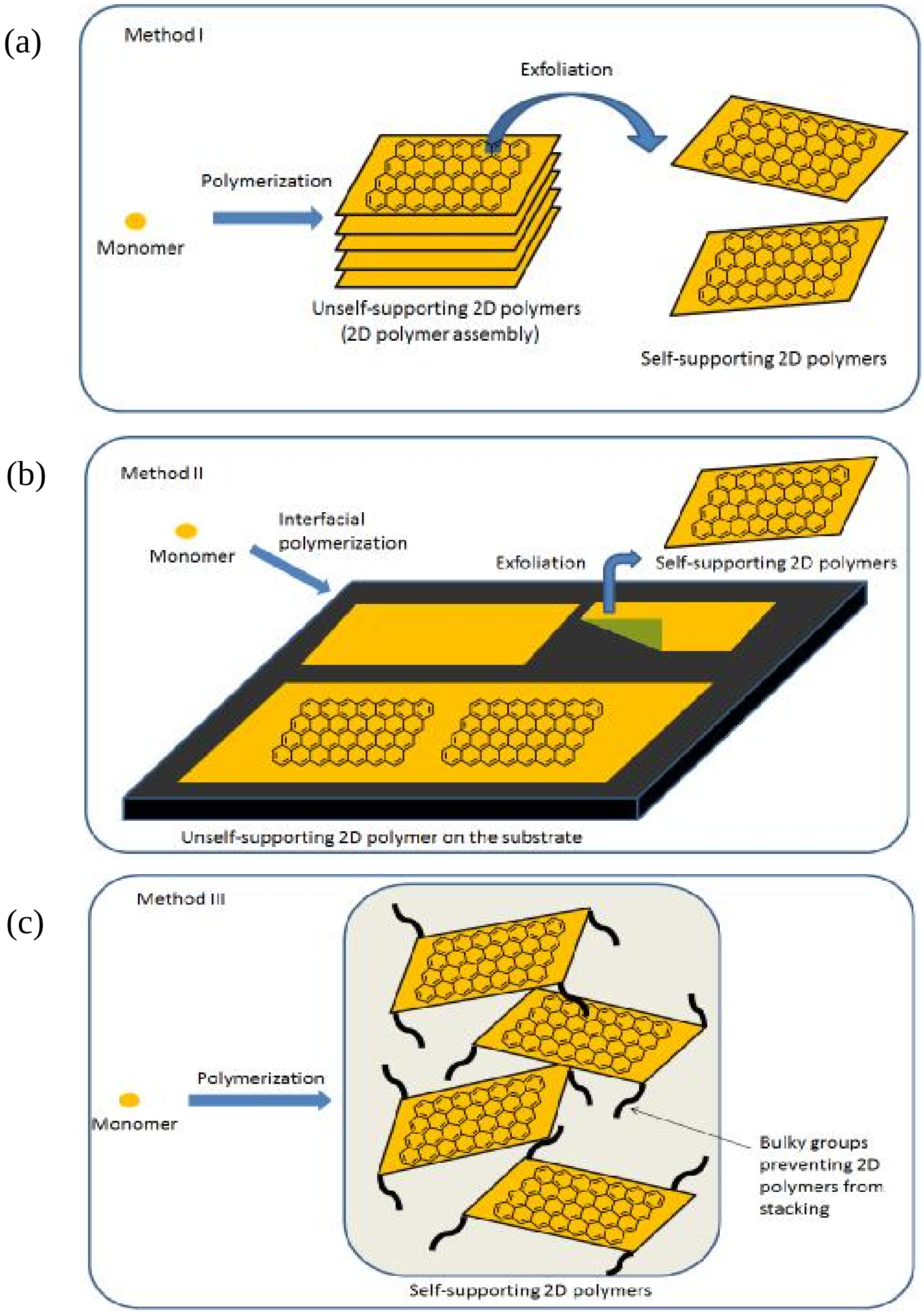


Figure 1. Synthetic methods of self-supporting 2D polymers: (a) via exfoliation from the assembly (Method I), (b) via exfoliation from substrates (Method II), (c) direct synthesis without exfoliation (Method III).

block dimensions, COFs can be categorized in to either 2D COFs and 3D COFs. Among them, 2D COFs were regarded as precursor of “substrate support” type “2D polymer”. [7-12]

There are three synthetic methods of “2D polymer” (Figure 1). Method I was exfoliation of one molecule from “self-assemble” type “2D polymer” precursor which was synthesized by solution polymerization (Figure 1 (a)). Usually, the resulting “2D polymer” precursor precipitated during the polymerization due to the formation of layered structures by stacking, and became insoluble in common solvents. Actually, there are many examples have been reported. [7-17] In order to obtain one molecule “2D polymer” from the “2D polymer” precursor, the chemical exfoliation [13-15] by chemical modification and the physical exfoliation [6, 16-17] by using ultrasonic waves or heat to break the stacking layers of the polymers were considered. However, only one report which achieved in the separation of “2D polymer” to one molecule has been published by Sakamoto and co-workers [6] (Table 1).

Table 1. Estimation of the size of 2D like polymers prepared by Method I (See Figure 1)

2D compound	Size (x×y)[a] /μm	Thickness [a] /nm	The number of molecular layers [b]
3 5b)	No data	<1	1
4 5c)	0.1×0.1	3.0	10
5 6a)	4.0×5.0	4 - 10	10 - 25
6 6b)	0.7×1.8	2 - 3	5 - 6
7 3)	1.2×1.2	<2.5	1

[a] After exfoliation. [b] Calculated from the thickness.

Method II was exfoliation of one molecule from “substrate support” type “2D polymer” precursor which was synthesized by interfacial polymerization on graphite or a metal substrate, such as copper and gold (Figure 1 (b)). For example, many studies on boroxine COF by interfacial polymerization of boronic acids have been reported. COF sheets prepared by this method have been devoted exclusively to the application to gas adsorption. However, the separation of one molecule from substrate hasn’t been reported to our knowledge.

Method III is one step synthesis leading to “2D polymer”, that is, a “2D polymer” is directly synthesized without exfoliation from precursor (Figure 1 (c)) which has not been reported so far. This method must be devised to meet the conflicting of the design point of the polymer backbone with a high flatness, and to prevent stacking between the polymers. Usually, since the reaction proceeds spread to three-dimension, the polymerization of trifunctional monomer is caused normal three-dimensional cross-linking structure. To synthesis of regular two-dimensional structure polymer, the precise design of the monomer structure and the controlling polymerization condition are necessary. Therefore, the research on the 2D synthesis is charming and challenge for field of polymer synthesis.

Here, some reports of synthesis of “2D polymer” precursor (“self-assemble” type and “substrate support” type “non-self-supporting” “2D polymer”) will be introduced. In the Part 9.3.1 and 9.3.2, synthesis of “self-assemble” type “2D polymer” precursor and the exfoliation of one molecule from “self-assemble” type “2D polymer” precursor by the chemical exfoliation or physical exfoliation will be reported, respectively.

9.3.1 Synthesis of “self-assemble” type “2D polymer” precursor [9-12]

Bojdys and co-works have reported the synthesis of “2D polymer” precursor (layered “2D polymer” frameworks) made up from heptazine unit using triazine derivatives as a monomer. [9] Three kinds of triazine derivatives were used as monomers, the reactions were carried out under inert atmosphere at 430 ℃ for 48 h. The resulting macrocycle **1**(Figure 2 (a)) was characterized by infrared spectroscopy (IR), solid-state ^{13}C MAS NMR, elemental analysis (EA), X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The interplanar stacking distance was 3.3 Å which was similar to that of graphite (3.35 Å). From the images of SEM, the thinnest "2D polymer" precursor 6.4 Å was observed equal to 2-4 layers. A "2D polymer" precursor **2** (Figure 2 (b)) has been reported by Lotsch and co-workers which was synthesized by heating 5,5"-dicyano-2,2"-bipyridine to 400 ℃ for 48 h. The resulting "2D polymer" precursor **2** was characterized by IR, solid-state NMR (^{13}C, ^{15}N) and XRD. The interplanar stacking distance was 3.6 Å. [10] Dichtel and co-workers have reported a 2D COF with the biggest pores (4.7 nm) from 2,3,6,7,10,11-hexahydroxytriphenylene (HHTP). The structures of the 2D COF were confirmed by IR, solid-state NMR (^{1}H, ^{11}B, ^{13}C) and XRD. Molecular mechanics (MM3) and density functional theory (DFT) modeling analysis of the interlayes potential energies of various stacking conformation of the 2D COF were calculated. The interplanar stacking distance was 3.42 Å and the thickness was 132 nm. Microcrystalline borazine-linked polymer has been reported by El-Kaderi and co-workers for the first time. The borazine-linked polymer prepared by the thermal decomposition of 1,3,5-(p-aminophenyl)benzene-borane in a solvent mixture of mesitylene–toluene at 120 ℃/150 mTorr in a sealed tube for three days which a orded the borazine-linked polymer as a white microcrystalline powder in yield of 72%. [12] The formation of the borazine ring was investigated by IR, solid-state NMR (^{11}B, ^{13}C) and EA. The XRD pattern of the borazine-linked polymer showed the interplanar stacking distance was 3.82 Å indicated that the packing of the 2D layers.

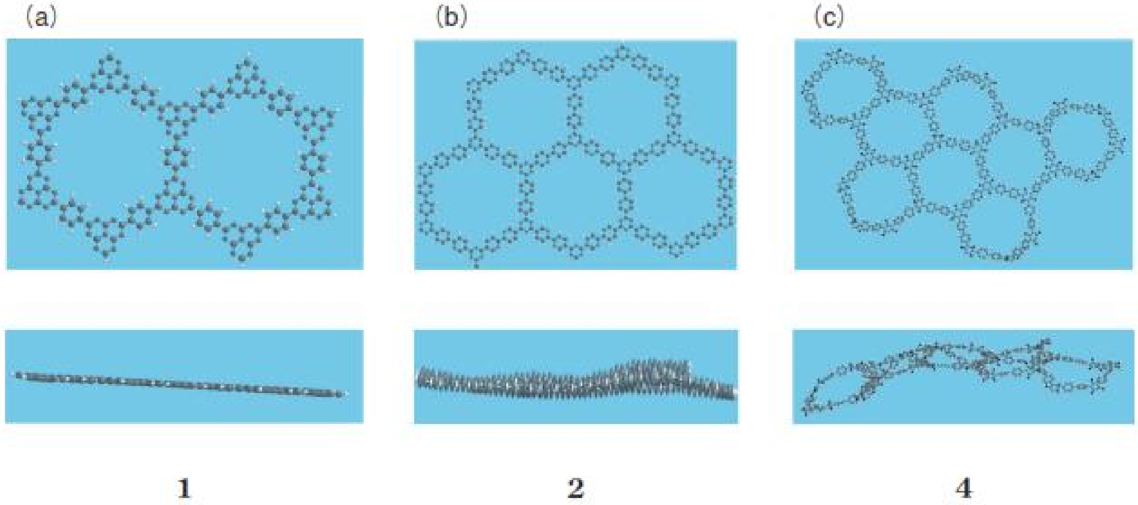


Figure 2. 3D structures of **1** (A), **2** (B), and **3** (C) (upper: top view; lower: side view)

9.3.2 Synthesis of “2D polymer” by exfoliation of one molecule from “self-assemble” type “2D polymer” precursor [6, 13-17]

Usually, “self-assemble” molecular aggregate of “2D polymer” generated due to the stacking during polymerization. Exfoliation of one molecular from the “self-assemble” “2D polymer” precursor after polymerization is another method. The chemical exfoliation of oxidation of the graphite is well known. [13]

9.3.2.1 One molecular exfoliation by chemical modification (chemical exfoliation) [13-15]

Ruoff and co-workers have reported thin graphene-based nanosheets **3** (Table 1) prepared by reduction of a colloidal suspension of exfoliated graphene oxide sheet in water with hydrazine hydrate. [14] The resulting material was characterized by atomic force microscopy (AFM), EA, solid-state ^{13}C MAS NMR and X-ray photoelectron spectroscopy (XPS). 10 Å layers were observed (the thickness of graphene is 3.4 Å). The problem of chemical exfoliation is that the planarity of the compound decreased by introducing the substituent. The thickness increased which can be observed from the AFM image. The trade-off between exfoliation and the 2D integrity is an important point for chemical exfoliation.

Zhang and co-workers have reported 2D covalent frameworks (“2D polymer” precursor) of poly(isocyanurate) by cyclotrimerization of diisocyanate in *N*, *N*-dimethylformamide (DMF) at 80 ℃. The chemical exfoliation of organic nanosheet **4** was achieved by the interaction of amine of the terminal groups.[15] Form the characterization result of AFM, the thickness of the nanosheet was 3.0 nm, and the size of naosheet was 150 nm by TEM measurement.

9.3.2.2 One molecular exfoliation by physical force (physical exfoliation) [6, 16-17]

Zomora and co-workers have reported a COF **5** (Table 1) based on the condensation of 2,3,6,7,10,11-hexahydroxytriphenylene (HHTP) and 1,3,5-tris(4-phenylboronic acid)benzene (BTPB) and then physical exfoliation by sonication of the resulting COF **5** in CH_2Cl_2 was carried out for 15 min. [16]

From the results of IR, XPS and AFM, 4×5 μm size, 4-10 nm thickness (10-25 layers) thin layered nanostructures polymers were obtained. In addition, Zamora and co-workers also succeeded in exfoliating of polyacetylene type COF **6** (Table 1) by sonication in CH_2Cl_2 for 45-180 min. The maximum level of exfoliation was 2-3nm (5-10 layers thickness). The resulting materials were cast onto the mica and examined by AFM, 2.4 nm thickness, 0.7×1.8 μm size layers were obtained. However, one molecule exfoliation has not been achieved. Sakamoto and co-workers have reported a complete exfoliated “2D polymer” **7** (Table 1) by photopolymerization of a two-dimensional per-organization of photoreactive monomer under LEDs (470 nm). To achieve full exfoliation down to individual monolayers, the crystals were heated at 150 ℃ in 1-methyl-2-pyrrolidone (NMP) for 3 days. The resulting material was around 2.5 nm by AFM characterization which thickness showed a good agreement with the theoretical value of one molecule (2.4nm), a “2D polymer” was synthesized successfully. From the AFM image, the area of the “2D polymer” was more than

1 μm^2, if it is one molecule, more than 4×10^5 unit (degree of polymerization) it must be contain. This paper is the only one which has the description on the degree of polymerization of the "2D polymer". It indicated that to synthesis of "2D polymer" is very difficult.

As a method to synthesize "2D polymer", synthesis and exfoliation of one molecule from "self-assemble" type "2D polymer" precursor (method I) were summarized. Table 1 shows the data about size (area, thickness, the numbers of layers) of the "2D polymer" in the literatures which introduced in Part 9.3.2 from the author's view point. The areas were calculated from the images of the literatures. The "2D polymer" (one molecule thickness planar organic polymer) in this review have not been obtained until now. In addition, it is unknown for the area whether the size is one molecule or not.

9.4 The author's challenge

—Synthesis of the "2D polymer" or "2D polymer" supramolecular and the property of the polymer membrane

As described above, the synthesis of original sense of the "2D polymer" has not been reported. Recently, as the goal, we have started the research on the "2D polymer", although the results are far from real "2D polymer", the following three cases will be introduced as a result at this stage.

9.4.1 Synthesis of multi-strand polymer as a prototype of "2D polymer"

A perfect "2D polymer" was thought to be insoluble, and the higher the planarity it is, the stronger the stacking will be. Therefore, as intermediate between "1D polymer" and "2D polymer", strip (ribbon) polymer was regarded as a prototype rather than planar (sheet) polymer. Strip polymer is multi-stranded polymer which is synthesized from double-stranded polymer (ladder-like polymer). About this kind of polymers, the insolubilization is easily to occur and the relative report was few. We have begun to synthesis of the hetero-multi-stranded polymers as a prototype of "2D polymer". For example, soluble helical polymers having double-stranded, triple-stranded, quadruple-stranded were synthesized by ADMET polycondensation of a stereoregular helical polymer having ultrahigh molecular weight as a template (Figure 3). Although the degree of polycondensation was not very high, the hetero-multi-stranded polymers were synthesized successfully. [18] In addition, we also succeeded in the synthesis of quadruple-stranded polymer by selective photocyclic aromatization (SCAT) reaction. [19]

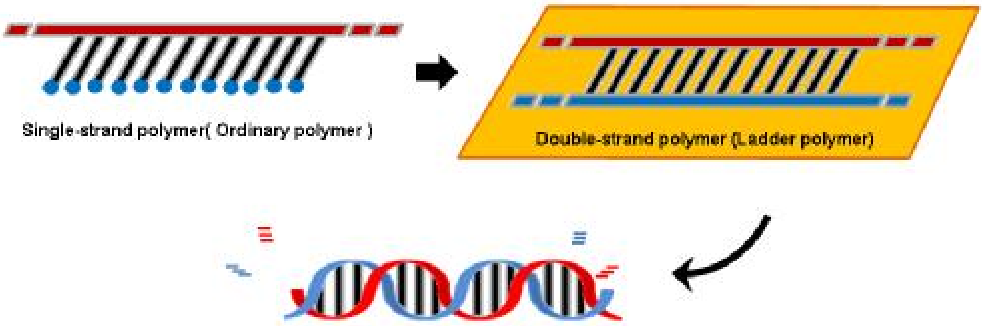


Figure 3. Synthesis of double-strand polymer (Hetero-ladder polymer).

9.4.2 Synthesis and the application of "2D polymer" supramolecular membranes from amphiphilic 2D monomer (2D surface modification)

The realization of the ideal separation membrane is a challenge for energy, environmental and water problems. Generally, separation membrane has a problem that there is a trade-off between permeability and selectivity. Therefore, to realized a defect-free "2D polymer" membrane is one method to solve the problem above. As mentioned in Part 9.2 and 9.3, it is a long way and valuable work before the completion of the synthesis of the real "2D polymer". Therefore, we tried to synthesize the "2D polymer" not from the traditional polymer (organic polymer) which contain covalent bond but from a supramolecular polymer. In that case, considering the difficulty of the formation of the self-supporting membrane, we designed a blend membrane with common polymer (Figure 4). By blending an amphiphilic 2D compound on the surface of substrate polymer, the membrane having 2D surface was prepared (Figure 5).[20] The gas separation efficiency and ability were improved successfully by this method. In other words, the permselectivity was improved without decrease the permeability. The good property was caused by the molecular sieving effect of the blend membrane.[21]

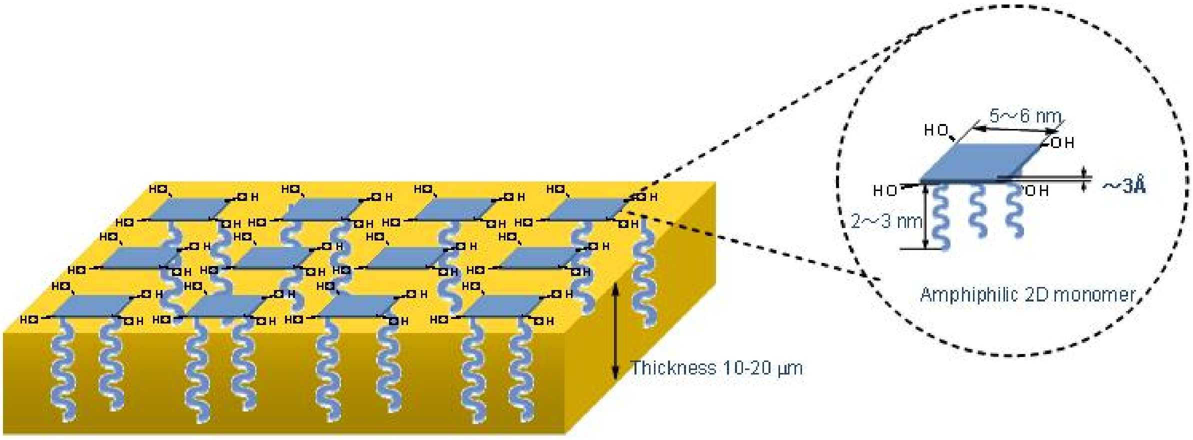


Figure 4. 2D supramolecular polymer membrane from amphiphilic 2D monomer on a substrate polymer (Concept).

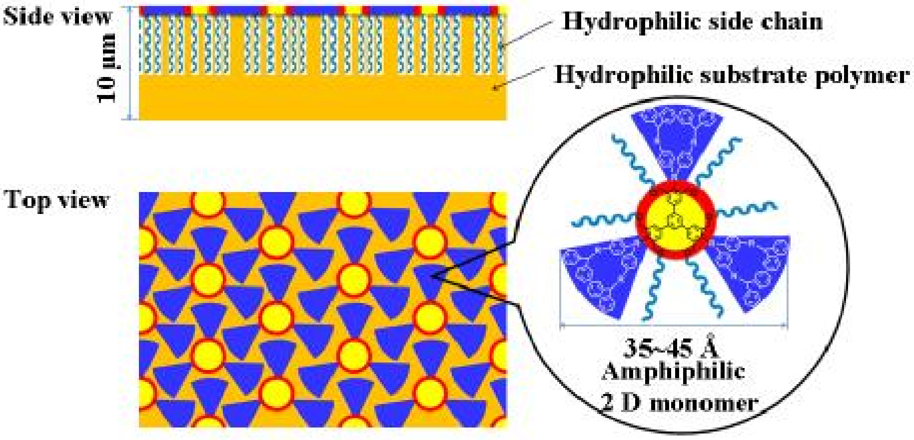


Figure 5. 2D supramolecular polymer membrane from amphiphilic dendronized 2D monomer on a substrate polymer (Example).

9.4.3 Synthesis of "2D polymer" by chemical exfoliation of one molecule from two-dimensional oriented polymer which was prepared by 2D polymerization and selective photocyclic aromatization (SCAT)

The synthetic methods of "2D polymer" described in Part 9.4.1 and 9.4.2 are temporary from the view point of real "2D polymer". Here, we will report a method for synthesizing a real "2D polymer" (Figure 6) [22] by using our original techniques helix-sense-selective polymerization (HSSP) [23] and SCAT [24] (Figure 7). First of all, HSSP was carried out to synthesis of cis-cisoid π-conjugated polymer. Hexagonal columnar oriented self-supporting membrane **8** was obtained, and then 2D polymerization was used to fix the surface direction (two dimensional) of self-supporting membrane (Figure 6 (a)). The resulting hexagonal columnar oriented self-supporting membrane **9** was treated by topochemical reaction (SCAT) (Figure 6 (b)). From the current results, the formation of "2D polymer" precursor **10** (2D polymer-stacking assembly) with relatively large area was achieved. The next step—physical exfoliation (Figure 6 (c)) is a challenge, it is expected that atom thick order two-dimensional polymer membrane **11** can be obtained by adding a polar solvent to cut the hydrogen bond. [2]

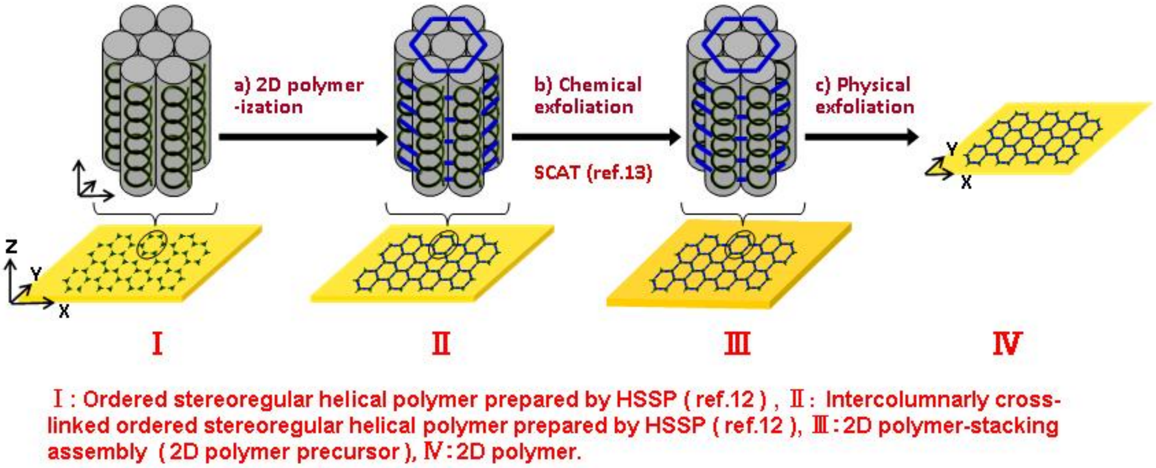


Figure 6. A new strategy of synthetic route to a 2D polymer via exfoliation using SCAT from stereoregular polymer by HSSP a) 2D polymerization on X-Y plane (intercolumnar cross-linking reaction), b) highly selective photocyclic degradation, SCAT (ref. 13) in Z direction, c) exfoliation of a 2D polymer.

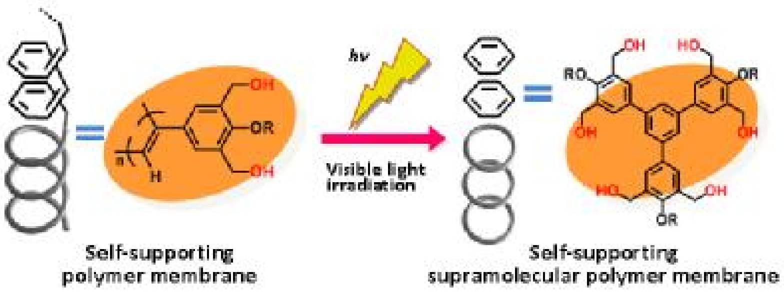


Figure 7. Highly selective photocyclic aromatization (SCAT) (ref. 13)

9.5 For the future

—To the realization of the “2D polymer” as a ultra-thin separation membrane

A number of polymer membranes have been used for the separation and removal of harmful molecules from the atmosphere and water. However, the complete separation (100% selectivity) and high permeability has never been achieved. Until now, the polymer membranes, which have been reported, have been prepared by solution casting of one-dimensional polymers (=linear or branch polymer) or by molding of two-dimensional polymers (= film or sheet polymer). Usually most of the membranes contain large irregular defects due to the thickness which were higher than nanometer order. The higher thickness decreased the permeability (permeability rate) and the defects reduced the selectivity (isolation ability). As a result, the thickness and the defect determined the separation property rather than the molecular structure. As a thin membrane, aggregation of two molecules which thickness is 10 nm and no bond in the two-dimensional direction, is impossible to be used as a separation membrane due to the low strength. The membranes which are fixed by covalent bonds showed no regularity in the planar direction.

The “2D polymer” in this review is a sheet-like, self-supporting membrane at the molecule level, the thinnest one, people can image. In addition, the structure of the membrane can be controlled to the atomic order, therefore, the ultimate pores in the membrane framework are expected to be used as a molecular sieving membrane to enhance the permeability and permselectivity. For synthesis of “2D polymer”, the well-balanced design of the formation of planar part and enhancement of the solubility part is very important. Moreover, the elimination of the part which used to enhance the solubility after the formation of 2D structure is also thought to be important for synthesis of “2D polymer”. The supramolecular polymer introduced in the Part 9.4 can be expected as a new direction.

The sheet type “2D polymer” is possible to be used for preparing polymer tube by winding or origami of a sheet polymer. Furthermore, it is possible to build a structure or assembly of the three-dimensional polymer which primary structure is highly controlled, such as a two-dimensional polymer laminate chiral helix. “2D polymer” can be applied not only to the academic study, but also to various field of material.

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Conclusions of Part Ⅱ

The applications of helical polymers prepared by the HSSP for membranes were achieved. The resulting polymer membrane prepared by HSSP or PHSSP can be used for preparation of supromolecular/polymer blend membrane by the surface modification using the SCAT products. By introducing a high planarity and π- conjugated imino structure, the rigidity of the polymer increased. As a result, a higher regularity polymer membrane and 2D membrane were expected to be synthesized. The resulting polymer membranes were expected to show the highest permselectivity.

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Yu Zang

February 2013

List of Publications and Presentations

Original Papers

1. Yu Zang, Toshiki Aoki, Lijia Liu, Yunosuke Abe, Yuriko Kakihana, Masahiro Teraguchi, Takashi Kaneko, Pseudo helix-sense-selective polymerization of achiral substituted acetylenes, *Chem. Commun.*, **48**(3), 4761-4763 (2012).
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4. Yu Zang, Toshiki Aoki, Masahiro Teraguchi, Takashi Kaneko, Helix-sense-selective polymerization using catalytic amount of chiral cocatalyst of substituted acetylenes containing bulky π-conjugated planar substituents yielding highly stable one-handed helical polymers, *ACS Macro Lett.*, submitted for publication.

5. Yu Zang, Guanwu Yin, Toshiki Aoki, Masahiro Teraguchi, Takashi Kaneko, Helix-sense-selective polymerization of fluorine containing achiral phenylacetylenes, *Macromolecules*, in preparation.
6. Yu Zang, Toshiki Aoki, Masahiro Teraguchi, Takashi Kaneko, Structures and mechanism of helix- sense-selective polymerization of various achiral phenylacetylenes, *J. Am. Chem. Soc.*, in preparation.
7. Yu Zang, Toshiki Aoki, Masahiro Teraguchi, Takashi Kaneko, Application of the one-handed helical polymers prepared by the HSSP to polymer membranes for gas separation, *J. Membr. Sci.*, in preparation.
8. Yu Zang, Toshiki Aoki, Masahiro Teraguchi, Takashi Kaneko, Application of the amphiphilic SCAT products for surface modified membranes, *J. Membr. Sci.,* in preparation.

Others publications

9. Lijia Liu,Yoshiyuki Oniyama, Yu Zang, Shingo Hadano, Toshiki Aoki, Masahiro Teraguchi, Takashi Kaneko, Takeshi Namikoshi, Edy Marwanta, Synthesis and helix-sense-selective polymerization of a novel phenylacetylene having a trisiloxanyl group and two hydroxyl groups and enantioselective permeability of the resulting chiral polymeric membrane: Effect of the trisiloxanyl group on the polymerization and enantioselective permeability, *Polymer (communications)*, **51**(12), 2460-2464 (2010).
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Review

藏雨, 王健軍, 中尾和樹, 宮田真理, 棚木宏幸, 寺口昌宏, 青木俊樹,「２Ｄポリマー」膜の合成-----究極の分子分離膜をめざして, *未来材料*, **13**(2), 31-37 (2013).

Award

- Poster award, Pseudo helix-sense-selective polymerization of achiral phenylacetylene, *International Chiral Meeting (ICM 2012),* Zhangjiajie, China, 2-3 August, 2012.
- ポスター賞, 両親媒性環化三量体を用いた表面修飾による酸素選択透過性の改良, 膜シンポジウム 2012, 神戸, 日本, 11 月 14 日 2012 年。

Invited presentation

1. Yu Zang, Jun Li, Masahiro Teraguchi, Takashi Kaneko, and Toshiki Aoki, Comparison of asymmetric polymerization of substituted phenylacetylenes to yield static one-handed helical polymers, *IUPAC 8th International Conference on Novel Materials and Synthesis (NMS-VIII) & 2 2nd International Symposium on Fine Chemistry and Functional Polymers (FCFP-XXII),* Xi'An, China, 14-19 October, 2012.
2. Yu Zang, Masahiro Teraguchi, Takashi Kaneko, and Toshiki Aoki, New approach to asymmetric polymerizations of substituted phenylacetylenes to yield static one-handed helical polymers, *Asian International Symposium,* Kusatu, Japan, 24 March, 2013.

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1. Yu Zang, Masahiro Teraguchi, Takashi Kaneko, Toshiki Aoki, Pseudo helix-sense-selective polymerization of substituted phenylacetylenes having two hydroxyl groups and a dynamic covalent bond of imino group, *Taiwan-Japan Bilateral Polymer Symposium*, Hsinchu, Taiwan, 16 September, 2011.
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3. Yunosuke Abe, Takeshi Namikoshi, Yu Zang, Masahiro Teraguchi, Takashi Kaneko, Toshiki Aoki, Asymmetric-induced polymerization and polymer reaction of the resulting one-handed helical polymer membranes, *ACS Spring 2012 National Meeting & Exposition*, San Diego, California, USA, 27 March, 2012.
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ADVANCED HELIX-SENSE-SELECTIVE POLYMERIZATION OF ACHIRAL PHENYLACETYLENES CONTAINING IMINO GROUPS AND APPLICATION OF THE RESULTING HELICAL POLYMERS FOR MEMBRANES

YU ZANG