Feature Article

Synthesis of functional π-conjugated polymers from aromatic acetylenes

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Abstract

Because of their unique structures and properties, π-conjugated polymers have attracted the attention of scientists and engineers. The authors have studied the synthesis of two kinds of π-conjugated poly(aromatic acetylene)s, i.e. poly(arylacetylene)s and poly(aryleneethynylene)s with the aim of obtaining new polymers having novel functions or higher performances. This review mainly concerns the authors' results, as follows: first, we describe the synthesis and properties of achiral poly(arylacetylene)s, containing trimethylsilyl groups, oligodimethylsiloxanyl groups, dendritic groups, and glavinoxyl groups, for application as oxygen permselective membrane materials. Their self-membrane-forming abilities and high oxygen permeabilities are presented. Second, the synthesis by asymmetric-induced polymerization of chiral poly(arylacetylene)s having both a main-chain chirality and chiral pendant groups and their application as optical resolution membranes are described. Third, two new synthetic methods for preparing chiral helical poly(phenylacetylene)s without the coexistence of any other chiral moieties are presented. One is helix-sense-selective addition polymerization and the other is in situ removal of chiral pendant groups from membranes of poly(arylacetylene)s that also contain a main-chain chirality. The chiral helical poly(arylacetylene)s were tested as optical resolution membranes. The chiral and achiral poly(arylacetylene)s were synthesized by addition polymerization using metathesis catalysts or rhodium complexes. Finally, the synthesis of regiospecific poly(aryleneethynylene)s bearing stable radicals by the polycondensation of bromoethynylanthracene derivatives using a Pd(0) complex is described. The magnetization and the static magnetic susceptibility of the polyradicals are explained.
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1. Introduction

π-Conjugated polymers have attracted much attention among numerous scientists and engineers because they offer many possibilities of having useful properties such as electric conductivity, optical nonlinear susceptibility, electroluminescence, molecular magnetism, photoluminescence, high gas permeability and so on. One of the most famous π-conjugated polymers is polyacetylene, the well-known electrically conductive polymer discovered by Prof. Shirakawa, who received the Nobel Prize for Chemistry in 2000. The chemical structure of this compound,

which is synthesized by the addition polymerization of acetylene [1,2], is very simple, allowing for no variation. To introduce variations into the structure and properties of

H————H

Acetylene

R————R'

Substituted acetylene

polyacetylene, other synthetic methods, especially employing new initiators of addition polymerizations of substituted acetylenes, including aromatic acetylenes, have been developed by excellent researchers, for example, Prof. Masuda [3–5], and Prof. Grubbs [6,7] and Prof. Schrock [8–10] who received Nobel Prize for Chemistry in 2005. Therefore, the extent of availability of many kinds of conjugated polymers has been increasing. In particular, poly(substituted acetylene)s were intensively studied by Masuda et al. [3–5]. The record

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oxygen permeability of polySP and the relatively high permselectivities of poly(substituted acetylene)s relative to those of other polymers have excited the attention of membrane scientists [11,12]. Organic magnetism in poly(substituted acetylene)s bearing radical pendant groups was also investigated by Nishide [13] and Iwamura [14].

$$CH_3 - \!\!\equiv\!\! - \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}} - CH_3$$

SP
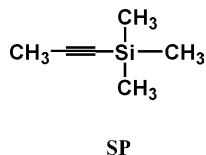
The π-conjugated polymers obtained by the addition polymerization of substituted acetylenes contain alternating double bonds and are usually called 'substituted polyacetylenes', although they are systematically named as 'substituted poly(vinylene)s' (Scheme 1(a)). Another type of conjugated polymer is obtained from substituted aromatic acetylenes by condensation polymerization. In this case, the substituted aromatic acetylene monomers need to have a halogen atom present on the aromatic ring. The resulting π-conjugated polymers, which contain alternating triple and double bonds, are systematically named 'substituted poly(aryleneethynylene)s' (Scheme 1(b)). For instance, poly(phenylenevinylene) is an example of one of these conjugated polymers prepared by polycondensation that was investigated for use as an organic magnetic material by Nishide [15] and Rajca [16].

Poly(arylacetylene)s have highly controlled chemical structures, such as a high cis-content and helical main chains. One result is the main chains are very rigid and, therefore, poly(arylacetylene)s tend to exhibit good membrane-forming abilities. High-ordered membrane structures were reported by Tabata [17,18]. In addition, if the helical sense of the π-conjugated polymers is controlled, the polymer backbone itself becomes optically active. Such one-handed helical polymers were researched by Akagi [19–21] and Yashima [22,23]. The backbone chirality of the π-conjugated polymers can be detected directly by measuring their CD behavior, because the main-chain itself is a chromophore. Therefore, such polymers

are likely sources of main-chain chiralities. Poly(aryleneethynylene)s can also form precise molecular architectures such as molecular-rods, foldamers, macrocycles and dendrimers, through control of the linkage-position of the aromatic units.

This review describes the author's investigation into synthesis and properties of poly(arylacetylene)s and poly(aryleneethynylene)s, and, through suitable macromolecular design, their applications as oxygen permselective membranes, optical resolution membranes, and organic magnetic materials.
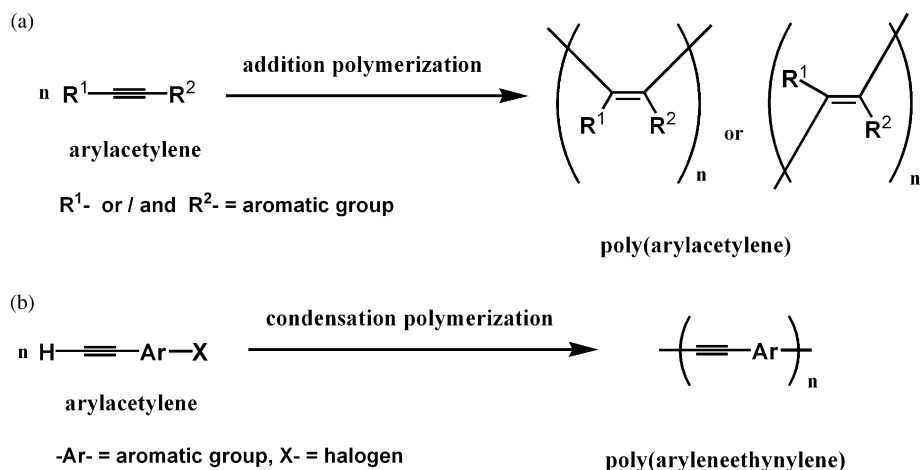
2. Achiral addition polymers from aromatic acetylenes for use as oxygen permselective membranes

2.1. Introduction—oxygen permselective membranes from poly(aromatic acetylene)s

Up to now, syntheses of many functional substituted polyacetylenes have been achieved. Among them, poly(aromatic acetylene)s are useful because they are usually more stable than other substituted polyacetylenes in air and often can form self-supporting membranes [24,25]. Masuda et al. have made extensive investigations of the synthesis and oxygen permeability of various aromatic polyacetylenes having bulky spherical substituents such as tris(trimethylsilyl)silyl groups [26], trialkylsilyl groups [27–30] or adamantyl groups [31,32]. However, the oxygen permeabilities of these polymers are low compared with that of polySP, which has the highest oxygen permeability of any synthetic polymer. The key structural features of the highly oxygen permeable polymers have been investigated from various viewpoints using positron annihilation lifetime [33], quasielastic neutron scattering [34,35], and spin probe techniques [36].

Recently, some insoluble polymeric membranes bearing no substituents [37–39], fluorine [40] or hydroxyl group [41] were synthesized by Masuda et al. by means of in situ desubstitution of trialkylsilyl groups or trialkylsiloxyl groups from substituted poly(diphenylacetylene) membranes. The resulting membranes showed high oxygen permeabilities.

Addition polymers from substituted aromatic acetylenes, especially from phenylacetylenes, possessed high molecular weights, good solubility, and subsequent good membrane-


(a)

n R¹ ——≡—— R² → **addition polymerization** → poly(arylacetylene)

arylacetylene

R¹- or / and R²- = aromatic group

(b)

n H ——≡—— Ar—X → **condensation polymerization** → poly(aryleneethynylene)

arylacetylene

-Ar- = aromatic group, X- = halogen

Scheme 1. Synthesis of two types of π-conjugated polymers from aromatic acetylenes. (a) Poly(arylacetylene) prepared by addition polymerization, (b) poly(aryleneethynylene) prepared by condensation polymerization.

forming abilities, even if the substituents were bulky. In addition, the aromatic group is suitable for introducing various other substituents, such as silicon- or fluorine-containing groups, dendritic groups, or galvinoxyl groups, that affect the permeabilities of the resulting membranes. Therefore, substituted arylacetylenes were synthesized, polymerized, and then fabricated into self-supporting membranes. In this section, we discuss the author's results concerning the effect of the shapes, numbers, and positions of the substituents on the membranes' oxygen permeabilities.

2.2. Polymers from phenylacetylenes (PA) and diphenylacetylenes (DPA) containing one to three trimethylsilyl groups

The presence of trimethylsilyl groups in polymeric dense membranes is known to enhance oxygen permeability. For example, Masuda et al. reported that polySP membranes have the highest oxygen permeability of all the dense membranes [42].

SP
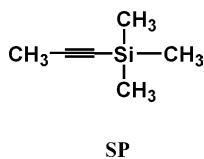
One of the reasons for the record permeability of polySP was thought to be that the trimethylsilyl groups have a high mobility and are located in a space between the main chains where oxygen molecules permeate [11,12,24]. The authors thought that, because polySP has a compact main-chain, a high density of the groups in the membrane was important to achieve even higher permeabilities. Therefore, the authors tried to synthesize poly(phenylacetylene)s having more than two trimethylsilyl groups in the monomer unit.

o,p-BSPA bearing two trimethylsilyl groups was synthesized and polymerized by WCl_6 to yield a soluble polymer having a high molecular weight. The self-supporting membrane from the polymer showed a higher oxygen permeability than that from poly(*o*-SPA) or poly(*p*-SPA) [43]. In addition, its permselectivity was also quite high and the permeability was similar to that of polySO, which has the highest permeability of all the commercially available dense polymeric
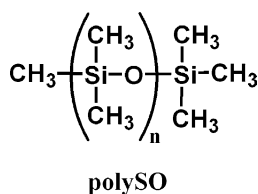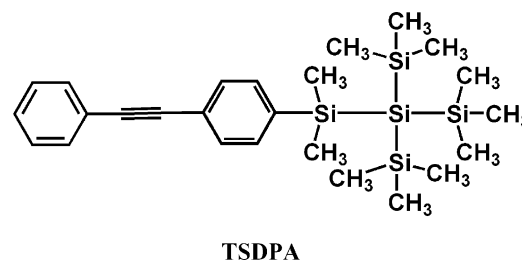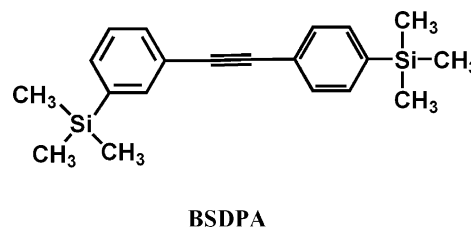
polySO

membranes. However, the permeability of poly(*o,p*-BSPA) was around six times lower than that of polySP.

o,p-BSPA

o-**SPA**

p-**SPA**
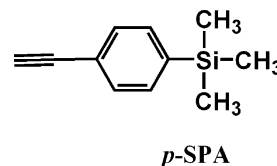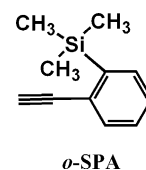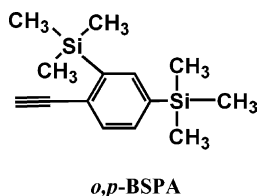
To enhance its permeability to a similar order of magnitude as that of polySP, three trimethylsilyl groups were introduced in the phenylacetylene in the form of tris(trimethylsilyl)silyl groups [26]. The homopolymer (polyTSPA) obtained by a Rh complex was insoluble, but judging from the data of the membranes from the copolymers with *p*-SPA, the authors estimated that the permeability of the homopolymer was of a similar order of magnitude as that of polySP.

TSPA
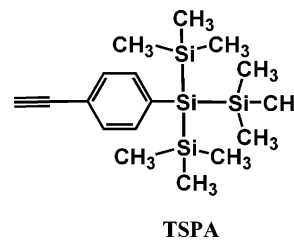
It was already known that poly(diphenylacetylene)s had a high oxygen permeability similar to polySP. Therefore, the authors selected poly(diphenylacetylene) as a main-chain instead of poly(phenylacetylene) and introduced more than two trimethylsilyl groups into the monomer unit [44]. The authors synthesized and polymerized BSDPA, having two trimethylsilyl groups, and TSDPA, having three trimethylsilyl groups, and obtained good self-supporting membranes from the polymers by a solvent cast method. They showed a quite high oxygen permeability, very similar to that of polySP. In addition, these membranes exhibited a higher degree of stability in permeability than polySP.

BSDPA

TSDPA

## 2.3. Polymers from phenylacetylenes (PA) containing a linear or branched oligodimethylsiloxanyl group

Polydimethylsiloxane (polySO) shows the highest permeability of all the commercially available polymers because the siloxane (Si–O–Si) bonds in that material are very flexible. However, pure linear polySO lacks the ability to form a self-supporting membrane. To remedy this disadvantage, the authors selected a poly(phenylacetylene) backbone as a rigid component, and then synthesized and (co)polymerized phenylacetylenes having an oligodimethylsiloxane chain at the para position. The homopolymers of TeSOPA and TSOPA showed higher oxygen permeabilities and permselectivities than polySO. As the Si–O bond content
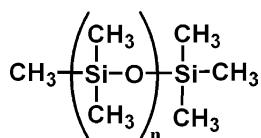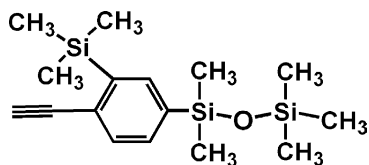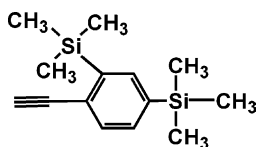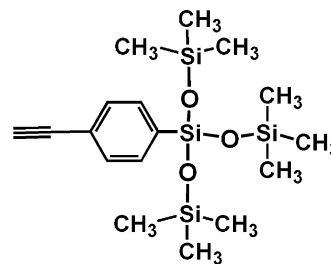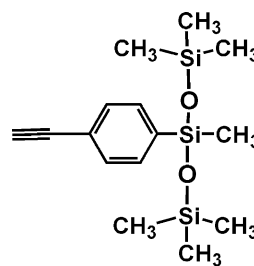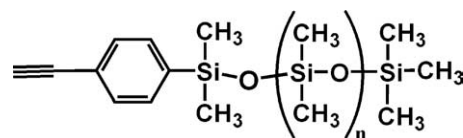

polySO
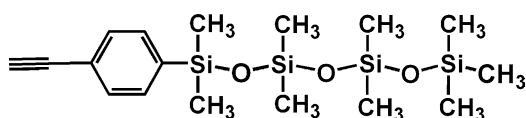
TeSOPA
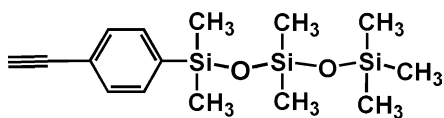
TSOPA

increased, so did the oxygen permeability. The rigid main-chain was effective in producing a self-supporting membrane and relatively high permselectivity. On the other hand, the oxygen permeability of poly(*o*-S-*p*-DSOPA) was lower than poly(*o*,*p*-BSPA), which were prepared by metathesis catalysts [45]. In this case, the extremely large spaces between the macromolecules in poly(*o*,*p*-BSPA) were filled by the disiloxane chains of poly(*o*-S-*p*-DSOPA).


o-S-p-DSOPA

o,p-BSPA

Branched oligosiloxane chains were introduced to poly(phenylacetylene)s. They showed high oxygen permselectivities maintaining high oxygen permeabilities [46].

t-TSOPA

s-DSOPA

The authors also synthesized polySO-*graft*-poly(phenyla-cetyelne) by copolymerization of a SOPA macromonomer with SPA. The graft copolymers formed good self-supporting membranes in spite of having a high polySO content, and a higher oxygen permeability and permselectivity were observed than with polySO [47].

SOPA macromonomer
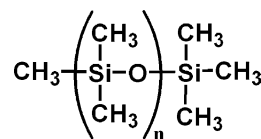
polySO

2.4. Polymers from phenylacetylenes (PA) containing one to three trifluoromethyl groups or a perfluroalkyl group

As fluorine-containing compounds have an oxygen affinity, it is expected to enhance oxygen permeability. Therefore, the authors introduced two or three trifluoromethyl groups onto the benzene ring of phenylacetylene and polymerized the resulting monomers (*o*,*p*-BFPA and *o*,*m*,*p*-TFPA) [48]. The polymeric membranes showed high oxygen permeabilities, similar to that of polySO, and a higher permselectivity than that compound.
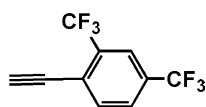
o,p-**BFPA**
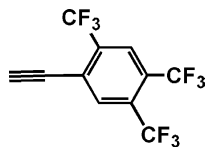
o,m,p-**TFPA**

To further enhance the fluorine content of the compounds, we planned to introduce perfluoroalkyl groups. However, perfluoroalkyl groups tend to form crystalline regions, which lower the permeability. To prevent this crystallization, the authors synthesized OFOSPA and TeFOSPA, which have perfluoroalkyl groups linked via an alkoxysilyl (Si–O–C) bond as a flexible spacer [49]. The polymeric membranes showed good performance.
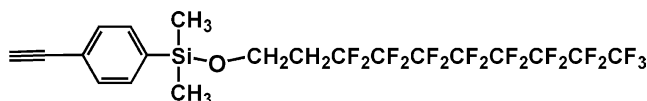
OFOSPA
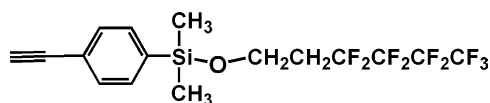

TeFOSPA

2.5. Polymers from phenylacetylenes having a dendritic group

Recently, dendrimers have been used for nanotechnological innovation in various fields [50–53]. A new class of dendrimers, known as side-chain dendritic or dendronized polymers, have a polymer backbone as a core group, instead of a dot-like core [54–56]. However, it has proved difficult to effect homopolymerization of dendron monomers beyond the second generation, thereby producing a polydendron having a high degree of polymerization (DP), owing to the steric hindrance of the bulky dendritic groups. The authors selected a poly(phenylacetylene)-backbone as the central core because it was known that poly(phenylacetylene)s having high degrees of polymerization and high cis-transoidal structures were generated by a rhodium complex, even if they had very bulky substituents. Monodendron monomers (DENPA) consisting of *m*-linked phenyleneethynylene repeating units were synthesized, and the corresponding polydendrons were obtained by polymerization of the monomers using a rhodium catalyst [54,57–60]. The resulting polydendrons exhibited a high degree of polymerization (DP $> 10^3$), and were soluble in common organic solvents such as chloroform and tetrahydrofuran.
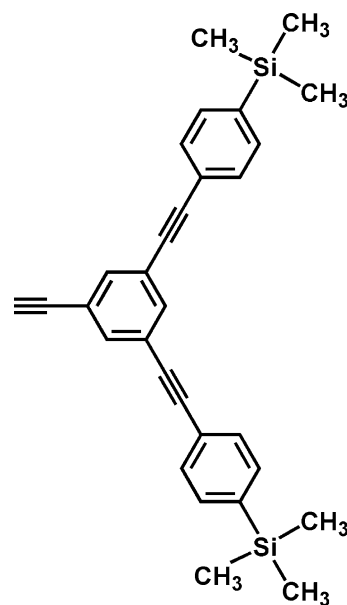

DENPA

The structural features of the polydendrons were investigated by ^{1}H, ^{13}C NMR, and UV–vis spectrometries, wide angle X-ray scattering (WAXS) and atomic force microscopy (AFM), and combined gel permeation chromatography and low angle laser light scattering (GPC-LALLS), among others. The results indicated that the polydendrons possessed rod- or worm-like structures, which had a cis-transoidal main-chain and a well-defined monodendron plane. The presence of the bulky monodendron substituents made the dihedral angle between the main-chain and the attached monodendron plane highly twisted. However, steric repulsios between the monodendron substituents resulted in the main-chain adopting an extended conformation with slightly or moderately twisted single bonds. These combination of these steric effects resulted in the dendron planes arranged in a regular fashion along the main-chain.

The polydendrons showed a good membrane-forming ability, depending on their degree of polymerization. The self-supporting membranes prepared by the solvent-casting method were orange due to the presence of the π-conjugated main-chain chromophore. The first generation polydendron, polyDENPA, showed a higher oxygen permselectivity than those of the corresponding zero generation poly(phenylacetylene) derivatives [60].

2.6. Polymers from phenylacetylenes having a galvinoxyl group

Poly(phenylacetylene)s had been investigated as a backbone structure of the polyradicals used for magnetic materials [15,61]. However, the difficulties involved in synthesizing and stabilizing these types of polyradicals has meant that their abilities to form thin membranes are not known. In order to obtain a new polyradical having a good membrane forming ability, the authors synthesized copolymers of HGPA with SPA, and oxidized the copolymers to yield the corresponding

polyradicals, poly(*p*-SPA-*co*-GPA) [62]. The oxygen perms-electivities of the resulting copolymer membranes were also evaluated.
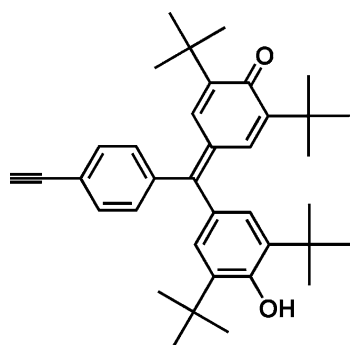
HGPA
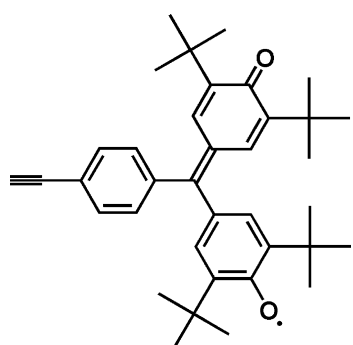
GPA

Copolymerization of HGPA and *p*-SPA was initiated by [Rh(nbd)Cl]$_2$ in chloroform, and the corresponding high molecular weight ($M_n \approx 10^5$) copolymer, poly(*p*-SPA-*co*-HGPA), was obtained in a good yield. Poly(SPA-*co*-HGPA) was the more soluble in organic solvents such as chloroform, benzene and THF, in spite of its higher molecular weight compared to polyHGPA. Poly(*p*-SPA-*co*-HGPA) gave the corresponding polyradical, poly(*p*-SPA-*co*-GPA), by chemical oxidation with fresh PbO$_2$ or alkaline K$_3$Fe(CN)$_6$ in an oxygen-free atmosphere. These copolymers and polyradicals could be fabricated to self-supporting membranes. The polyradical membranes were so stable that the initial spin concentration was maintained for a few days. The rigid character of the galvinoxyl moiety resulted in the oxygen permselectivity increasing and the oxygen permeability decreasing as the amount of galvinoxyl units increased.

3. Chiral addition polymers having both bulky chiral groups and a chiral main-chain prepared by asymmetric-induced polymerization of chiral aromatic acetylenes for use as optical resolution membranes

3.1. Introduction—asymmetric-induced polymerization and optical resolution membranes

To realize good optical resolution membrane materials, the authors thought that the polymers should possess the following

properties: (1) the polymers should have a self-membrane-forming ability, thereby eliminating domains and defects having no recognition ability. (2) The polymers should have a high content of chiral structures to enhance the amount of chiral recognition sites.

The authors reported that polyPSP gave a self-supporting membrane, which showed enantioselective permeation for many kinds of racemates. Notably, the enantioselectivity was almost 100% in the initial period. Since, the polymer powder had no enantioselectivity in adsorption, the enantioselectivity appeared only in permeation (diffusion) through the pure membrane [63–65].
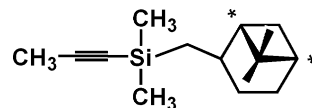

PSP

Subsequently, the authors selected other poly(substituted aromatic acetylene)s, especially poly(substituted phenylacety-lene)s, many newly synthesized by homopolymerization of the corresponding new monomers, for use as enantioselective membranes. The reasons for the selection of chiral substituted poly(aromatic acetylene)s were as follows. (1) Many kinds of substituted aromatic acetylenes can polymerize to yield soluble high molecular weight polymers, even if the monomers bear bulky groups. Therefore, they have a self-membrane-forming ability. (2) When substituted aromatic acetylenes have chiral substituents, the monomers can polymerize to yield one-handed helical polymers. Therefore, the membranes can have a high chiral content [24,54].

In this section, monomers suitable for asymmetric-induced polymerization are discussed, and enantioselective permeation through the resulting polymeric membranes presented.

3.2. Polymers from phenylacetylenes (PA) having one or two bulky chiral groups

In 1993, during the course of an investigation into the synthesis of a new enantioselective permeability membrane material, the authors accidentally discovered an asymmetric-induced polymerization in which one-handed helical chirality was induced in the main-chain during polymerization of a phenylacetylene (MCPA) having a bulky chiral L-menthox-ycarbonyl group [66]. The polymer could be fabricated to a self-supporting membrane, which showed a CD spectrum similar to that of the solution. The membrane showed enantioselectivity in permeation.
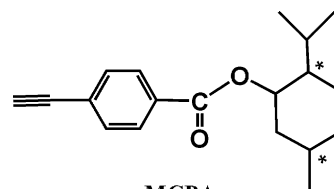
MCPA

After this discovery, the authors synthesized and polymer-ized many other phenylacetylenes and diphenylacetylenes

having a chiral substituent to check whether any main-chain chirality was induced. As a result, many chiral monomers were found to be suitable for the one-handed-helix induced polymerization. For example, the homopolymers of *p*-PSPA and PCPA obtained with a Rh complex showed strong CD absorptions similar to that of MCPA, while BCPA and 3-PDSOPA showed very weak CD absorptions [66–68]. Interestingly, the homopolymers of *p*-PSPA prepared using WCl$_6$ showed much weaker CD absorptions than that of *p*-PSPA prepared by a Rh complex [67].

p-PSPA

PCPA

BCPA

3-PDSOPA
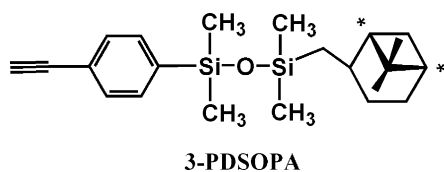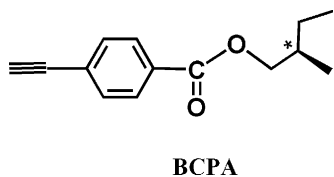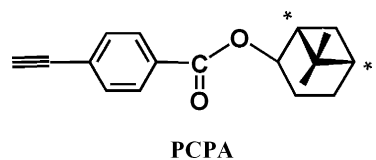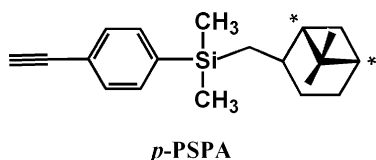
o-PSPA, *m*-PSPA, and *o,p*-BPSPA were synthesized and polymerized using WCl$_6$ [69]. PolyPSPAs having pinanylsilyl group at ortho position showed very weak CD absorptions similar to poly(*p*-PSPA) prepared with WCl$_6$. Poly(PSPA)s made using a rhodium complex had a high cis content, whereas polyPSPAs made with WCl$_6$ did not. Therefore, cis–trans regularity was found to be an important factor to make one-handed chiral conformations.

o-PSPA

m-PSPA

o,p-BPSPA

Some of these polymeric membranes showed enantioselectivities in permeation.

3.3. Polymers from linear or branched oligosiloxanylphenylacetylenes (SOPA) having one to three bulky chiral groups

To investigate the effects of the chemical structures of the chiral groups, including the number and position of the chiral groups in the monomers, on the induction of chirality in the main-chain during polymerization and on the degree of enantioselectivity in the permeation of the polymeric membranes, oligosiloxanylph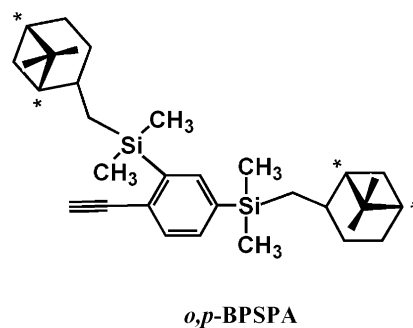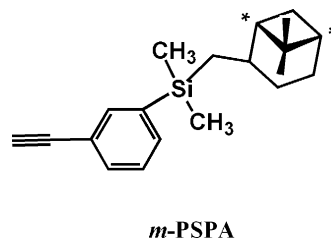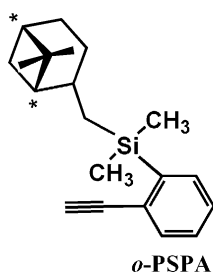enylacetylenes having one or two bulky chiral pinanyl groups at the 1-, 3-, and/or 5-position of an oligosiloxane chain were polymerized with a Rh complex to produce high molecular weight polymers. With the exception of the polymers with very bulky substituents, polymers with a chiral pinanyl group at the 1-position of an oligosiloxanyl group, such as 1,3-BPDSOPA and 1-PDSOPA, showed high molar ellipticity in the main-chain region in the CD spectra. The exceptional polymers with very bulky substituents had UV–vis absorptions at longer wavelengths. On the other hand, the polymers from monomers with a chiral pinanyl group at the 3- or 5- position of an oligosiloxanyl group (3-PDSOPA and 5-PTSOPA) showed almost no CD absorptions. The flexible Si–O spacer did not transmit the chiral information to the main-chain [69,70].

1,3-BPDSOPA
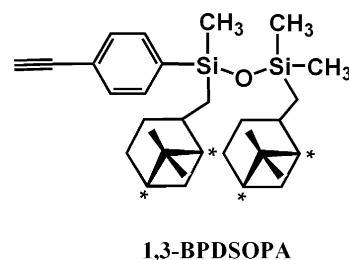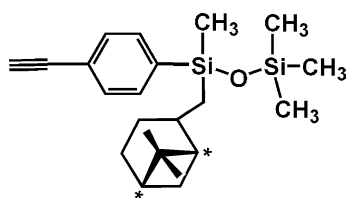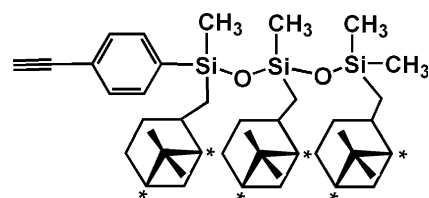
1-PDSOPA

1,3,5-TPTSOPA
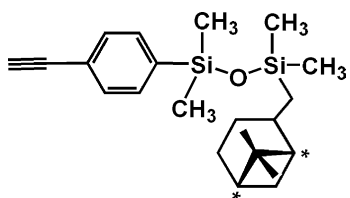
3-PDSOPA
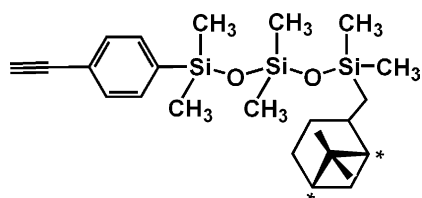
5-PTSOPA
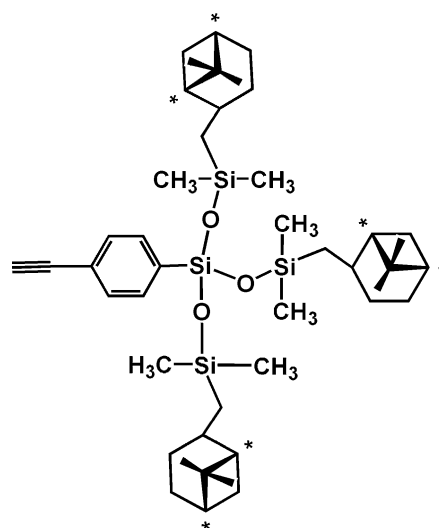
t-TPSOPA

All these membranes showed enantioselective permeabilities for two amino acids and an alcohol. To construct the best optical-resolution membranes, the authors found that the most effective chemical structures of the pinanyl-group-containing poly(phenylacetylene)s were as follows: (1) a chiral helical backbone, (2) a high content of chiral pinanyl groups, and (3) an absence of oligodimethylsiloxane moieties [69,70].

Although the polymers of 1,3-BPTSOPA and 1,3,5-TPTSOPA had a pinanyl group at the 1-position, they showed almost no CD absorptions. In this case, their UV–vis absorptions shifted to longer wavelengths than those of the corresponding polymers having disiloxanyl groups. On the other hand, the case of polyphenylacetylenes having a branched oligopinanylsiloxane(*t*-TPSOPA), showed CD absorptions in spite of having no pinanyl group at the 1-position [71]. This may be because their bulky substituents changed the main-chain structure. Similar findings were observed in Section 3.2.
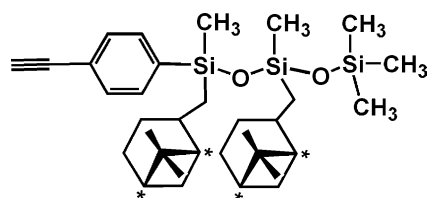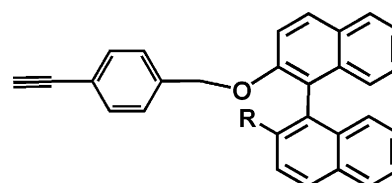
3.4. Polymers from aromatic acetylenes having a binaphthol group

The authors synthesized and polymerized two kinds of aromatic acetylenes having an axial chirality, which were derived from binaphthol. One has a binaphthol residue connected with phenylacetylene via an ether linkage (NOPA) and the other has a binaphthol residue directly connected to a triple bond by a C–C bond without any spacer (NA). Compared to the other polymers described above, both of these polymers showed relatively strong CD signals at longer wavelengths, around 450 and 550 nm, respectively [72].

1,3-BPTSOPA

NOPA

NA
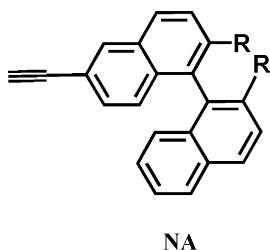
3.5. Polymers from diphenylacetylenes (DPA) having a bulky chiral group

Disubstituted acetylenes with bulky chiral pinanyl groups, *p*-PSDPA, *m*-PSDPA, polymerized with NbCl₅-, TaCl₅-, or MoCl₅-based metathesis catalysts to give high molecular weight polymers in good yields. Poly(*p*-PSDPA) and poly(*m*-PSDPA) showed intense CD effects in the UV–vis region, which suggests that these disubstituted acetylene polymers have helical conformations with an excess of one-handed helical sense [73].
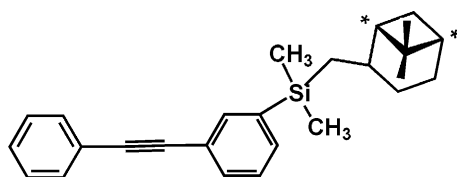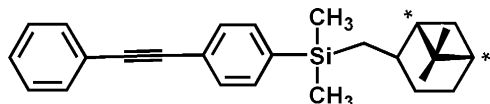
p-PSDPA

m-PSDPA

The lack of a significant decrease in the magnitude of the CD effects of poly(*p*-PSDPA) and poly(*m*-PSDPA) with increasing temperature indicated the relatively high stability of their helical conformations. On the other hand, the intensities of the CDs of poly[(−)-1-{4-(dimethyl(10-pinanyl)silyl)phenyl}-1-propyne] and poly[(−)-1-chloro-2-{4-(dimethyl(10-pinanyl)silyl)-phenyl}acetylene] were approximately 1/10 those of poly(*p*-PSDPA) and poly(*m*-PSDPA), which means that introduction of two aromatic side groups into the repeating unit is favorable for the induction of helical conformation to disubstituted acetylene polymers. The self-supporting membranes of poly(*p*-PSDPA) and poly(*m*-PSDPA) exhibited characteristic properties as optical resolution membranes.

3.6. Polymers from phenylacetylenes having a galvinoxyl group

Polyradicals possessing a one-handed helical structure would promise interesting magnetic and chiroptical properties. For example, the interchain magnetic interaction may be modified by the helicity of polyradical in the following manner.

A racemic helical polyradical has two types of interchain interaction, i.e. interactions between chains of the same helical sense and between chains of the opposite helical sense. If only the former shows ferromagnetic interaction, only the one-handed helical polyradical will show ferromagnetic property. Additionally, a magneto-chiral dichroism effect is expected in chiral magnetic materials [74–77]. To investigate such an effect, a poly(phenylacetylene)-based polyradical possessing an excess of one-handed helical backbone was synthesized by copolymerization of HGPA and a chiral acetylene monomer, *p*-PSPA, using a rhodium catalyst [78].

The copolymers were obtained in a good yield with high molecular weight ($M_n \approx 10^5$), and the compositions of the copolymers were almost the same as the feed compositions of monomers. The CD spectra of the poly(HGPA-*co*-*p*-PSPA) copolymers were different from that of the mixture of polyHGPA and poly(*p*-PSPA), being the same as that of poly(*p*-PSPA). A bathochromic shift of the absorption edge was observed in the UV–vis absorption spectra with increasing amounts of HGPA. In all the CD spectra of the copolymers, positive Cotton effects were observed in the absorption region (450–550 nm) of the backbone chromophore, and the peaks also shifted to longer wavelength with the bathochromic shift of the absorption edge, indicating an excess of one-handed helical polyacetylene backbone. With higher HGPA composition, a split-type CD signal appeared and increased its intensity in the absorption region (420 nm) of the hydrogalvinoxyl chromophore. The CD spectrum of the copolymer with a high HGPA content shows patterns similar to that of the polyHGPA obtained by the helix-sense-selective polymerization in the presence of a [Rh(nbd)Cl]₂ catalyst and (*R*)-PEA shown in Section 4.2.2.

HGPA

p-PSPA
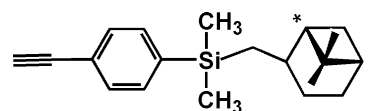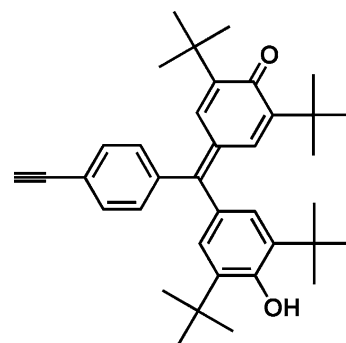
In the CD spectra of the polyradical poly(GPA-*co*-*P*-SPA) containing more than 20 mol% of *P*-SPA, a Cotton effect was observed in the absorption region (470 nm) of the galvinoxyl radical chromophore and in that (450–550 nm) of the backbone chromophore. This result indicates the maintenance of the

excess of one-handed helix even after the oxidation reaction, and the successful synthesis of an optically active polyradical. The static magnetic susceptibility of the powdered polyradical with 67 mol% galvinoxyl units was measured with a SQUID magnetometer at 2–250 K. The negative Weiss temperature ($\theta = -2.2$ K) indicated a antiferromagnetic interaction between unpaired electrons, but this negative θ value was larger than the value of $\theta = -0.7$ K [79] observed for the polyGPA that did not have an excess of one-handed helical structure. This result suggests that the excess of one-handed helix facilitated efficient packing of the polymer chains to give a more extensive and stronger antiferromagnetic through-space interaction between the radical units, although the effect of comonomer cannot be ruled out.

4. Chiral addition polymers having a chiral structure only in the main-chain

4.1. Introduction—one-handed helical substituted polyacetylenes having no other chiral moieties

As the authors described in Section 1, chiral substituted polyacetylenes have been synthesized by polymerization of monomers having bulky chiral substituents. However, after the chiral side groups were removed by hydrolysis or reduction, the resulting polymer did not show CD absorptions in the main-chain region in solution. A chiral helical nonsubstituted polyacetylene had been synthesized by polymerization of acetylene in a chiral nematic reaction field [19]. However, there were no reports of obtaining chiral helical substituted polyacetylenes having no other chiral moieties in the side or end groups.

4.2. One-handed helical poly(phenylacetylene)s synthesized by helix-sense-selective polymerization

4.2.1. One-handed helical poly(phenylacetylene)s stabilized by intramolecular hydrogen bonds

The authors have found a simple and novel synthetic method for obtaining such a chiral polymer from an achiral substituted acetylene monomer using a chiral catalytic system. In addition, the helical conformation was stable in solution. This is the first example of helix-sense-selective polymerization of substituted acetylenes whose chiral helicity is stable in solution without the aid of other chiral substituents or other small molecules [80].

The authors polymerized an achiral phenylacetylene having two hydroxyl groups and a dodecyl group (DHPA) using a chiral catalytic system consisting of a rhodium dimeric complex, [Rh(nbd)Cl]$_2$ (nbd = 2,5-norbornadiene), as a catalyst, and a chiral amine, (R)-1-phenylethylamine ((R)-PEA), as a cocatalyst. The polymer showed Cotton effects at wavelengths around 430 and 310 nm where there are no UV absorptions of DHPA and (R)-PEA (Fig. 1).
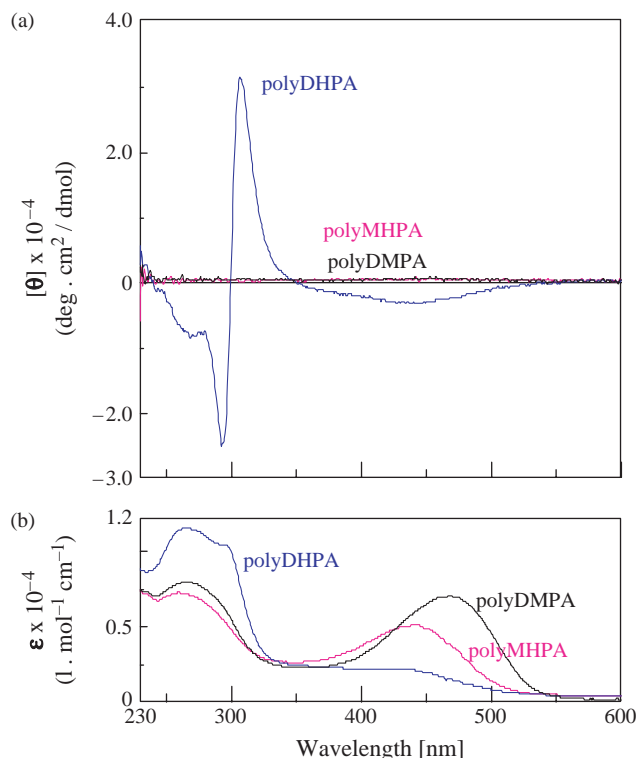
Fig. 1. CD and UV spectra of polyDHPA, polyDMPA, and polyMHPA in chloroform at 20 °C.
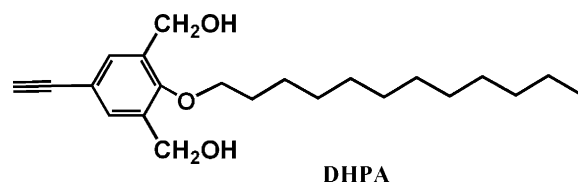
The absorption band at 430 nm is assigned to the conjugated main-chain, and the peak at 310 nm may arise from a chiral position between adjacent pendant groups. The intensity of the band at 430 nm was similar, and the peaks at 310 nm were a little stronger, compared with other chiral helical polyphenylacetylenes having chiral side groups. Therefore, the authors realized the first helix-sense-selective polymerization of a substituted acetylene using a chiral catalyst. On the other hand, no helix-sense-selective polymerizations occurred in the case of achiral phenylacetylenes, DMPA and DMHPA having two methoxy groups, and having one hydroxyl group and one methoxy group, respectively, instead of the two hydroxy groups in DHPA, and SPA that have no hydroxy groups (Fig. 1).
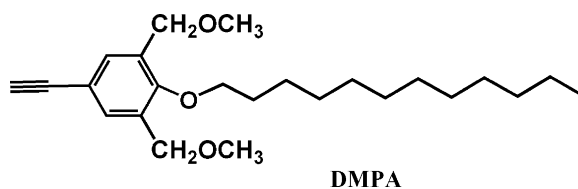
Fig. 2. Dependence of temperature on CD of polyDHPA in chloroform. Reprinted with permission from Ref. [80]. Copyright 2003, American Chemical Society, Washington, DC.

MHPA

_p_-SPA

The polyphenylacetylene without chiral substituents derived from the chiral homopolymer showed no CD as described above. On the other hand, the chiral structure of polyDHPA was stable in chloroform at room temperature for 5 months. Moreover, even when the solution was heated to 50 °C, almost no change was detected in the CD (Fig. 2). This stability may be caused by intramolecular hydrogen bonds between hydroxy groups in different monomer units.

To confirm this, the authors measured CD and IR data in various two-component solvents, which have different polarities. As the content of the polar DMSO solvent component increased, the CD signal became smaller and then disappeared (Fig. 3). Simultaneously, the OH absorption at 3300 cm^{-1} shifted to longer wavelength, indicating that the hydrogen bonds had become weaker (Fig. 4). Therefore, the intramolecular hydrogen bonds were found to be effective in stabilizing the chiral structure.

The authors have also examined the role of the chiral amine cocatalyst in the helix-sense-selective polymerization. Several chiral amines were effective for the polymerization reaction and their effectiveness depended on their bulkiness and ability to coordinate to rhodium. To determine the structure of the true active species in the catalytic system, the authors have synthesized a new chiral rhodium complex having two chiral amines as ligands $([Rh(nbd)((R)-PEA)_2]+BF_4^-)$. The

isolated chiral complex also catalyzed the helix-sense-selective polymerization. These findings suggest that a chiral rhodium complex having two chiral amines may be the true active species when using the catalytic system consisting of $[Rh(nbd)Cl]_2$ and a chiral amine [81].
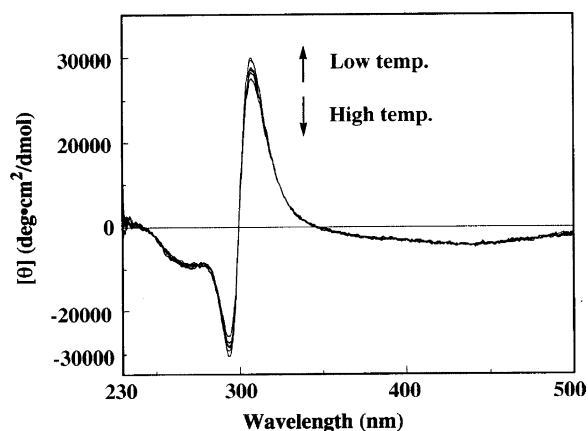
It was of interest to see whether acetylene monomers having the two hydroxyl groups, other than DHPA, could be adapted for the helix-sense-selective polymerization. To achieve such a polymerization of other achiral monomers by the chiral catalytic system, new achiral phenylacetylenes having two _N_-alkyamide groups (OAPA, DoAPA) were designed as monomers. The _N_-alkylamide groups in OAPA or DoAPA were thought to play two important roles, i.e. the formation of intramolecular hydrogen bonding between amide groups and the interruption of intermolecular hydrogen bonds made by long _N_-alkyl chains. Consequently, the polyOAPA or

OAPA

Fig. 3. CD and UV spectra of polyDHPA in various two-component solvents at 20 °C. (a) In CCl$_4$, (b) in CCl$_4$/DMSO(50/1), (c) in CCl$_4$/DMSO(30/1), (d) in CCl$_4$/DMSO(20/1), (e) in CCl$_4$/DMSO(10/1). Reprinted with permission from Ref. [80]. Copyright 2003, American Chemical Society, Washington, DC.
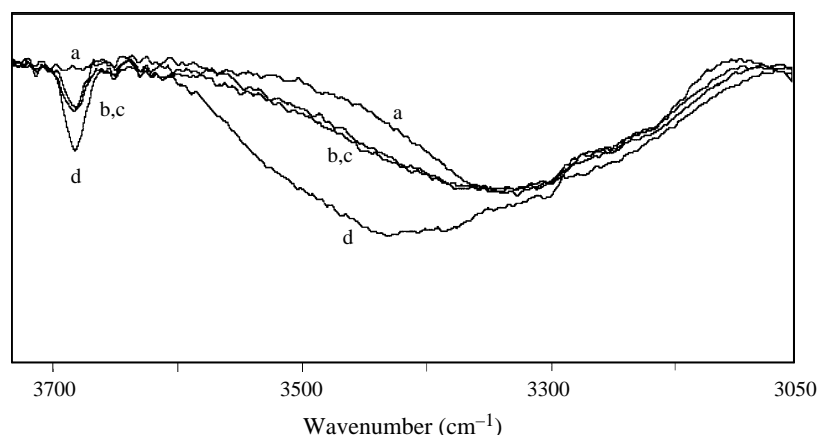
Fig. 4. Effect of the composition of two-component solvents on IR spectra of polyDHPA in CCl$_4$ and DMSO at rt (3.0 g/l). (a) In CCl$_4$, (b) in CCl$_4$/DMSO(50/1), (c) in CCl$_4$/DMSO(30/1), (d) in CCl$_4$/DMSO(20/1). Reprinted with permission from Ref. [80]. Copyright 2003, American Chemical Society, Washington, DC.

DoAPA

OEPA
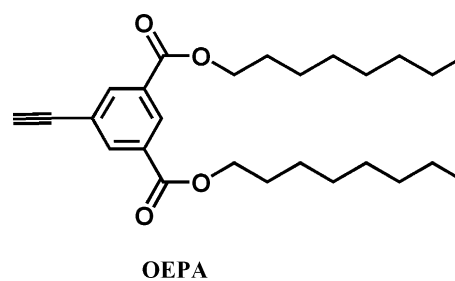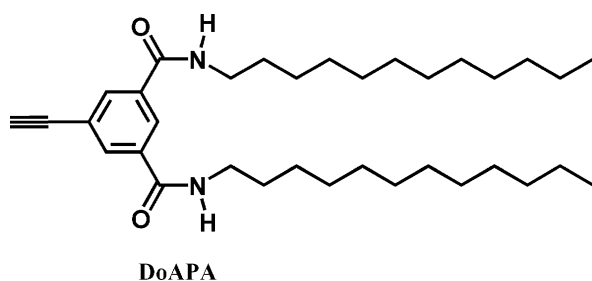
polyDoAPA obtained using the chiral catalytic system showed Cotton signals in CD measurements (Fig. 5). This result proved that the monomer having two amide groups could polymerize in a helix-sense-selective fashion. To confirm the importance of hydrogen bonding for this helix conformation, a polar solvent was added to the CD solution. As a result, the CD intensity of polyOAPA or polyDoAPA decreased significantly. A homopolymer of another achiral phenylacetylene (OEPA), having two alkyl ester groups, which cannot make hydrogen bonds instead of *N*-alkylamide groups, was obtained in a similar chiral condition, but showed no CD signal.

From the above experiments, it became clear that the hydrogen bonds in the helix conformation of the polyOAPA or polyDoAPA are crucially important [82].

4.2.2. One-handed helical poly(phenylacetylene)s stabilized by bulky substituents

In Section 4.2.1, the authors described the helix-sense-selective polymerization of DHPA and its rigid and one-handed helical conformation in solution, which was kinetically stabilized by intramolecular hydrogen bonds among hydroxyl groups in polyDHPA. Moreover, we have succeeded in the helix-sense-selective polymerization of the achiral and bulky monomer HGPA, which cannot make any intramolecular hydrogen bonds in the resulting polymer (Scheme 2) [83,84].
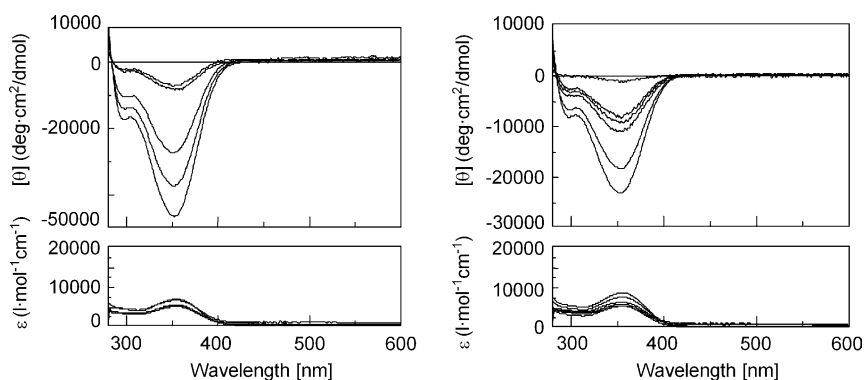
Fig. 5. CD (top) and UV–vis (bottom) spectra of polyOAPA and polyDoAPA in toluene at 20 °C.
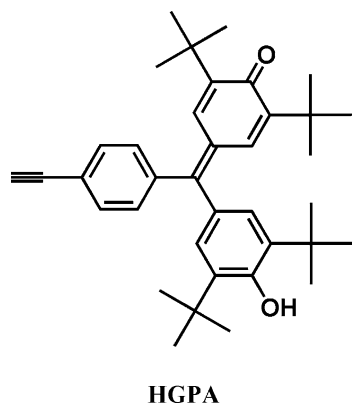
HGPA

Polymerization of the monomer HGPA was carried out in the presence of the [Rh(nbd)Cl]$_2$ catalyst and (*R*)- or (*S*)-PEA. A red solid polymer was obtained in a low yield with an average molecular weight of ca. 10^4, but in the CD spectrum taken in chloroform solution, clear Cotton effects were observed not only in the absorption region (450–600 nm) of the backbone chromophore but also in that (420 nm) of the hydrogalvinoxyl chromophore. The CD spectra of the polymers obtained by polymerization using (*R*)- and (*S*)-PEA as solvent presented mirror images of each other. These results indicate an excess of one-handed helical polyacetylene backbone. The Cotton effect at 420 nm showed split-type CD signals that were attributed to exiton coupling between the hydrogalvinoxyl chromophores. The sign of the CD signal in the absorption region (420 nm) of the hydrogalvinoxyl chromophore was calculated from the polymer geometry, and the result suggests that an excess of right-handed helix was induced by polymerization in the presence of a [Rh(nbd)Cl]$_2$ catalyst and (*R*)-PEA (Fig. 6) [84].

When excess amounts of (*R*)-PEA were added to the solution of achiral or racemic polyHGPA that were obtained by polymerization using triethylamine or racemic PEA as solvents, no Cotton effects were observed. Therefore, it was confirmed that the helix-sense-selective polymerization occurred in the presence of the chiral PEA. Since, the helical polyacetylenes possessing no chiral moieties except for helicity have two conformational enantiomers whose states are thermodynamically equivalent to one another, the conformational rotations of the polymers should lead to the full racemization of polymers on the intra- and/or inter-chain. However, it was found

that the optically active polyHGPA had an excess of one-handed helix kinetically stabilized by the achiral bulky side groups. The CD signals of optically active polyHGPA remained for a long time in chloroform solution, the half-life of the CD signal intensity being more than three days at room temperature [83]. However, CD and UV–vis absorption spectra of the optically active polyHGPA exhibited both thermo- and solvatochromism in the solution examined immediately after preparation [84]. The observation of chiroptical thermo- or solvatochromism is novel for the one-handed helical polymers possessing no chiral moieties in the polymer chains. This is because the helical polymers require both a high activation energy for the conformational rotations to the conformational enantiomer, and the availability of intermediate conformational states with lower activation energies, whose CD signals become of weak intensity or of opposite sign to those of the helical conformation of the ground state.

4.3. One-handed helical poly(phenylacetylene) membranes prepared by in situ desubstitution of chiral groups for use as optical resolution membranes

As mentioned in Section 2.1, the in situ desubstitution of the achiral groups of poly(diarylacetylene)s membranes and the oxygen permeabilities of the membranes thus obtained were investigated in detail by Masuda et al. Masuda and Teraguchi, one of the authors, also reported that removal of chiral pendant groups from poly(diphenylacetylene) membranes, which also contain an induced chiral helical backbone afforded chiral polymers having chiral structure only in the main-chain [37].

The authors examined the in situ desubstitution of chiral groups in the membrane made from various aromatic polyacetylenes and investigated the enantioselective permeabilities of the formed membranes, which have a chiral structure only in the main-chain [85].

First, the synthesis of poly(diphenylacetylene) having only a chiral helical structure as a chiral source by removal of the chiral auxiliary groups, accompanied by scission of the Si–C bond, and their optical resolution ability were investigated. Diphenylacetylenes having one or two pinayl silyl groups (*p*-PSDPA, BPSDPA) polymerized in the manner of asymmetric-induced polymerization to give chiral helical polymers with various chiral pinanyl contents (Scheme 3). Then, fabrication of
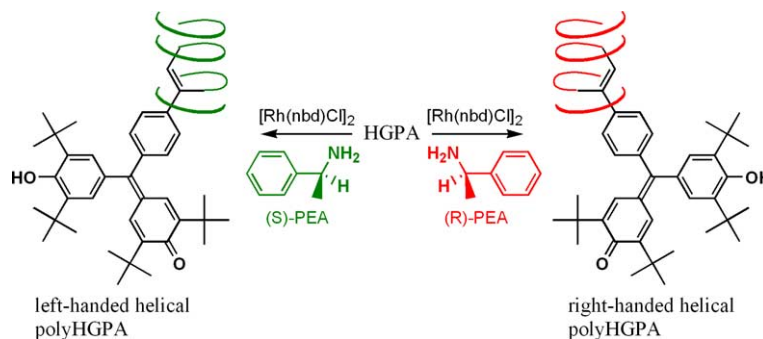
Scheme 2. Helix-sense-selective polymerization of HGPA.
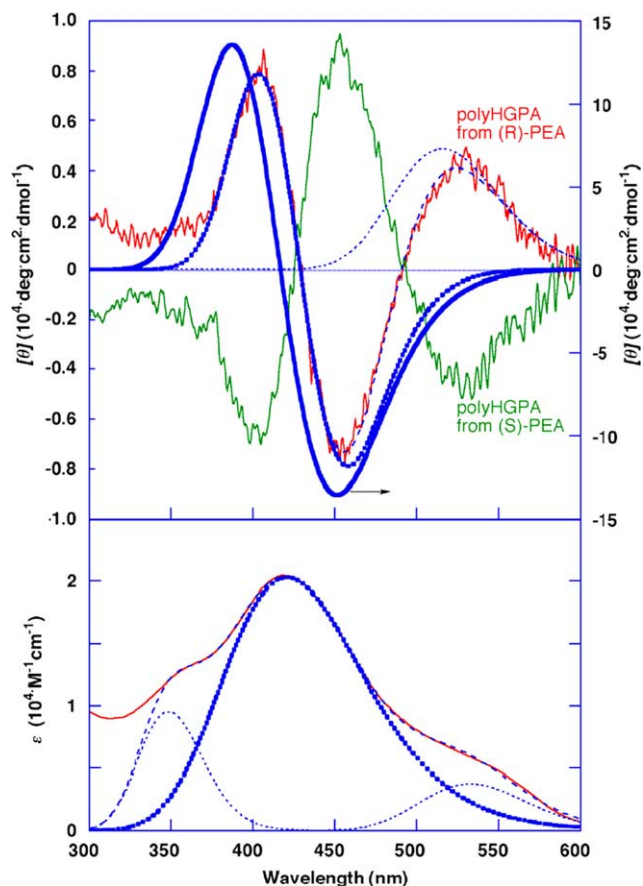
Fig. 6. CD and UV–vis absorption spectra of polyHGPA (by polymerization using (*R*)-PEA and (*S*)-PEA at 25 °C in chloroform (0.80 mM) (solid lines), and their curve-fitting (the broken line represents the result of the curve fitting; individual bands are shown with dotted lines). The theoretically calculated CD curve of the hydrogalvinoxyl chromophores using the conformational parameters, the dihedral angle of two neighboring double bonds in the backbone $\phi = 130°$ and the dihedral angle between the double bonds of backbone and the quinon methide of galvinoxyl unit $\psi = 170°$, is shown with a bold line, where ϕ and ψ are positive for a right handed helix.

chiral poly(diphenylacetylene) membranes was achieved via Si–C scission catalyzed by trifluoroacetic acid. As a result, chiral
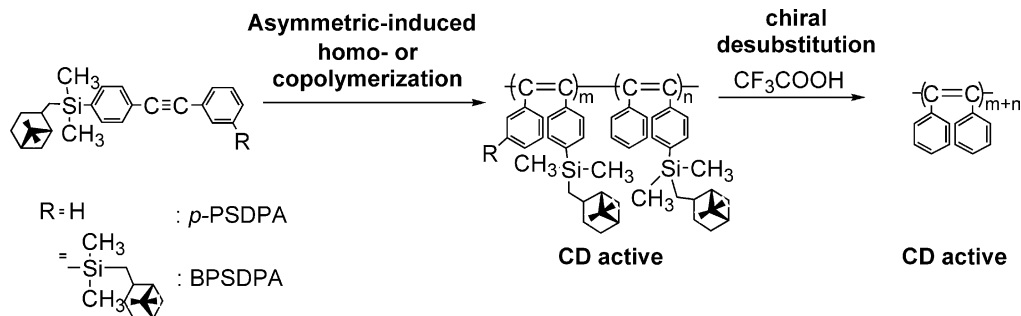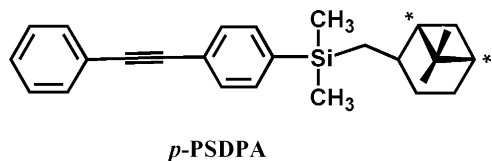
p-PSDPA

BPSDPA
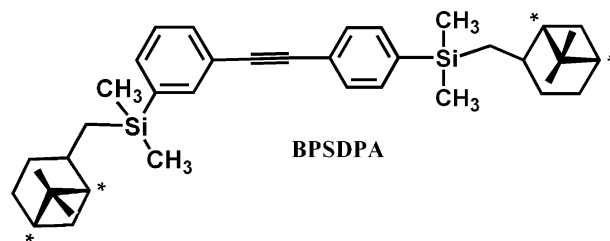
desubstitution in the membrane state proceeded quantitatively in spite of the reaction being heterogeneous. Completion of the reactions was confirmed by IR spectra of the membranes before and after reaction. Thus, the characteristic absorptions at 3060 ($\delta_{s,\ aliphatic\ C–H}$), 1250 ($\delta_{s,\ SiC–H}$), 1119 ($\nu_{as,\ Si–CH_3}$), 855 ($\nu_{as,\ Si–CH_3}$), and 812 ($\nu_{s,\ Si–CH_3}$) cm^{-1} completely disappeared in the IR spectrum of a polymer membrane, which agreed well with that of poly(diphenylacetylene) synthesized directly by polymerization of DPA. CD spectra of the desubstituted polymer membranes showed Cotton effects in the UV–vis region despite the absence of chiral pendant groups (Fig. 7). This fact indicates that the desubstituted polymer membranes retain the same chiral helical conformation as in the original polymer. We can conclude that we had obtained polymer membranes having a chiral structure that had only a chiral main-chain as the chiral source. Also, enantioselective permeations of the polymeric membranes were investigated. In permeation of ($\pm$)-tryptophan (0.5 wt% aqueous solution) through the depinanylsilylated polyPDPA, an enantioselectivity (α^R) of 2.89 (48.5% ee) was observed. In addition, the enantioselective pervaporation of ($\pm$)-2-butanol was achieved ($\alpha^R = 3.83$ (58.6% ee)) (Fig. 8).

Similarly, the Si–C bonds of the chiral pinanylsily groups of a chiral helical poly(phenylacetylene)(*p*-PSPA) were cleaved quantitatively in the membrane state. The desubstituted polymer had a CD signal in the UV–vis region in spite of the lack of any chiral pendant groups, so that a chiral structure resulting only from a main-chain was confirmed [85].

At the next level of investigation, the scission of a Si–O bond was examined as a second approach for in situ chiral desubstitution in a membrane. Thus, poly(phenylacetylene)s membranes having chiral pinanylsilyl groups tethered through Si–O bonds (PSOMPA, PSOPA), and having an induced chiral helical structure, were treated with trifluoroacetic acid to examine the effects in situ desubstitution (Scheme 4) [86]. The result was that chiral desubstitution in membrane state

Scheme 3. Asymmetric-induced polymerization of *p*-PSDPA and BPSDPA and in situ chiral desubstitution of the formed polymer in membrane.

Fig. 7. CD (top) and UV–vis (bottom) spectra of copoly(BPSDPA/*p*-PSDPA) and desubstituted copoly(BPSDPA/*p*-PSDPA) in membrane at 20 °C. Reprinted with permission from Ref. [85]. Copyright 2003, American Chemical Society, Washington, DC.

proceeded quantitatively in spite of the heterogeneous reaction. The IR spectra of the desubstituted polymers showed absorptions at 3300 cm^{-1} ($\nu_{s, O-H}$), 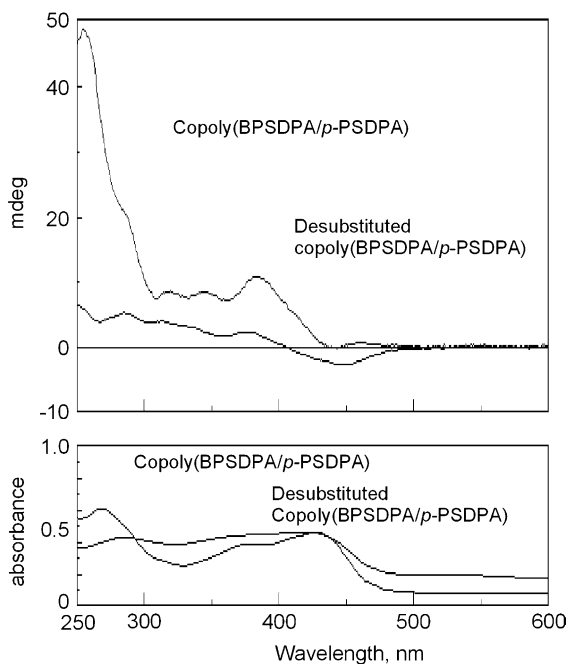indicating the formation of the hydroxyl groups, and the absorptions at 3010 ($\nu_{s, \text{aliphatic C–H}}$), 1210 ($\delta_{s, \text{SiC–H}}$), 1150 ($\nu_{as, \text{Si–CH}_3}$), 925 ($\nu_{as, \text{Si–CH}_3}$) and 900 ($\nu_{s, \text{Si–CH}_3}$) cm^{-1} present in the IR spectra of the original polymer membranes, which indicated the presence of pinanylsilyl groups, completely disappeared (Fig. 9). The desubstituted polymer membranes showed CD signals in the UV–vis region similar to those of the original polymer (Fig. 10) despite the absence of the chiral substituents, a fact indicating that the main chains of the polymers retained their chiral helicity.

PSOMPA

PSOPA
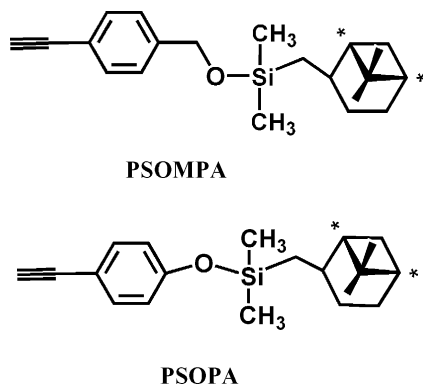
Enantioselective permeation of an aqueous solution of a racemic phenylalanine (Phe) through these desubstituted polymer membranes was examined (Fig. 11). In a manner similar to the original polymer membranes, all the desubstituted polymer membranes showed (*R*)-isomer enantioselec-

tivity in permeation. This result directly indicates the importance of the contribution of the chiral main-chain for enantioselective permeation. Enhancements of the permeation rate were observed in the permeation through the desubstituted polymer membranes. These results show that molecular-scale voids generated by depinanylsilylation were retained and effective in enhancement of permeation. This method shows great promise to improve membranes that suffer from low permeability.

5. Polycondensation polymers from arylacetylene derivatives for use as molecular magnets

5.1. Introduction—synthesis of well-controlled poly(aryleneethynylene)s

Poly(aryleneethynylene)s [87,88] are classified as π-conjugated polymers, and have various structures depending on the nature of the arylene unit, which can be a heterocyclic [89–105] or polycyclic [106–109] aromatic. There are three main synthetic approaches to making poly(aryleneethynylene)s: (A) formation of triple bonds from precursor polymers [110,111], (B) polycondensation by cross-coupling reaction between ethynyl groups and aryl groups [95,112–123], and (C) polymerization forming triple bonds [124–126] (Scheme 5). As shown in Scheme 5 (B), the Sonogashira cross-coupling reaction [127] is most typically used for poly(aryleneethynylene)s synthesis, although the use of other cross coupling reactions [112,114–116,119,120,122] has been reported. Recently, poly(aryleneethynylene)s with a high degree of polymerization were synthesized using alkyne metathesis polymerization [125,126], which is categorized under method (C).

Of the three synthetic methods for producing poly(aryleneethynylene), method (B) is the best for controlling the regioregularity and configurational sequence, i.e. alternating sequences of aryl units produced by the coupling between diethynyl-arene derivatives and dihalogeno-arene derivatives (Scheme 5 (B)(a)), and head-to-tail bonds formed by the self-condensation of ethynylhalogeno-arene derivatives (Scheme 5 (B)(b)), respectively.

The molecular shapes and electronic states of poly(aryleneethynylene)s are strongly affected by their geometric connectivity. In the case of the poly(phenyleneethynylene)s, the poly(1,4-phenyleneethynylene)s are rigid rods [128,129] or wormlike chains [130–132] depending on their degree of polymerization, and the poly(1,3- and 1,2-phenyleneethynylene)s form random-coil [133,134] or foldamer [135–139] structures. On the other hand, the poly(1,4- and 1,2-phenyleneethynylene)s have an extensively conjugated structure, and the absorption spectra of their oligomers usually show a bathochromic shift with increasing degree of polymerization [129,140], while the poly(1,3-phenyleneethynylene)s are cross-conjugated polymers whose electronic structure are less affected by the degree of polymerization [141].
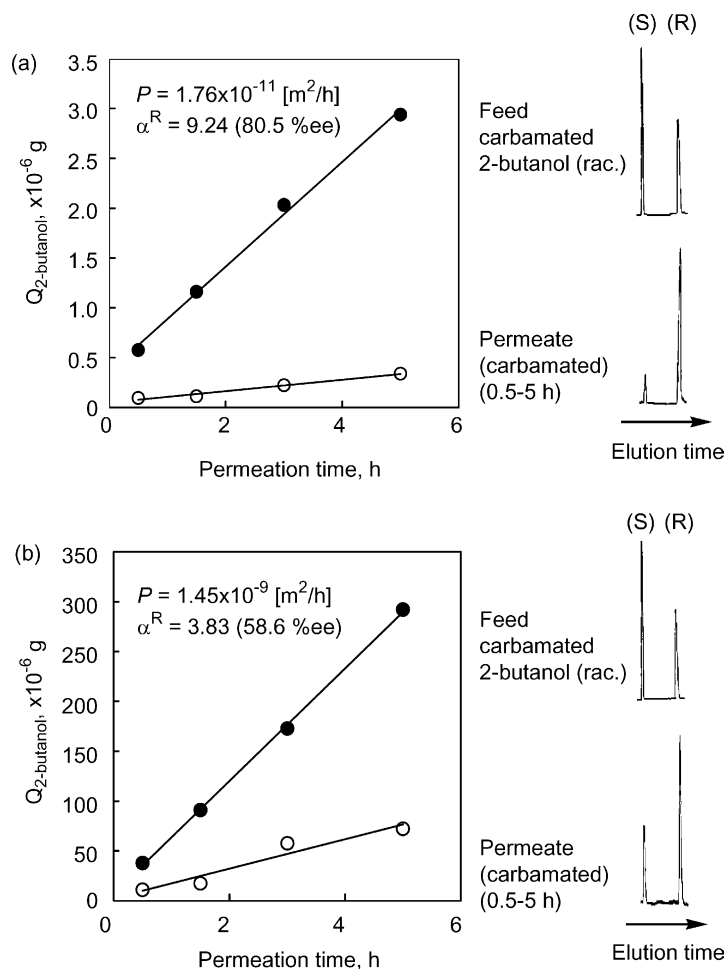
Fig. 8. (Left) plots of quantity ($Q_{2\text{-butanol}}$) of permeated ($\bullet$)-(R)-(+)- and ($\circ$)-(S)-(−)-2-butanol vs permeation time through (a) poly(p-PSDPA) membrane (top) and (b) desubstituted poly(p-PSDPA) membrane (bottom), respectively. (right) HPLC chromatogram of carbamated 2-butanol. Column, CHIRALCEL OD-H; eluent, n-hexane/2-propanol = 9:1 (v/v). Reprinted with permission from Ref. [85]. Copyright 2003, American Chemical Society, Washington, DC.

5.2. Molecular design of poly(aryleneethynylene)-based polyradicals

The π-conjugated polymers have attracted much attention as a possible structural route to organic magnetic materials. Many π-conjugated polyradicals that have stable radicals as pendant side groups and a π-conjugated chain as a backbone, were synthesized and their magnetic properties investigated [13–16,142–147]. The degree of coplanarity of the π-conjugated pendant polyradicals throughout the backbone chain and pendant side chains significantly affects the magnitude of the spin polarization and the spin-exchange coupling constant (J) [79,148,149]. Poly(aryleneethynylene)s is one of the favored choices as a π-conjugated backbone for the polyradicals, because they possess a ethynylene bridge characterized by a sterically compact and a hydrogen-free structure. These characteristics help to avoid a highly twisted dihedral angle between the backbone and the pendant radical groups, even if the pendant radicals were bulky [148,150].

On the basis of molecular topology and spin polarization, theory predicts a ferromagnetic through-bond interaction between the pendant spins [151–159]. To satisfy this condition,

poly(1,4- and 1,2-phenyleneethynylene) requires a regioregular head-to-tail linkage and poly(1,3-phenyleneethynylene) an alternating copolymer (Fig. 12). On the basis of the above prediction, some poly(phenyleneethynylene)s bearing stable radicals were synthesized, and their magnetic properties

Scheme 4. Scission of Si–O bonds of chiral helical polyPSOPA and polyPSOMPA by in situ chiral desubstitution in membrane.

Fig. 9. IR spectra of the membranes of (a) polyPSOPA and (b) desubstituted polyPSOPA. Reprinted with permission from Ref. [86]. Copyright 2005, American Chemical Society, Washington, DC.

5.3. Poly(anthryleneethynylene)-based polyradicals

A benzene ring is rigid and planar, but it cannot be substituted by more than three radical units while maintaining ferromagnetic connectivity. On the other hand, in polycyclic compounds many radical units can be inserted into ferromagnetic positions. For example, the ferromagnetic connective sites of naphthalene, anthracene, and polyacene ($n \geq 2$), are four, five, and $n+4$, respectively, (Fig. 13). Additionally, the polycyclic ladder compounds have a rigid and coplanar structure, and the incorporation of the polycyclic units to the backbone chain should reinforce the spin coupling through the π-conjugated chain [174]. Therefore, the poly(9,10-anthryleneethynylene) shown in Fig. 14, bearing 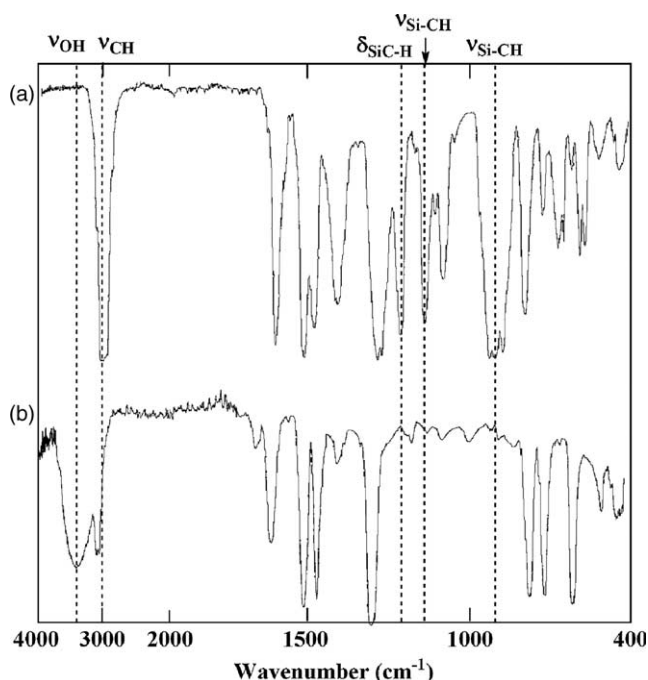side-chain radicals at the β-position, which will probably receive less steric hindrance from the poly(9,10-anthryleneethynylene) backbone, has been proposed [150].

Although they did not satisfy the connectivity constraints outlined in Section 5.2 for ferromagnetic spin coupling through the π-conjugated backbone (Scheme 6), we synthesized poly(MHOA-alt-EAE), poly(BHOA-alt-EAE) and poly(HGA-alt-EAE) by polymerization of MAcOA, BAcOA and AcGA with EAE, as examples of easily accessible polymers bearing stable radicals, whose electronic states we could investigate [175]. The average molecular weight of the polymers were determined to be ca. 1×10^4 from polystyrene gel permeation chromatography calibrated using a polystyrene standard. On the other hand, polymerization of monomers MAcOAE, EMAcOA, MAcOAEp, EpMAcOA and BAcOAEp, which had ethynyl and bromo groups to be linked with head-to-tail bonds by self-condensation, yielded the corresponding polymers polyMAcOAE, polyEMAcOA, polyMAcOAE, polyEMAcOA and polyBAcOAE, respectively, as purple solids (Scheme 7) [176,177]. The average molecular weight of these polymers reached $M_n = 3–6 \times 10^3$ after polymerization for a few hours. There was not difference in

The following poly(phenyleneethynylene)s were investigated, including 2,6-di-tert-butylphenoxyl [160,161], galvinoxyl [162], tert-butylnitroxide [163,164], nitronyl nitroxide [164–166], iminonitroxide [166], aminium cationic radical [167], nitrene [168], and semiquinone [169]. These magnetic properties of these poly(phenyleneethynylene)s involved through-bond intramolecular spin alignments. In addition, through-space, or intermolecular, spin interaction was also investigated [170,171], and poly(aryleneethynylene)s containing heterocyclic compounds were synthesized [172,173].
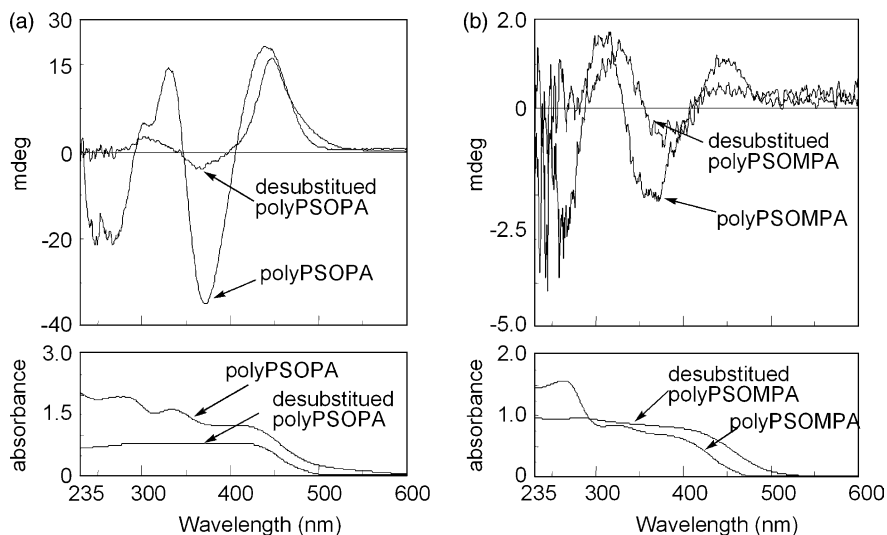

Fig. 10. CD (top) and UV–vis (bottom) spectra of the polymer membranes at 20 °C before and after in situ chiral desubstitution: (a) polyPSOPA and desubstituted polyPSOPA; (b) polyPSOMPA and desubstituted polyPSOMPA. Reprinted with permission from Ref. [86]. Copyright 2005, American Chemical Society, Washington, DC.

Fig. 11. Plots of quantity (Q) of permeated of permeated (R)- and (S)-phenylalannine vs permeation time through polyPSOPA membrane and desubstituted polyPSOPA membranes. Feed: 0.50 wt% racemic aqueous solution. (●,○) (R)- and (S)-isomer through polyPSOPA membrane, respectively; (▲,△) (R)- and (S)-isomer through desubstituted polyPSOPA membrane, respectively. Reprinted with permission from Ref. [86]. Copyright 2005, American Chemical Society, Washington, DC.

the polymerization activity between two isomers, i.e. MAcOAE and EMAcOA [176]. The polymers were soluble in chloroform, tetrahydrofuran and especially in aromatic solvents such as benzene and toluene, but insoluble in alcohols and aliphatic hydrocarbons.

In the palladium-catalyzed coupling of terminal alkynes to aromatic halides, there is an oxidative coupling side reaction to produce diyne linkages. The presence of diyne defects has an important consequence in polymerization, as they necessarily decrease the degree of polymerization and disturb the regioregularity of the pendant groups [88]. Heitz et al. reported that the deprotection of an ethynyl group combined with cross-coupling to an aromatic halide can circumvent the diyne defect problem. Since this method reduces the concentration of acetylenic protons, the oxidative coupling side reaction was suppressed [117,118]. The degree of polymerization of polyEMAcOA (from EpMAcOA) calculated from the integrated peak area of the acetylenic proton at 4.15 ppm in the ^{1}H NMR ($DP_n = 5.9$) agreed with that from Br analysis ($DP_n \approx 4$), and can be compared with ^{1}H NMR DP_n values of 9.6 and 12, respectively, for polyMAcOAE (from MAcOAE) and poly-EMAcOA (from EMAcOA) [176]. A short-time polymerization of the monomer protected in the ethynyl group, EpMAcOA, gave a resulting polymer with almost no diyne defects. This behavior is in marked contrast to the polymerization of MAcOAEp and EpMAcOA for 48 h, which resulted in diyne-defective polymers and/or the polymers with a high degree of polymerization, as evidenced by the missing acetylenic proton peak at 4.15 ppm in the ^{1}H NMR [176].

The presence of a precise regioregular head-to-tail structure in these polymers was confirmed by fractionation of the monodisperse oligomers polyBAcOAEp (n=2–5) as follows [178]. The polymerization of BAcOAEp was carried out in the

(A) Formation of triple bonds from precursor polymers
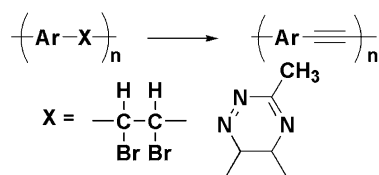
(B) Cross-coupling reaction between an ethynyl group and an aryl group
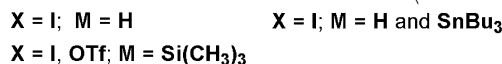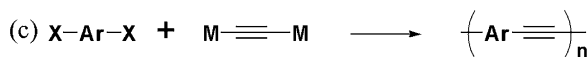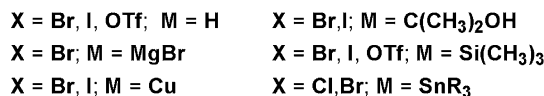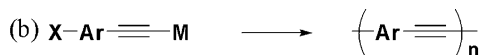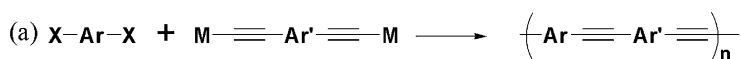
(C) Polymerization forming triple bonds
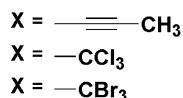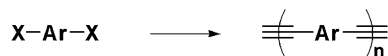
Scheme 5. Synthetic methodology of poly(aryleneethynylene)s.

Head-to-tail   **Head-to-head**   **Tail-to-tail**

(a)

Ferromagnetic   **Antiferromagnetic**   **Antiferromagnetic**
Coupling   **Coupling**   **Coupling**

(b)

Ferromagnetic   **Antiferromagnetic**   **Antiferromagnetic**
Coupling   **Coupling**   **Coupling**

Alternating copolymer   **Homopolymer**

(c)

Ferromagnetic   **Antiferromagnetic**   **Antiferromagnetic**
Coupling   **Coupling**   **Coupling**
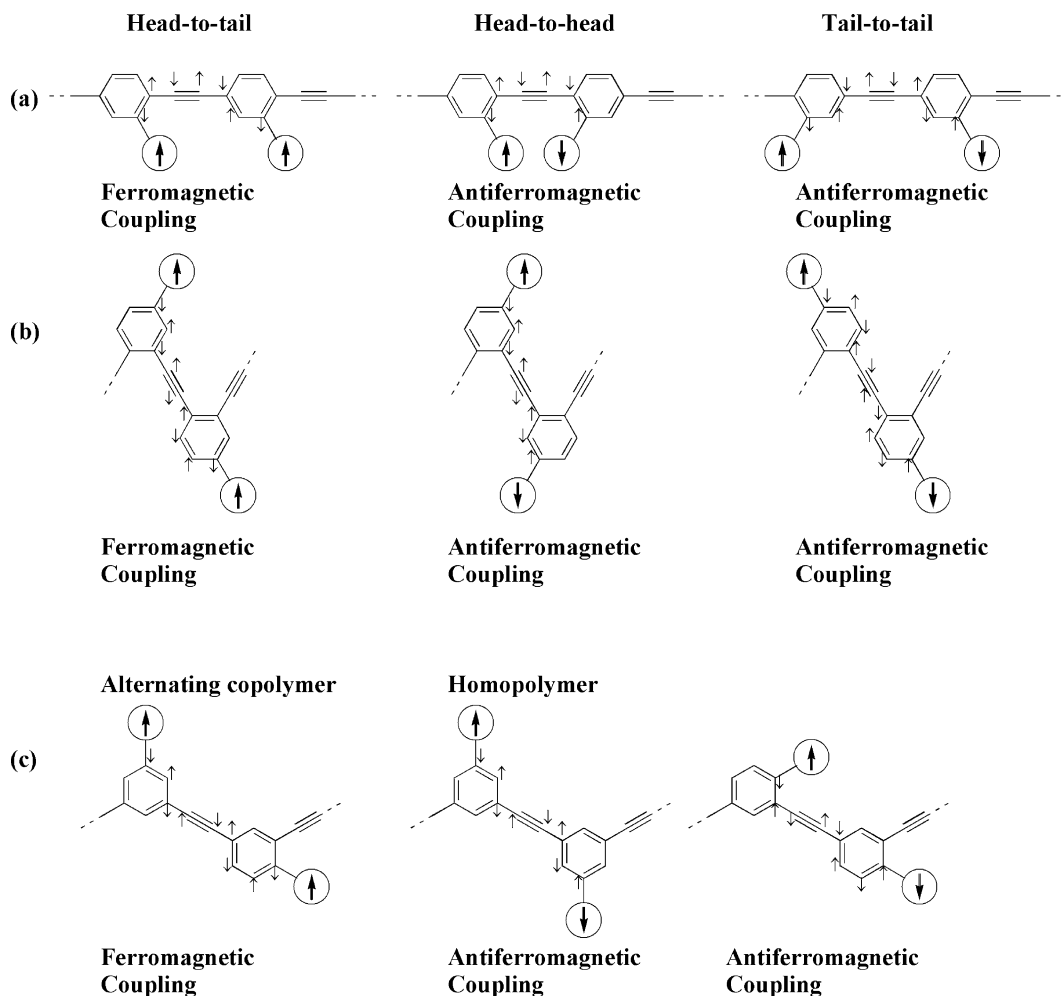
Fig. 12. The theoretical magnetic interaction between the contiguous radicals through the π-conjugation system in (a) poly(1,4-phenyleneethynylene)-, (b) poly(1,2-phenyleneethynylene)-, and (c) poly(1,3-phenyleneethynylene)-based polyradical with three different regiochemical diad linkages.

presence of the Pd(0) complex catalyst and the appropriate base. The degree of polymerization was controlled by amount of the base. A methanol-soluble reddish brown solid and a methanol-insoluble dark blue solid were obtained by precipitation from the polymerization mixtures into methanol. The

methanol-soluble fraction was further purified by silica gel column separation to give the dimer and trimer. The monodisperse oligomers polyBAcOAEp ($n=2$–5) were fractionated from the methanol-insoluble fraction by preparative GPC. The precise degree of polymerization was determined

$$S = \frac{6 - 3}{2} = \frac{3}{2}$$ $$S = \frac{9 - 5}{2} = \frac{4}{2}$$ $$S = \frac{12 - 7}{2} = \frac{5}{2}$$

$$S = \frac{(9+3n) - (5+2n)}{2} = \frac{4+n}{2}$$

Fig. 13. The theoretical ground state spin quantum number S of the polycyclic compounds possessing radical units to be ferromagnetic position. The S values are calculated from $S = |N^* - N|/2$, where N^* and N are the numbers of starred and unstarred centers, respectively.
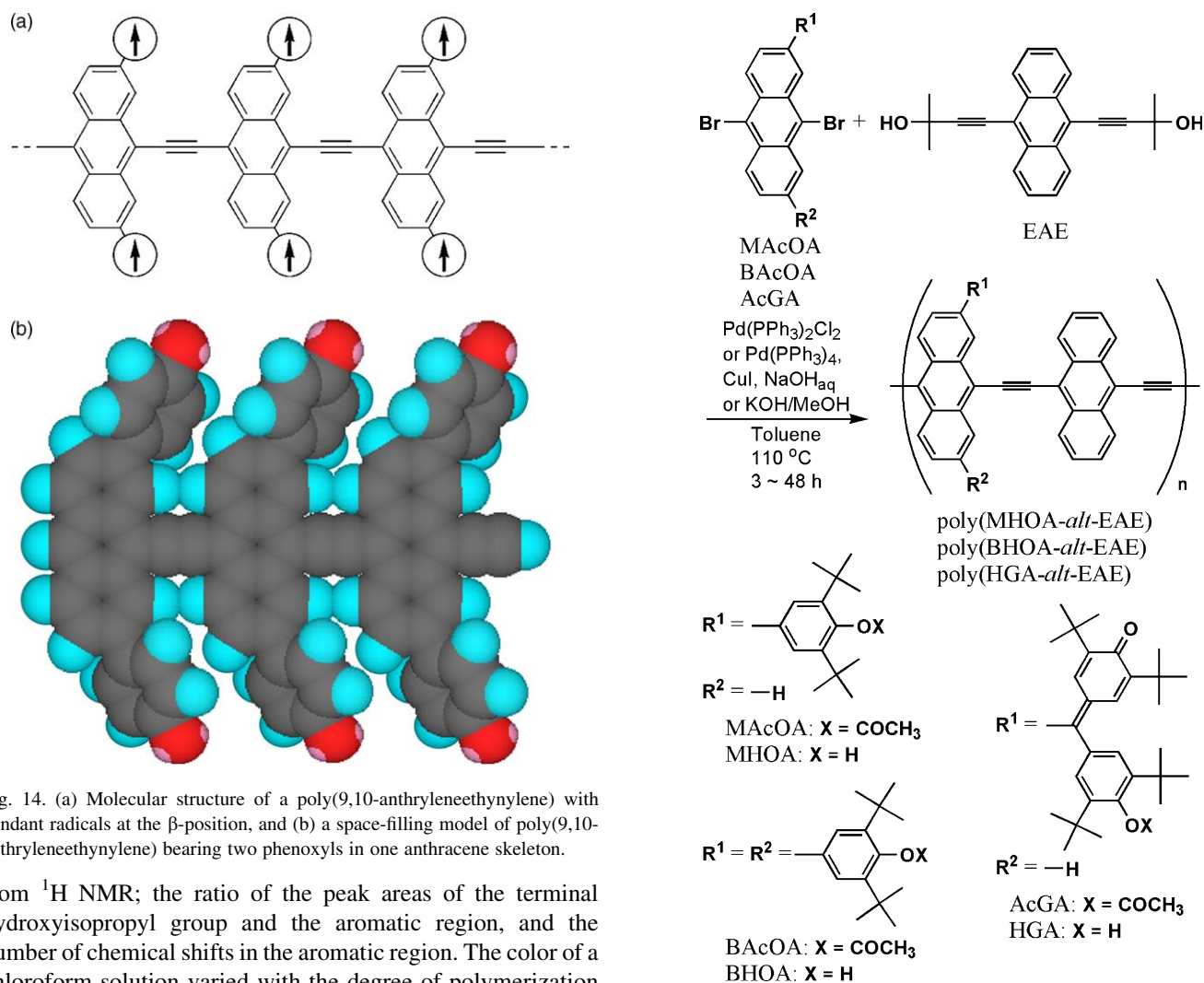
Fig. 14. (a) Molecular structure of a poly(9,10-anthryleneethynylene) with pendant radicals at the β-position, and (b) a space-filling model of poly(9,10-anthryleneethynylene) bearing two phenoxyls in one anthracene skeleton.

from ^{1}H NMR; the ratio of the peak areas of the terminal hydroxyisopropyl group and the aromatic region, and the number of chemical shifts in the aromatic region. The color of a chloroform solution varied with the degree of polymerization from orange (dimer) to reddish orange (trimer), red (tetramer) and reddish violet (pentamer). The UV–vis spectra of the oligomers showed absorption maxima (λ_{max}) at 480 (dimer), 515 (trimer), 534 (tetramer) and 543 (pentamer) nm, respectively. The λ_{max} of the pentamer was shifted to longer wavelength compared with the previously reported values of λ_{max} for poly(1,4-phenyleneethynylene)s (360–450 nm) and poly[(9,10-anthryleneethynylene)-alt-(1,4-phenyleneethynylene)]s (450–540 nm) [87,88], which suggests that the electronic structure of the planar and π-conjugated anthracene skeleton contributes to developing the π-conjugation system throughout the backbone.

The polymers thus obtained were converted to the corresponding hydroxyl polymers polyEMHOA and poly-BHOAE after complete elimination of the protecting acetyl group by treatment with alkaline solution followed by precipitation into methanol [176,177]. The resulting modified polymers were soluble in chloroform, tetrahydrofuran, and aromatic solvents, but insoluble in alcohols and aliphatic hydrocarbons. The number average molecular weight and molecular weight distribution of the polymers were measured as $M_n = 4.8 \times 10^3$ and $M_w/M_n = 1.4$ for polyEMHOA, and $M_n = 4.8 \times 10^3$ and $M_w/M_n = 1.5$ for polyBHOAE, using GPC
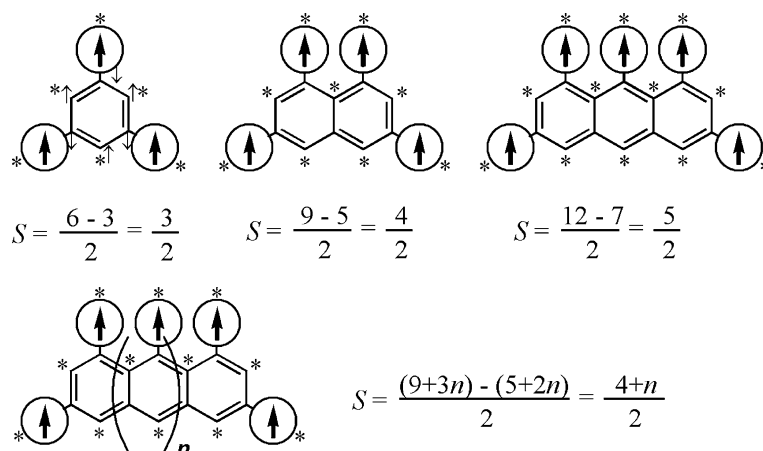

Scheme 6. Polymerization of MAcOA, BAcOA and AcGA with EAE.

calibrated relative to polystyrene standards. The degrees of polymerization calculated from Br analysis ($DP_n \approx 4$ for polyEMHOA, and $DP_n \approx 6$ for polyBHOAE) are in reasonable agreement with the GPC data when one takes into account that GPC using polystyrene standards tends to overestimate the average molecular weight of poly(aryleneethynylene)s. The polyradicals polyEMOA and polyBOAE were obtained by oxidizing polyEMHOA and polyBHOAE, by treatment of the polymer solution with fresh PbO$_2$.

The static magnetic susceptibility (2–100 K at 0.5 T) and magnetization (0–7 T) of polyEMOA and polyBOAE were measured using a SQUID magnetometer [176,177]. The samples were diluted in diamagnetic toluene or 2-methyltetrahydrofuran to minimize intermolecular interactions. The susceptibility data are frequently plotted as $\chi_{mol}T$ vs T in order to analyze the magnetic interaction, where χ_{mol} is the molar paramagnetic susceptibility. The average spin coupling constant was approximately determined as the average value (J_i; positive for ferromagnetic) by curve fitting of the $\chi_{mol}T$ vs T data assuming that spin exchange coupling only occurs between neighboring units. The resulting $2J_i$ values were

R³

Br ⎯⎯≡⎯ Y

R¹ R²

R³

Br (⎯⎯≡⎯ Y)ₙ

R¹ R²

R¹ = R³ = H, R² = [di-tert-butylphenol-OX group]

MAcOAE: **X = COCH₃, Y = H**
MAcOAEp: **X = COCH₃, Y = C(CH₃)₂OH**
MHOAE: **X = H, Y = H**

R¹ = [di-tert-butylphenol-OX group], R² = R³ = H

EMAcOA: **X = COCH₃, Y = H**
EpMAcOA: **X = COCH₃, Y = C(CH₃)₂OH**
EMHOA: **X = H, Y = H**
EMOA: **X = · , Y = H**

R¹ = H, R² = R³ = [di-tert-butylphenol-OX group]

BAcOAE: **X = COCH₃, Y = H**
BAcOAEp: **X = COCH₃, Y = C(CH₃)₂OH**
BHOAE: **X = H, Y = H**
BOAE: **X = · , Y = H**

MAcOAE   Pd(PPh₃)₄,
EMAcOA   PPh₃, CuI
⎯⎯⎯⎯⎯⎯⟶   polyMAcOAE   Pd(PPh₃)₄,
⎯⎯⎯⎯⎯⎯⟶   polyEMAcOA   PPh₃, CuI,
          NEt₃   polyBAcOAE   KOH   MAcOAEp
                                      EpMAcOA
                              toluene   BAcOAEp

polyEMAcOA   KOH aq   polyEMHOA   PbO₂   polyEMOA
polyBAcOAE   ⎯⎯⎯⟶   polyBHOAE   ⎯⎯⎯⟶   polyBOAE
             THF/
             DMSO

Scheme 7. Polymerization of MAcOAE, EMAcOA, MAcOAEp, EpMAcOA and BAcOAEp, and formation of their polyradicals.

summarized in Table 1. The $2J_1$ value of polyEMOA agreed with the $2J_1$ value of the corresponding oligomeric diradical DEMOA [175]. This large $2J_1$ value of polyEMOA was explained as a consequence of less steric hindrance between the side-chain radicals and the poly(9,10-anthryleneethynylene) backbone. The $2J_i$ values of diradicals BOA [177] and DEBOA [178] indicate that polyBOAE has both very strong ferromagnetic coupling through the anthracene unit and moderately strong ferromagnetic coupling through the dianthrylacetylene unit. PolyBOAE has relatively low degree of steric hindrance between the side-chain radicals and the poly(9,10-anthryleneethynylene) backbone even when the polyradical has two pendant phenoxyls in one anthracene unit.

The magnetization (M) normalized to the saturation magnetization (M_s), M/M_s, of polyEMOA and polyBOAE are plotted vs the ratio of magnetic field (H) and the effective temperature ($T - \theta$), and compared with the theoretical Brillouin curves in Fig. 15. In spite of the

fact that the polyradicals have the same spin concentration (polyEMOA: 0.36, polyBOAE: 0.37 spin/phenoxyl unit), the plots of polyBOAE fall almost on the theoretical Brillouin curve for $S = 5/2$ at 2 K, while the plots of polyEMOA correspond to a theoretical curve of $S = 2/2$. A statistical simulation of the ground spin states supported the contention that the average ground state spin quantum number of polyradical polyBOAE ($S = 5/2$) is larger than that of polyEMOA ($S = 2/2$) at the same spin concentration because polyBOAE consists of a ladder-like spin coupling network of the type depicted in Fig. 16 [179]. The measured average S value of polyBOAE coincides with the S value calculated on the assumption that the ferromagnetic spin coupling network of the polyradical has spread throughout the π-conjugated chain, considering the degree of polymerization and the spin concentration of polyBOAE ($DP_n \approx 5.7$ and spin conc. $= 0.37$ spin/phenoxyl unit) [177]. This result indicates that this type of one-dimensional

Table 1
Average spin coupling constants (J_i) of polyradical polyEMOA and the oligoradicals of polyEMOA and polyBOAE

Polyradical or oligoradical	J_1 (cm^{-1})[a]	J_2 (cm^{-1})[b]
PolyEMOA	39±3	
DEMOA	31±3	
BOA		>10^2
DEBOA	34±1	–

[a] The spin coupling constant through the dianthrylacetylene unit.
[b] The spin coupling constant through the anthracene unit.

DEMOA

BOA				DEBOA
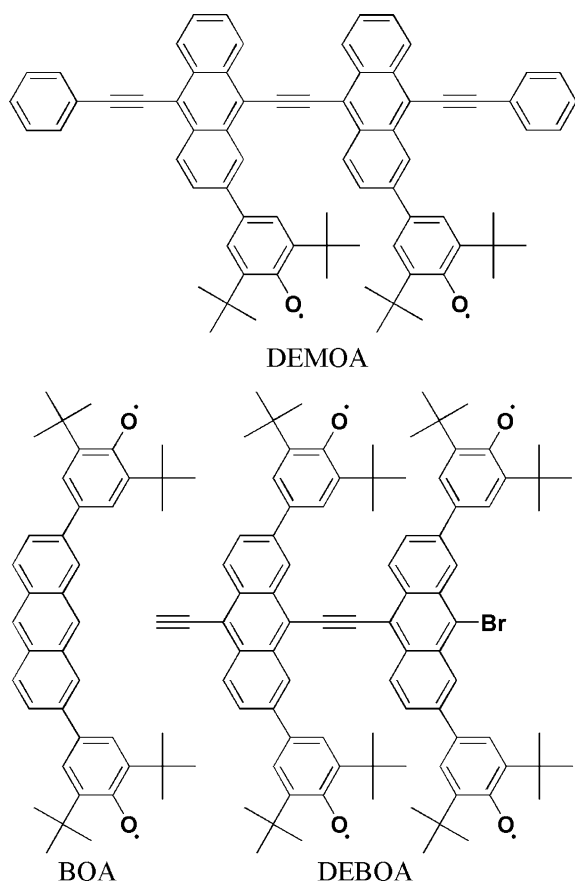
linear π-conjugated polyradical with the ladder-like spin coupling network is less sensitive to spin-defects.

6. Codes of the monomers

(1) SP, 1-trimethylsilyl-1-propyne; S, trimethylsilyl; (2.2) polySO, polydimethylsiloxane; SO, (oligo)siloxanyl; *o,p*-BSPA, *o,p*-bis(trimethylsilyl)phenylacetylene; PA, phenylacetylene; *o*-SPA, *o*-trimethylsilylphenylacetylene; *p*-SPA, *p*-trimethylsilylphenylacetylene; TSPA, *p*-tris(trimethylsilyl)silylphenylacetylene; BSDPA, 1-(*m*-trimethylsilyl)phenyl-2-(*p*-trimetylsilyl) phenylacetylene; DPA, diphenylacetylene; TSDPA, 1-[*p*-{2′, 2′-bis(trimethylsilyl)pentamethyltrisilanyl}phenyl]-2-phenyla-cetylene; (2.3) polySO, polydimethylsiloxane; TeSOPA,

p-(nonamethyltetrasiloxanyl)phenylacetylene; TSOPA, *p*-(heptamethyltrisiloxanyl)phenylacetylene; *o*-S-*p*-DSOPA, {*o*-trimethylsilyl-*p*-(pentamethyldisiloxanyl)}phenylacetylene; *t*-TSOPA, *p*-{tris(trimethylsiloxy)silyl}phenylacetylene; *s*-DSOPA, *p*-{bis(trimethylsiloxy)methylsilyl} phenylacetylene; SOPA macromonomer, *p*-(polydimethylsiloxanyl)phenylacety-lene macromonomer; (2.4) *o,p*-BFPA, *o,p*-bis(trifluoromethyl)-phenylacetylene; *o,m,p*-TFPA, 2,4,5-tris(trifluoromethyl) phenylacetylene; OFOSPA, *p*-[1H,1H,2H,2H-perfluorodecylox-ydimethylsilyl]phenylacetylenes; TeFOSPA, *p*-[1H,1H,2H,2H-perfluorohexyloxydimethylsilyl]phenylacetylenes; (2.5) DENPA, 3,5-{[4-(trimethylsilyl)phenyl]ethynyl}phenylacety-lene (dendronized phenylacetylene); (2.6) HGPA, (4-ethynyl-phenyl)hydrogalvinoxyl; GPA, (4-ethynylphenyl)galvinoxyl; G, galvinoxy; HG, hydrogalvinoxy; (3.1) PSP, (−)-1-{dimethyl(10-pinanyl)silyl}-1-propyne; P, (−)-(10-)pinanyl; PS, (10-pinanyl)silyl; (3.2) MCPA, *p*-{L-(−)-menthoxycarbo-nyl}phenylacetylene; *p*-PSPA, (−)-*p*-(dimethyl(10-pinanyl)si-lyl)phenylacetylene; PCPA, (+)-*p*-(10-pinanyloxycarbonyl) phenylacetylene; BCPA, *p*-(L-(−)-2-methylbutylcarbonyl)phe-nylacetylene; 3-PDSOPA, *p*-{tetramethyl-3-(10-pinanyl)disilox-anyl}phenylacetylene; *o*-PSPA, *o*-{dimethyl(10-pinanyl) silyl}phenylacetylene; *m*-PSPA, *m*-{dimethyl(10-pinanyl)silyl}-phenylacetylene; o,p-BPSPA, o,p -bis{dimethyl(10-pinanyl)si-lyl}phenylacetylene; (3.3) 1,3-BPDSOPA, *p*-{trimethyl-1,3-bis(10-pinanyl)disiloxanyl}phenylacetylene; 1-PDSOPA, *p*-{tetramethyl-1-(10-pinanyl)disiloxanyl}phenylacetylene; 3-PDSOPA, *p*-{tetramethyl-3-(10-pinanyl)disiloxanyl}phenyla-cetylene; 5-PTSOPA, *p*-{hexamethyl-5-(10-pinanyl)trisilox-nyl}phenylacetylene; 1,3-BPTSOPA, *p*-{pentamethyl-1, 3-bis(10-pinanyl)trisiloxanyl}phenylacetylene; 1,3,5-TPTSOPA, *p*-{tetramethyl-1,3,5-tris(10-pinanyl)trisiloxanyl}-phenylacetylene; *t*-TPSOPA, *p*-[tris{dimethyl(10-pinanyl)
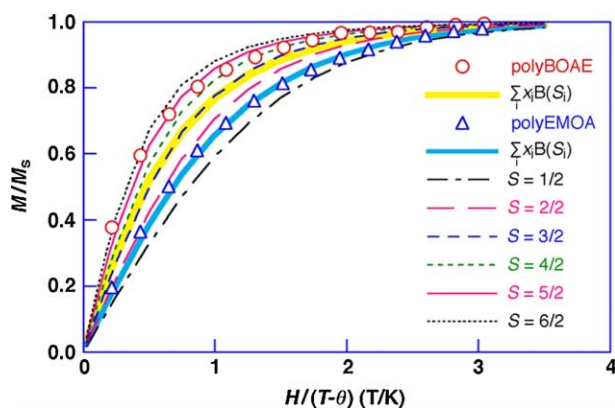
Fig. 15. Normalized plots of magnetization (M/M_s) vs the ratio of magnetic field and the effective temperature ($H/(T-\theta)$) for polyBOAE (spin conc.=0.37 spin/phenoxyl unit) in frozen 2-methyltetrahydrofuran glass (10 mM) at T= 2 K (○) and for polyEMOA (spin conc.=0.36 spin/phenoxyl unit) in frozen toluene glass (50 mM) at T=2 K (△), and theoretical curves corresponding to S=1/2, 1, 3/2, 2, 5/2 and 3 Brillouin functions, where θ is a weak antiferromagnetic term, and was determined to be −0.3 K from the $\chi_{mol}T$ vs T plots. Bold line: statistical simulation curve for polyEMOA with 0.36 spin/phenoxyl unit and DP=4, and for polyBOAE with 0.37 spin/phenoxyl unit and DP=6, respectively, [179].
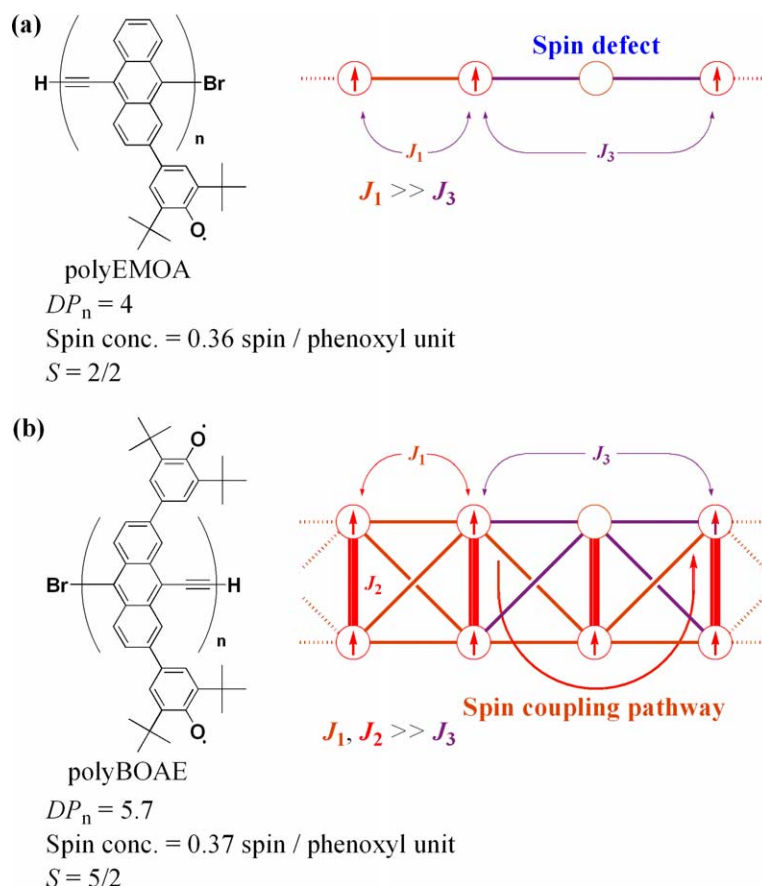
Fig. 16. Molecular structures of poly(9,10-anthryleneethynylene)-based polyradicals and their spin coupling pathway; (a) polyEMOA and one-dimensional spin coupling system, and (b) polyBOAE and ladder-like spin coupling network.

siloxy}silyl]phenylacetylene; (3.4) NOPA, *p*-{1,1′-binaphthoxymethyl}phenylacetylene; NA, 5-ethynyl-1,1′-binaphthol; (3.5) *p*-PSDPA, (−)-1-[*p*-{dimethyl(10-pinanyl)silyl}phenyl]-2-phenylacetylene; *m*-PSDPA, (−)-1-[*m*-{dimethyl(10-pinanyl)silyl}phenyl]-2-phenylacetylene; (4.2.1) DHPA, 3,5-bis(hydroxymethyl)-4-dodecyloxyphenylacetylene; DMPA, 3,5-bis(methoxymethyl)-4-dodecyloxyphenylacetylene; MHPA, 3-hydroxymethyl-5-methoxymethyl-4-dodecyloxyphenylacetylene; OAPA, 3,5-bis(octylaminocarbonyl)phenylacetylene; DoAPA, 3,5-bis(dodecylaminocarbonyl)phenylacetylene; OEPA, 3,5-bis(octyloxycarbonyl)phenylacetylene; (4.3) BPSDPA, (−)-1-[*p*-{dimethyl(10-pinanyl)silyl}phenyl]-2-[3-{dimethyl(10-pinanyl)silyl}phenyl]acetylene; PSOMPA, (−)-*p*-{dimethyl(10-pinanyl)siloxymethyl}phenylacetylene; PSOPA, (−)-*p*-{dimethyl(10-pinanyl)siloxy}phenylacetylene; (5) MAcOA, 2-(4-acetoxy-3,5-di-*tert*-butylphenyl)-9,10-dibromoanthracene; MHOA, 9,10-dibromo-2-(3,5-di-*tert*-butyl-4-hydroxyphenyl)anthracene; BAcOA, 2,7-bis(4-acetoxy-3,5-di-*tert*-butylphenyl)-9,10-dibromoanthracene; BHOA, 2,7-bis(3,5-di-*tert*-butyl-4-hydroxyphenyl)-9,10-dibromoanthracene; AcGA, 2-[(4-acetoxyphenyl-3,5-di-*tert*-butyl)(3,5-di-*tert*-butyl-4-oxocyclohexa-2,5-dien-1-ylidene)methyl]-9,10-dibromoanthracene; HGA, 9,10-dibromo-2-[(3,5-di-*tert*-butyl-4-hydroxyphenyl)(3,5-di-*tert*-butyl-4-oxocyclohexa-2,5-dien-1-ylidene)methyl]anthracene; MAcOAE, 2-(4-acetoxy-3,5-di-*tert*-butylphenyl)-10-bromo-9-ethynylanthracene; MAcOAEp, 2-(4-acetoxy-3,5-di-*tert*-butylphenyl)-10-bromo-9-(3-hydroxy-3-methyl-1-butynyl)anthracene; MHOAE, 10-bromo-2-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-9-ethynyl anthracene; EMAcOA, 2-(4-acetoxy-3,5-di-*tert*-butylphenyl)-9-bromo-10-ethynylanthracene; EpMAcOA, 2-(4-acetoxy-3,5-di-*tert*-butylphenyl)-9-bromo-10-(3-hydroxy-3-methyl-1-butynyl)anthracene; EMHOA, 9-bromo-2-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-10-ethynylanthracene; EMOA, phenoxyl radical from EMHOA; BAcOAE, 2,7-bis(4-acetoxy-3,5-di-*tert*-butylphenyl)-10-bromo-9-ethynylanthracene; BAcOAEp, 2,7-bis(4-acetoxy-3,5-di-*tert*-butylphenyl)-10-bromo-9-(3-hydroxy-3-methyl-1-butynyl)anthracene; BHOAE, 2,7-bis(3,5-di-*tert*-butyl-4-hydroxyphenyl)-10-bromo-9-ethynylanthracene; BOAE, phenoxyl radical from BHOAE; DEMOA, phenoxyl radical from 2-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-10-({9-[2-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-10-(phenylethynyl)anthryl]}ethynyl)-9-(phenylethynyl)anthracene; BOA, phenoxyl radical from 2,7-bis(3,5-di-*tert*-butyl-4-hydroxyphenyl)anthracene; DEBOA, phenoxyl radical from 2,7-bis(3,5-di-*tert*-butyl-4-hydroxyphenyl)-10-({9-[2,7-bis(3,5-di-*tert*-butyl-4-hydroxyphenyl)-10-ethynylanthryl]}ethynyl)-9-bromoanthracene

7. Conclusions

This article has reviewed the synthesis of two kinds of π-conjugated polymers from aryl acetylenes, i.e. poly(arylacetylene)s and poly(aryleneethynylene)s and the relationship between their chemical and electronic structures and their performance as oxygen permselective membranes, optical resolution membranes, and organic magnetic materials. We can expect to make unique new materials by suitable combinations of the properties of these π-conjugated polymers.

The chemical structures of the biopolymers in living organisms are organized with an extremely high degree of order and the molecules act cooperatively to generate elaborate functions. If we can generate artificial functional polymers with higher-ordered structures, they may perform at a high level comparable to the biopolymers. Since, the two kinds of poly(aromatic acetylene)s, highlighted in this review can be made with precisely defined three-dimensional structures, they are likely candidates for the role of highly-organized organic nanomaterials exhibiting novel properties. Hence, the authors expect further extensive development of the field of π-conjugated polymers synthesized from aromatic acetylenes.

Acknowledgements

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