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Synthesis of the Optically Active Polymer Consisting of Chiral Phosphorus Atoms and *p*-Phenylene-ethynylene Units

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Summary

We successfully synthesized optically active polymer **4** by using chiral bisphosphine, (*S,S*)-1,2-bis(boranato(*t*-butyl)methylphosphino)ethane (*S,S*)-**1**, as a key building block. The structure of the polymer was characterized by ^{1}H, ^{13}C, and ^{31}P NMR spectra. According to the CD spectra, the *p*-phenylene-ethynylene unit in the polymer main chain exhibited Cotton signals around the area of π–π* transition band.

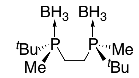
Introduction

Polymers containing inorganic elements in the main chain have been widely synthesized, and have attracted considerable attention due to their unique properties and potential applications [1]. For example, polymers consisting of inorganic elements in their main chain, polysiloxane (–Si–O–) [2], polysilane (–Si–) [3], polyphosphazene (–P=N–) [4], polyphosphinoborane (–P=B–) [5], polythionylphosphazene (–P=N–S–) [6], and polythiazyl (–N–S–) [7], have been well studied, and polymers containing inorganic elements alternately in their main chain have also been reported. Manners and co-workers have carried out the ring-opening polymerization of heteroatom-bridged ferrocenophane to obtain ferrocene-based polymers with Si, Ge, Sn, and P atoms [8]. Among them, the anionic polymerization of silicon-bridged ferrocenophane enabled living polymerization and produced block copolymers [8c]. The morphologies of ferrocene-based copolymers that contain dimethyl siloxane blocks have been examined [9]. On the other hand, since the synthesis and physical properties of conjugated polymers have attracted increasing attention, heteroatoms in their main chain, such as B [10], Si [3,11], P [12,13], As [14], and Bi [15], have been reported; these polymers show specific characteristics derived from each inorganic element.

Although many polymers containing heteroatoms have been synthesized as described above, few polymers containing chiral heteroatoms in their main chain have been reported to date [16,17]. Fujiki and co-workers have pioneered the synthesis of optically active polysilanes with a one-handed helix [3d,e]. In addition, the helical-sense programming of polysilane–*b*–poly(triphenylmethyl methacrylate) has been reported [18]. However, the helices of these polysilanes and polysilane–*b*–

poly(triphenylmethyl methacrylate) are derived from chiral carbons in the alkyl side chain or a right-handed helix of a poly(triphenylmethyl methacrylate) segment, respectively.

Recently, we have focused on chiral phosphine as the key component of chiral oligomers and polymers [19]. It is known that chiral trialkylphosphines hardly racemize even at considerably high temperature due to high inversion energy [20]. In a previous study, we have successfully synthesized optically active oligophosphines [19], which contain four and eight chiral phosphorus atoms by the stepwise oxidative coupling reaction of (*S,S*)-1,2-bis(boranato(*t*-butyl)methylphosphino)ethane (*S,S*)-**1** [21]. It is revealed that oligophosphine with eight chiral phosphorus atoms acquires the characters of the polymer. In addition, Wild and co-workers reported the synthesis and isolation of three types of optically active hexaphosphines with four chiral phosphorus atoms; they have also synthesized a unique double-stranded parallel helicate by complexation with Cu(I) [22].



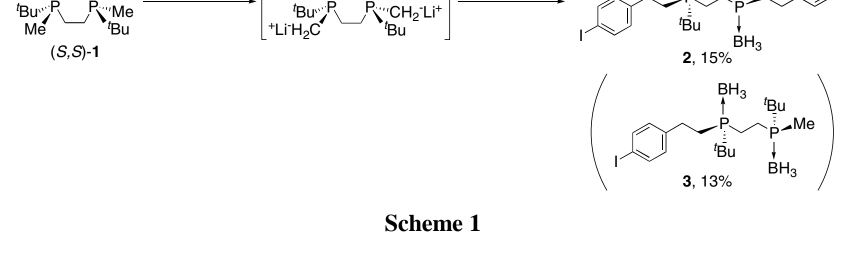
(*S,S*)-**1**

In this paper, we report the synthesis and characterization of an optically active co-polymer that contains chiral phosphorus atoms and rigid *p*-phenylene-ethynylene units alternately in the main chain. The synthesized polymer was confirmed by ^{1}H, ^{13}C, and ^{31}P NMR spectra and characterized by UV-vis and circular dichroism (CD) spectra. It is inferred that the optically active higher-ordered structure of the polymer is produced by chiral phosphorus units.

Results and Discussion

Synthesis of monomer 2

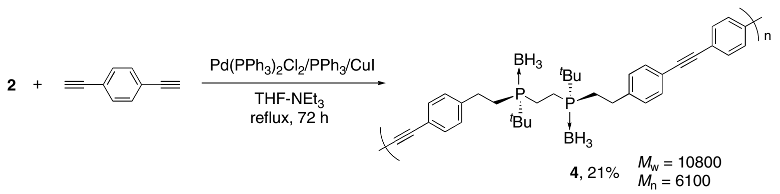
We focused on compound (*S,S*)-**1** as a chiral component of the polymer because it can be prepared easily with high enantiomer excess (*ee* > 99%), as reported by Imamoto and co-workers [21]. The synthetic procedure of optically active monomer **2** is shown in Scheme 1. The dianion of (*S,S*)-**1** was generated by the lithiation of methyl groups by *sec*-BuLi with (–)-sparteine under a nitrogen atmosphere. Subsequently, 4-iodobenzyl bromide was added to this solution. Although the reaction process did not involve the asymmetric reaction, (–)-sparteine was used only for the activation of *sec*-BuLi. After workup, the residue was purified by silica gel column chromatography to obtain monomer **2** in 15% yield. Monosubstituted compound **3** was also obtained as a by-product in 13% yield; it could be readily removed by column chromatography. (Scheme 1). Monomer **2** was characterized by ^{1}H, ^{13}C, ^{31}P NMR, HRMS, and elemental analysis.



Scheme 1

*Synthesis of polymer **4***

The polymerization of **2** with 1,4-diethynylbenzene was carried out by the Sonogashira coupling reaction [23] to obtain the corresponding polymer **4** in 21% yield, as shown in Scheme 2. Polymer **4** and monomer **2** were air stable in the solution and the solid state because of the phosphine-borane complex. Molecular weight measurements were performed by gel permeation chromatography (GPC) in a DMF eluent (containing 10 mM LiBr) using the calibration curve of polystyrene standards. The number-average molecular weight (M_n), weight-average molecular weight (M_w), and molecular weight distribution (M_w/M_n) of polymer **4** obtained were 6100, 10800, and 1.8, respectively.



Scheme 2

Polymer **4** was soluble in common organic solvents and was characterized by ^1H, ^{13}C, and ^{31}P NMR spectra. The ^1H NMR spectrum of polymer **4** in $CDCl_3$ is shown in Figure 1. As shown in this figure, a sharp single peak for *tert*-butyl protons appeared at δ 1.2 ppm. The methylene proton peaks for $–CH_2–P–CH_2–$ and $–CH_2–C_6H_4–CH_2–$ were observed at δ 1.6–1.9 ppm and δ 2.7–2.9 ppm, respectively. The aromatic proton peaks appeared in the range of δ 7.2–7.6 ppm. The ^{31}P NMR spectrum exhibited a peak at +35.6 ppm, and the chemical shift of polymer **4** was the same as that of monomer **2** (δ +35.5 ppm), thereby indicating that the environment around the phosphorus atom did not change due to polymerization. The carbon-carbon triple bond of **4** was confirmed by the ^{13}C NMR spectrum (δ 89.2 and 90.9 ppm). Additionally, we speculate that most of terminal groups are a phenyl group, because ^1H and ^{13}C NMR signals of terminal acetylene groups as well as ^{13}C NMR signals of iodine substituted carbons were not detected.

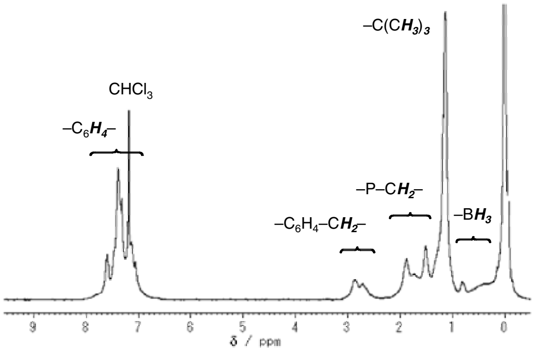
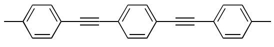


Figure 1. ^1H NMR spectrum of polymer **4**.

UV-vis and CD measurements

The UV-vis absorption spectrum of polymer **4** in $CHCl_3$ solution is shown in Figure 2. The spectrum shows an absorption maximum at 327 nm (ε = 5.75 × 10^{-4} $L \cdot mol^{-1} \cdot cm^{-1}$) derived from the absorption of the PPE backbone, which was in agreement with that of bis(*p*-tolylethynyl)benzene **5** (λ_{max} = 325 nm and ε = 6.20 × 10^{-4} $L \cdot mol^{-1} \cdot cm^{-1}$ in $CHCl_3$)



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reported previously [24]. Figure 3 shows the CD spectrum of polymer **4** in $CHCl_3$ at room temperature. The *p*-phenylene-ethynylene unit in the polymer main chain exhibited Cotton signals around the area of the π–π^* transition band. This indicates that the chirality of phosphorus atoms affects the *p*-phenylene-ethynylene moieties of polymer **4**; more specifically, polymer **4** adopts an optically active structure such as a helix conformation.

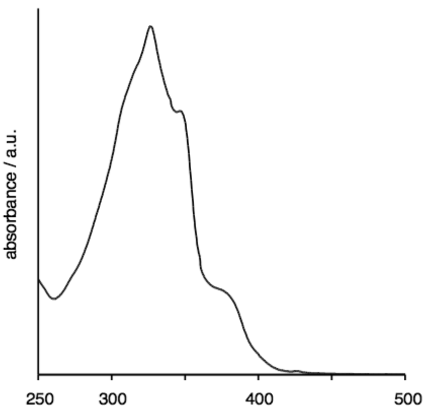

Figure 2. UV-vis absorption spectrum of polymer **4** in $CHCl_3$.

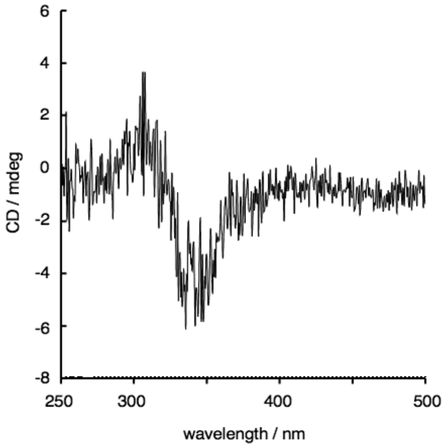

Figure 3. CD spectrum of polymer **4** in $CHCl_3$.

Conclusion

In summary, novel optically active polymer **4** containing chiral phosphorus atoms and *p*-phenylene-ethynylene units was successfully prepared. Polymer **4** exhibited the Cotton effect in the region of the π–π^* band of the phenylene-ethynylene moieties in $CHCl_3$ solution due to the chiral optically active higher-ordered structure induced by chiral phosphorus atoms. Further studies will attempt to remove the boranato groups from polymer **4** and investigate the effects of additives such as transition metals.

Experimental Section

General

^1H (400 MHz) and ^{13}C (100 MHz) NMR spectra were recorded on JEOL EX400 spectrometer, and samples were analyzed in $CDCl_3$ using Me_4Si as an internal standard. ^{31}P (161.9 MHz) NMR spectra were also recorded on JEOL EX400 spectrometer, and samples were analyzed in $CDCl_3$ using H_3PO_4 as an external standard. The following abbreviations are used; d: doublet, m: multiplet, br: broad. Gel permeation chromatography (GPC) was carried out on a TOSOH UV-8020 and RI-8020 (TSK-GEL α-3000) using DMF containing 10 mM of LiBr as an eluent after calibration with standard polystyrene. The UV-vis absorption spectra were obtained on a JASCO V-530 spectrometer with $CHCl_3$ as a solvent. The circular dichroism (CD) spectra were recorded on a JASCO J-600 spectropolarimeter with $CHCl_3$ as a solvent. High-resolution mass spectra (HRMS) were obtained on a JEOL JMS-SX102A spectrometer. Column chromatography was performed with Wakogel C-300 silica gel. The removal of low molecular weight compounds was carried out on a recycling preparative HPLC (Japan Analytical Industry Co. Ltd., Model 918R) equipped with JAIGEL-1H and 2H columns (GPC) using $CHCl_3$ as an eluent. Elemental analysis was performed at the Microanalytical Center of Kyoto University.

Materials

THF was distilled from sodium benzophenone ketyl under nitrogen. (–)-Sparteine and NEt_3 were distilled from KOH under nitrogen. *sec*-BuLi (1.0 M in cyclohexane and *n*-hexane solution), $Pd(PPh_3)_2Cl_2$, PPh_3, and CuI, were obtained commercially, and used without further purification. 1,4-Diethynylbenzene was obtained commercially, and used after sublimation. (*S,S*)-1,2-Bis(boranato(*t*-butyl)methylphosphino)ethane (*S,S*)-**1** was prepared as described in the literature [21]. 4-Iodobenzyl bromide was prepared from 4-iodotoluene with NBS according to the literature [25]. All reactions were performed under nitrogen using standard Schlenk techniques.

*Synthesis of Monomer **2***

A solution of (–)-sparteine (1.8 mL, 8.0 mmol) in THF (40 mL) was cooled to –78°C under nitrogen. To this solution with stirring, *sec*-BuLi (1.0 M in cyclohexane and *n*-hexane solution, 8.0 mL, 8.0 mmol) was added by a syringe. After 15 minutes, a solution of (*S,S*)-**1** (0.20 g, 0.76 mmol) in THF (8.0 mL) was added dropwise, and the mixture was stirred at –78°C over 3 h. A solution of 4-iodobenzyl bromide (2.6 g, 8.8 mmol) in THF (10 mL) was added, and the reaction mixture was allowed to slowly warm to room temperature. After 15 h, the reaction was quenched by the addition of 2 N HCl and extracted with CH_2Cl_2 (40 mL x 3). The combined extracts were washed with aqueous $NaHSO_3$ and brine. The organic layer was dried over $MgSO_4$. After the solvent was removed under reduced pressure, the crude compound was purified by column chromatography on silica gel with hexane-CH_2Cl_2 (v/v = 2:1 to 1:1) to give monomer **2** as a colorless solid (0.23g, 0.34 mmol, 17%).
^{1}H NMR (400 MHz, $CDCl_3$) δ 0.12–0.79 (br, $-\mathrm{B}H_3$, 6H), 1.16-1.25 (m, $-Bu^t$, 18H), 1.85 (br, $-\mathrm{C}H_2-\mathrm{P}-\mathrm{C}H_2-$, 8H), 2.79 (br, $-\mathrm{C}H_2-\mathrm{C_6H_4I}$, 4H), 6.96 (d,$-\mathrm{C_6}H_4\mathrm{I}$, 4H), 7.61 (d, $-\mathrm{C_6}H_4\mathrm{I}$, 4H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.2 (d, $-C\mathrm{H_2}-\mathrm{P}-$, J_{CP} = 31.5 Hz), 22.8 ($-C\mathrm{H_2}-\mathrm{C_6H_4I}$), 25.5 ($-\mathrm{C}(C\mathrm{H_3})_3$), 29.3 ($-C(\mathrm{CH_3})_3$), 91.5 ($-C_6\mathrm{H_4}-$), 129.9 ($-C_6\mathrm{H_4}-$), 137.5 ($-C_6\mathrm{H_4}-$), 140.5 ($-C_6\mathrm{H_4}-$) ppm; ^{31}P{^{1}H} NMR (161.9 MHz, $CDCl_3$) δ +35.5 ppm. HRMS (FAB) calcd for $C_{26}H_{43}B_2I_2P_2$ [M-H$^+$]: 693.1116, found 693.1113. Anal. calcd for $C_{26}H_{44}B_2I_2P_2$: C, 44.99%; H, 6.39%. Found: C, 44.78; H, 6.16.

*Synthesis of Polymer **4***

To a solution of **2** (0.21 g, 0.30 mmol) in THF (2.0 mL) were added 1,4-diethynylbenzene (0.038 g, 0.30 mmol), $Pd(PPh_3)_2Cl_2$ (0.042 g, 0.060 mmol), PPh_3 (0.031 g, 0.12 mmol), CuI (0.11 g, 0.060 mmol), and NEt_3 (4.0 mL). The reaction was carried out at reflux temperature for 72 h. After the reaction, this solution was passed through Celite column, and the filtrate was washed with aqueous NH_3 and brine. The organic layer was dried over $MgSO_4$. After the solvent was removed under reduced

pressure, crude polymer was purified by using HPLC to remove the low molecular weight compound to obtain polymer **4** as an yellow powder (0.047g, 21%).
^{1}H NMR (400 MHz, $CDCl_3$) δ 0.21–0.68 (br, $-BH_3$), 1.13–1.29 (brs, $-Bu^t$), 1.63–1.87 (br, $-CH_2-P-CH_2-$), 2.70–2.85 (br, $-CH_2-C_6H_4-$), 7.18–7.60 (br, $-C_6H_4-$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.1 ($-CH_2-P-CH_2-$), 22.6 ($-CH_2-C_6H_4-$), 25.5 ($-C(CH_3)_3$), 28.5 ($-C(CH_3)_3$), 89.2 ($-C\equiv C-$), 90.9 ($-C\equiv C-$), 121.3 ($-C_6H_4-$), 122.9 ($-C_6H_4-$), 128.2–132.9 ($-C_6H_4-$), 137.7 ($-C_6H_4-$) ppm; ^{31}P{^{1}H} NMR (161.9 MHz, $CDCl_3$) δ +35.6 ppm.

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