# SYNTHESIS OF OPTICALLY ACTIVE POLYMERS USING P-CHIRAL BISPHOSPHINES AS ANIONIC INITIATORS[1]

**Y. Morisaki (✉), K. Saito, H. Imoto, K. Suzuki, Y. Ouchi, and Y. Chujo (✉)**

*Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University, Katsura, Nishikyo-ku, Kyoto 615-8510, Japan.*

*e-mail: ymo@chujo.synchem.kyoto-u.ac.jp, chujo@chujo.synchem.kyoto-u.ac.jp*

**Abstract**—Anionic polymerization of triphenylmethyl methacrylate (TrMA) was performed by using P-chiral bisphosphine initiators. According to the optical rotation analysis and circular dichroism (CD) measurements, the poly(TrMA) obtained by using the initiator (*S,S*)-1,2-ethanebis(*t*-butylmethylphosphineborane) exhibited one-handed helical conformation induced by the chirality of phosphorus atoms in the polymer terminal. The enantiomer (*R,R*)-1,2-ethanebis(*t*-butylmethylphosphineborane) gave the opposite one-handed helical poly(TrMA). Optically active bisphosphine (*S,S*)-1,2-ethanebis(methylphenylphosphineborane) was employed for the helix-sense-selective polymerization of TrMA in order to obtain the poly(TrMA) with the same helix sense as the polymer obtained from the initiator (*S,S*)-1,2-ethanebis(*t*-butylmethylphosphineborane). Further, removal of the coordinated boranes and complexation with platinum(II) on the chiral phosphorus atoms were carried out in order to yield the corresponding polymer-platinum(II) complex without loss of its chiral higher-ordered structure.

[1]This work was supported by Grant-in-Aid for Science Research on Priority Areas (No. 20036027, Synergy of Elements) from Ministry of Education, Culture, Sports, Science and Technology, Japan. Y.O. appreciates Research Fellowships from the Japan Society for the Promotion of Science for Young Scientists.

# INTRODUCTION

In polymer chemistry, helical conformation of polymers and macromolecules, such as the double helix of DNA [1] and α-helix of natural polypeptides [2], is the most characteristic chirality derived from a second-ordered structure. The helical structures have been extensively studied since they were discovered in the early 1950s [1–5]. The synthesis of optically active polymers and the construction of helical structures have attracted considerable attention due to their high functionality, molecular recognition, and potential application for asymmetric catalysis. Optically active polymers have been prepared by the polymerization of a chiral monomer and the stereoselective polymerization of racemic or prochiral monomers by using specific chiral sources such as chiral initiators, catalysts, solvents, and ligands [6–14]. In addition, the helical induction and chiral amplification of optically inactive polymers by external stimuli or chiral additives have been investigated in detail [15–21]. Most of the chiralities of the optically active polymers have been attributed to chiral carbon atoms or chiral axes of binaphthyl structures. However, thus far, heteroatom chirality has rarely been incorporated into the polymer main chain for the construction of optically active polymers [22–35].

The phosphorus atom, similar to the carbon atom, can act as a chiral center because the inversion energy of tri- or pentavalent phosphorus compounds is generally much higher than that of the nitrogen analogues [36, 37]. The tri- and pentavalent phosphorus atoms are known to adopt the pyramidal structure, and thus, several P-chiral phosphine compounds have been reported so far [38–54]. Among such compounds, as an example of stable chiral phosphine compounds, (*S,S*)-1,2-ethanebis(*t*-butylmethylphosphineborane) (*S,S*)-**1** [55–57] was reported by Imamoto and co-workers as a chiral ligand precursor for asymmetric hydrogenation reactions; this compound can be easily prepared with high enantiomer excess (*ee* > 99%). We have recently focused on (*S,S*)-**1** as a building block for new phosphorus compounds, and we have synthesized optically active homo-oligomers of (*S,S*)-**1** by means of a step-by-step oxidative coupling reaction of (*S,S*)-**1** [58–60]. In addition, we have reported the copolymers [33–35] and dendrimers [61] containing the (*S,S*)-**1** unit as a key component. The oligomers, copolymers, and dendrimers exhibited the chiral higher-ordered structure derived from the chirality of the phosphorus atoms in the main chain.

(Structures of (*S,S*)-**1** and (*S,S*)-**5**)

In this research, triphenylmethyl methacrylate (TrMA) was polymerized by anionic polymerization using chiral phosphine compounds (*S,S*)-**1** [55] and

(*S,S*)-1,2-ethanebis(methylphenylphosphineborane) (*S,S*)-**5** [62] as initiators in order to investigate the ability of the chiral phosphorus atoms as a driving force for induction of helical conformation. Chiral sulfur atom was employed for a chiral source of asymmetirc polymerization of unsaturated monomers such as 1,3-pentadiene [63]; however, there have been no report on chiral phosphorus atom-induced asymmetric polymerization. Poly(TrMA) is known to form a nearly complete isotactic configuration and one-handed helical conformation, which are stabilized by the steric repulsion of the bulky groups [6, 7, 64–68]. Such a one-handed helical conformation is achieved by using (–)-sparteine as a chiral ligand of lithium species. Chiral anionic initiator, lithium (*R*)-*N*-(1-phenylethyl)anilide, was also reported to be utilized to obtain one-handed helical poly(TrMA) [65]. Additionally, in the present study, the complexation behavior of the obtained poly(TrMA) with platinum(II) was observed by utilizing the coordination ability of phosphorus atoms at the initiation point.

## RESULTS AND DISCUSSION

### *Synthesis and Characterization of the Monomers and Polymers **2**–**4**.*

P-Chiral bisphosphines (*S,S*)-1,2-ethanebis(*t*-butylmethylphosphineborane) (*S,S*)-**1** can be synthesized by the oxidative homocoupling reaction of *t*-butyldimethylphosphineborane by utilizing (–)-sparteine with high enantiomer excess (*ee* > 99%) [55]. However, optically active bisphosphine (*R,R*)-**1**, which is the enantiomer of (*S,S*)-**1**, cannot be synthesized by the procedure used for (*S,S*)-**1** because (+)-sparteine is not readily available [69]. Therefore, (*R,R*)-**1** was synthesized by employing another strategy reported in the literature [70]. In order to study the influence of the P-chirality on the higher-ordered structure of the polymers, optically inactive bisphosphine **1′** was prepared by the treatment of *t*-butyldimethylphosphineborane without (–)-sparteine, as shown in Scheme 1 [60]. Thus, bisphosphine **1′** was obtained as a mixture of *rac*-**1** ((*S,S*)-**1** and (*R,R*)-**1**) and *meso*-**1** ((*S,R*)-**1** = (*R,S*)-**1**).

(Structures of (*S,S*)-**1** and (*R,R*)-**1**)
(Scheme 1)

The typical polymerization procedure of TrMA is shown in Scheme 2. To a THF solution of optically active bisphosphine (*S,S*)-**1**, 1 equivalent of *s*-BuLi was added at −78 °C, and the reaction mixture was stirred for 3 h to generate a monoanion of (*S,S*)-**1**. This initiator solution was added into a THF solution of TrMA. After 2 h, a few drops of MeOH were added in order to quench the polymerization reaction, and the resulting polymer **2** was obtained by reprecipitation with hexane twice. Polymers **2a-c** were prepared by changing the feed ratio of the initiator and monomer. Polymers **3** and **4** were also synthesized from optically active bisphosphine (*R,R*)-**1** and optically inactive bisphosphine **1′**, respectively. The polymerization results are summarized in Table 1. The molecular weight measurements were performed by gel permeation chromatography (GPC) in eluent DMF at 40 °C by using the calibration curve of polystyrene standards. For example, the number-average molecular weight ($M_n$) and the molecular weight distribution ($M_w/M_n$) of polymer **2c** obtained in run 3 were 4200 and 1.3, respectively. The number-average degree of polymerization (DP) of **2c** was estimated to be approximately 11. Bisphosphine (*R,R*)-**1** certainly exhibited the same reactivity (run 5) as that of the enantiomer (*S,S*)-**1**, and optically inactive bisphosphine **1′**, including *meso*-**1**, provided the polymer with almost the same molecular weight, $M_n$ = 2400 and DP = 6 (Table 1, run 5). In the present study, increase of the feed ratio of TrMA over 20 formed a large amount of white

precipitate, which was insoluble in THF, $CHCl_3$, and toluene. Thus, we decided to investigate their properties, especially chiroptical property, by using THF– and $CHCl_3$–soluble polymers.

(Scheme 2)
(Structures of polymers **3** and **4**)
(Table 1)

It is known that poly(TrMA) can be converted to poly(MMA) by a polymer reaction. In order to calculate a more accurate molecular weight as well as to examine tacticity (*vide infra*), polymer **2c** was reacted with MeOH followed by the treatment with trimethylsilyldiazomethane (TMS–$CHN_2$) to obtain the corresponding poly(MMA). The molecular weight was calculated to be $M_n$ = 1400 ($M_w/M_n$ = 1.2) relative to the standard poly(MMA), indicating DP = 11.5.

Polymers **2a-c**, **3**, and **4** were characterized by $^1$H, $^{13}$C, and $^{31}$P NMR. In the $^{31}$P NMR spectrum of polymer **2a** shown in Figure 1, two relatively broad peaks appeared at $\delta$ +28.4 ppm and $\delta$ +34.7 ppm, which were assigned to the phosphorus atom at the outer and inner sides, respectively (Figure 1), on the basis of the $^{31}$P NMR chemical shift of (*S,S*)-**1** ($\delta$ +30.6 ppm) [55].

(Figure 1)
(Figure 2)

Figure 2 shows the $^1$H NMR spectrum of poly(MMA) **2c** prepared from poly(TrMA) **2c**. In the $^1$H NMR spectrum in $CDCl_3$ at room temperature, signal at 1.21 ppm and signals at 1.52 ppm and 2.14 ppm were assignable to methyl and methylenes of the meso sequence, respectively. Peaks derived from the racemo sequence and meso–racemo–mixed chains were not observed at 1.52–2.14 ppm. This results in the formation of the isotactic polymer in the present system.

## *Studies on Chiral Structures of Polymers **2**–**4**.*

Polymers **2a-c** exhibited positive specific rotations (*c* 0.5, THF); (*S,S*)-**1** alone exhibited a negative specific rotation of $[\alpha]_D^{28}$ –8.6 (*c* 0.5, THF). A polymer with higher molecular weight exhibited a larger specific rotation, and polymers **2a-c** exhibited $[\alpha]_D^{25}$ +16.9, +83.3, and +109.6 (*c* 0.5, THF), respectively. It is well known that TrMA provides an optically active polymer with the stable one-handed helical structure by ligand- and initiator-controlled anionic polymerization [6, 7, 64, 67]. Therefore, the results suggest that polymers **2a-c** form the one-handed helical structure induced by chiral phosphorus atoms at the initiation point. The

screw sense of polymers **2a-c** was the same as that of polymers initiated by 9-fluorenyllithium or *n*-BuLi with (–)-sparteine according to the same positive specific rotation [6, 7, 64]. The values of specific rotation of polymers **2a-c** were smaller ($[\alpha]_D^{25}$ +109.6 for DP = 23) than that of the helical poly(TrMA) synthesized by ligand-controlled anionic polymerization, for example, $[\alpha]_D^{20}$ +262 for DP = 42 [64]. This is due to not only the shorter chain length of **2a-c**, but also that the initiator-controlled polymerization of TrMA proceeds with lower helix-sense selectivity as compared to the ligand-controlled polymerization [62, 71, 72]. On the other hand, polymer **3** synthesized from the enantiomer (*R,R*)-**1** exhibited a negative specific rotation of $[\alpha]_D^{25}$ –74.8 (DP = 14, *c* 0.5, THF); this indicates that the opposite helix sense was induced (Table 1, run 4). Additionally, polymer **4** obtained by the anionic polymerization of TrMA with optically inactive initiator **1′** did not rotate the plane of polarized light, as expected.

The circular dichroism (CD) and absorption spectra of polymers **2b**, **3**, and **4** in THF ($1.0 \times 10^{-5}$ M) are shown in Figure 3. Polymer **2b** from (*S,S*)-**1** exhibited positive Cotton effect in the range of the π–π* band of benzene rings of the TrMA unit. Helical poly(TrMA) is known to exhibit Cotton effect in this range [73], thereby indicating the one-handed helical conformation. Polymer **3** from (*R,R*)-**1** exhibited negative Cotton effect at around 240 nm, and the CD spectra of polymers **2b** and **3** were mirror images of each other. Polymer **4** from the optically inactive **1′** did not exhibit any Cotton effect. Since the (*S,S*)-**1** unit has no absorption at the above-mentioned wavelength, these results indicate that the poly(TrMA) main chain adopts the one-handed helix structure induced by the chirality of phosphorus atoms at the initiation point.

(Figure 3)

## *Synthesis and Chiral Structures of Polymer **6**.*

In order to achieve easy removal of coordinated boranes of the bisphosphine unit, chiral bisphosphine (*S,S*)-1,2-ethanebis(methylphenylphosphineborane) (*S,S*)-**5** possessing phenyl groups instead of *tert*-butyl groups was synthesized according to the procedure provided in the litterature [62] with minor modifications (Scheme 3) [74]. Although the 98% *ee* of (*S,S*)-**5** was reported in the literature [62], the *ee* of (*S,S*)-**5** could be enhanced up to almost 100% by repeated recrystallization (three or four times) from toluene/hexane [74]. The crystallization process caused the low isolated yield of 17%. The specific rotation $[\alpha]_D^{21}$ of (*S,S*)-**5** was +35.7 (*c* 0.5, THF). As shown in Scheme 4, TrMA could be polymerized by using (*S,S*)-**5** as the anionic initiator. The results of the polymerization are shown in Table 2. The molecular weight of the obtained polymers **6a-d** increased with the TrMA ratio. Further, polymers **6a-d** exhibited positive specific rotations similar to polymers **2a-c**. However, $[\alpha]_D^{25}$ of polymer **6** was smaller

than that of the corresponding polymer **2**. For example, $[\alpha]_D^{25}$ of polymer **6c** with $M_n$ = 2800 (DP = 7 estimated from poly(TrMA) using polystyrene standards; DP = 8 derived from poly(MMA) using poly(MMA) standards) was +57.2 (Table 2, run 3), whereas that of polymer **2b** ($M_n$ = 2700, DP = 15) was +109.6 (Table 1, run 2). The specific rotations did not increase with the DP, and those of polymers **6b-d** were similar (Table 2, runs 2-3). The bulky *tert*-butyl group of (*S,S*)-**1** is more effective for the helix-sense-selective polymerization of TrMA as compared to the phenyl group of (*S,S*)-**5**. According to the $^1$H NMR spectrum of poly(MMA) **6c** prepared from poly(TrMA) **6c**, signals of the atactic polymer in addition to those of the isotactic polymer chain were observed. The chiral bisphosphine unit at the polymer chain end affects the chirality of the polymer besides the total helix sense [7].

(Schemes 3 and 4)
(Table 2)

The CD spectrum of polymer **6d** is shown in Figure 4, which includes the CD spectra of polymer **2b** and the initiator (*S,S*)-**5**. Polymer **6d** exhibited a CD spectrum similar to that of polymer **2b** in the $\pi$–$\pi^*$ region of the benzene ring of the TrMA unit. The CD of polymer **6d** is weaker than that of polymer **2b** depending on the helical-sense excess ($[\alpha]_D^{25}$ +57.2 and +109.6 for **6d** and **2b**, respectively). The optically active initiator (*S,S*)-**5** containing two phenyl groups exhibited weak Cotton effect at around 225 nm, which differed from the Cotton effect of polymer **6d** at around 235 nm in Figure 4. Thus, it was confirmed that the chirality was attributed to the one-handed helical sense of the TrMA main chain induced by the chirality of phosphorus atoms at the initiation point.

(Figure 4)

## *Complexation Behavior of Polymer **6**.*

A coordinated borane on a trialkylphosphine compound can be removed by a strong acid and successive treatment with aqueous inorganic base [55, 75, 76], and the borane on aryl-substituted phosphine can be readily removed under milder conditions by organic bases such as diethylamine, pyrrolidine, and 1,4-diazabicyclo[2.2.2]octane (DABCO) [77]. As shown in Scheme 5, the deprotection of polymer **6d** and the successive coordination reaction with platinum(II) were carried out. First, the removal of boranes from polymer **6d** by treatment with DABCO in toluene at 50 °C proceeded smoothly overnight. The residual DABCO and by-product salts were removed by reprecipitation from $Et_2O$ in order to obtain

polymer **7d** in 49% isolated yield. The removal of boranes on the bisphosphine unit was confirmed by the $^{31}$P NMR spectrum (Figure 5). The $^{31}$P NMR signals of phosphines were shifted up-filed from $\delta$ +19.2 and $\delta$ +11.2 ppm to $\delta$ –19.6 and –32.8 ppm, respectively. Polymer **7d** underwent the reaction with excess amount of *cis*-$PtCl_2$(cod) (cod = 1,5-cyclooctadiene) in $CH_2Cl_2$ at room temperature to produce polymer **8d** with the platinum(II) complex unit as a white powder in 58% isolated yield. It was also confirmed that the complexation with platinum(II) proceeded according to the $^{31}$P NMR spectrum (Figure 5). The typical satellite signals derived from the phosphorus-platinum coupling ($J_{P\text{-}Pt}$) were observed at $\delta$ +45.1 and +37.5 ppm with $J_{P\text{-}Pt}$ = 3623 and 3564 Hz, respectively.

(Scheme 5)
(Figures 5–7)

The GPC curves of polymers **6d** and **8d** indicate that decomposition of the TrMA main chain did not occur during the removal of boranes and the complexation reactions (Figure 6). A slight shift in the GPC curve of polymer **8d** was observed, and the $M_n$ and PDI of polymer **8d** were found to be 3000 and 1.3, respectively. This is due to the prohibition of the rotary motion of the bisphosphine unit by the complexation (Figure 6). The CD spectra and specific rotations $[\alpha]_D^{25}$ (*c* 0.5, THF) of polymers **6d** and **8d** are shown in Figure 7. Polymer **8d** exhibited a Cotton effect almost similar to that of polymer **6d** regardless of the complex formation. The helical structure of poly(TrMA) was locked, and the helix sense was maintained. The specific rotation of polymer **8d** ($[\alpha]_D^{25}$ = +49.7) was smaller than that of polymer **6d** ($[\alpha]_D^{25}$ = +53.3) because of the larger molecular weight of **8d** as compared to that of **6d** with the same concentration (*c* 0.5) rather than the conformation change of the optically active bisphosphine unit.

# CONCLUSIONS

Helix-sense-selective anionic polymerization of TrMA was demonstrated by utilizing P-chiral bisphosphines (*S,S*)-**1**, (*R,R*)-**1**, and (*S,S*)-**5** as anionic initiators. Poly(TrMA)s from (*S,S*)-**1** and (*R,R*)-**1** produced one-handed helical polymers that were mirror images of each other. The higher molecular weight polymer exhibited a larger optical rotation value. Optically inactive bisphosphine **1′** was used for the initiator, and the resulting polymer did not exhibit optical activity. Optically active bisphosphine (*S,S*)-**5** was employed for the helix-sense-selective polymerization in order to obtain the poly(TrMA)s **6a-d** with the same one-handed helical structure as that of poly(TrMA)s **2a-c** obtained from (*S,S*)-**1**. However, $[\alpha]_D^{25}$ of **6** was smaller than that of **2**, thereby indicating that the bulky *tert*-butyl group of (*S,S*)-**1** is more effective for the helix-sense-selective polymerization of TrMA as compared to the phenyl group of (*S,S*)-**5**. The deprotection of **6d** and complexation with platinum on the chiral phosphorus atoms at the initiation point were also achieved to obtain the corresponding polymer complex **8d** without loss of the chiral higher-ordered structure.

# EXPERIMENTAL SECTION

## *General.*

$^{1}$H (400 MHz) and $^{13}$C (100 MHz) NMR spectra were recorded on a JEOL EX400 spectrometer, and samples were analyzed in $CDCl_3$ using tetramethylsilane as an internal standard. $^{31}$P (161.9 MHz) NMR spectra were also recorded on a JEOL EX400 spectrometer, and samples were analyzed in $CDCl_3$ using $H_3PO_4$ as an external standard. The following abbreviations are used; s: singlet, d: doublet, t: triplet, m: multiplet, and br: broad. Gel permeation chromatography (GPC) was carried out on a UV-8020 and RI-8020 [TSK-GEL α-3000(0.78 cm × 30 cm)] using DMF containing 10 mM LiBr as an eluent after calibration with 12 standard polystyrene samples ($M_n$ = 500-1090000). Analysis of poly(MMA) was carried out using three polystyrene gel columns [Shodex K-805L (0.80 cm × 30 cm) × 3] using $CHCl_3$ as an eluent after caribration with 12 standard poly(MMA) samples ($M_n$ = 630-1200000). Optical rotation values were measured with a RUDOLPH RESEACH Autopol IV polarimeter by using THF as a solvent. Circular dichroism (CD) spectra were recorded on a JASCO J-600 spectropolarimeter with THF as a solvent by using a cell with the path length of 1.0 cm. Chiral liquid chromatography was carried out on TOSOH UV-8020 equipped with Daicel Chiralcel OD-H column (0.46 cm × 25 cm) using 2-propanol/hexane (v/v = 10:90) as an eluent. The removal of the remained $PtCl_2$(cod) from the polymer 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.

## *Materials.*

Tetrahydrofuran (THF) and diethyl ether ($Et_2O$) were purchased and purified by passage through purification column under Ar pressure [78]. Dehydrated toluene and dichloromethane ($CH_2Cl_2$) were obtained commercially and used without purification. (−)-Sparteine was distilled from KOH under Ar atmosphere. *t*-Butyldimethylphosphineborane, (*S,S*)-1,2-ethanebis(*t*-butylmethylphosphineborane) (*S,S*)-**1** [55], (*R,R*)-1,2-ethanebis(*t*-butylmethylphosphineborane) (*R,R*)-**1** [70], optically inactive mixture of 1,2-ethanebis(*t*-butylmethylphosphineborane) **1′** [60], and triphenylmethyl methacrylate (TrMA) [79] were prepared as described in the literature. *s*-BuLi (1.0 M in cyclohexane and *n*-hexane solution), $CuCl_2$, $BH_3$·THF, 1,4-diazabicyclo[2.2.2]octane (DABCO), and *cis*-$PtCl_2$(cod) were purchased and used without further purification. All reactions were performed under Ar atmosphere using standard Schlenk techniques.

### *(S,S)-1,2-Ethanebis(methylphenylphosphineborane) (S,S)-**5**.*

This compound was prepared according to the procedure of Evans and coworkers [62], and $CuCl_2$ was employed instead of $Cu(OPiv)_2$. Enantiomerically pure (*S,S*)-**5** was obtained by repeat recrystallizations (at least four times) from toluene/hexane in 17% isolated yield with high enantiomer excess (ee > 99%), which was monitored by the chiral HPLC as shown in Figure 7 [73]. $[\alpha]_D^{21}$ +35.7 (c 0.5, THF). Spectral data were matched with the literature values [62].

### *Synthesis of polymers **2**–**4** and **6**.*

A solution of the bisphosphine (0.40 mmol) in THF (10 mL) was cooled to –78 °C under Ar atmosphere. To the stirred solution, *s*-BuLi (0.40 mmol, 1.0 M in cyclohexane and *n*-hexane solution) was added, and the mixture was stirred at –78 °C over 3 h. To a solution of TrMA (1.3 g, 4.0 mmol) in THF (20 mL), the initiator solution was added at –78 °C. After 2 h, the reaction was quenched by addition of a few drops of MeOH. The reaction mixture was concentrated *in vacuo* to give the white solid. This solid was dissolved in $CHCl_3$, filtrated, and poured into ca. 100 mL of hexane to reprecipitate the polymer twice. The white precipitate was collected by centrifugation and dried *in vacuo*.

**2a** 66%, **2b** 87%, **2c** 80%, **3** 80%, and **4** 76% yield. $^1$H NMR ($CDCl_3$) $\delta$ –0.05-2.60 (br, -B*H*$_3$ and aliphatic protons), 6.00-7.95 (br, aromatic protons); $^{13}$C NMR ($CDCl_3$) $\delta$ 5.3 (br, P-*C*H$_3$), 14.0-22.1 (br, P-*C*H$_2$- and C-*C*H$_3$), 24.5-26.4 (br, P-C(*C*H$_3$)$_3$), 27.6-29.5 (m, P-*C*(CH$_3$)$_3$ and P-*C*H$_2$-), 40.0-48.6 (br, -*C*H$_2$-*C*(CH$_3$)(COOCPh$_3$)-), 88.9-91.1 (br, -*C*Ph$_3$), 123.2-130.3 (br, -C*Ph*$_3$), 141.8-144.4 (br, -C*Ph*$_3$), 172.2-175.1 (br, -*C*(=O)-O-); $^{31}$P{$^1$H}NMR ($CDCl_3$) $\delta$ +28.4, +34.7 ppm.

**6a** 70%, **6b** 74%, **6c** 54%, and **6d** 51% yield. $^1$H NMR ($CDCl_3$) $\delta$ –0.25-2.60 (br, -B*H*$_3$ and aliphatic protons), 6.35-8.06 (br, aromatic protons); $^{13}$C NMR ($CDCl_3$) $\delta$ 10.8 (br, P-*C*H$_3$), 17.9-21.8 (br, P-*C*H$_2$- and C-*C*H$_3$), 42.7-48.5 (br, -*C*H$_2$-*C*(CH$_3$)(COOCPh$_3$)-), 88.1-90.8 (br, -*C*Ph$_3$), 123.9-130.1 (br, P-*Ph* and -C*Ph*$_3$), 131.0-133.1 (br, P-*Ph*), 141.6-144.7 (br, -C*Ph*$_3$), 172.0-175.1 (br, -*C*(=O)-O-); $^{31}$P{$^1$H}NMR ($CDCl_3$) $\delta$ +11.5, +19.2 ppm.

### *Synthesis of polymer **7d**.*

A solution of polymer **6d** (0.8 g, 0.24 mmol) and 1,4-diazabicyclo[2,2,2]octane (0.27 g, 2.4 mmol) in dry toluene (16 mL) was prepared under Ar atmosphere. The mixture was stirred at 50 °C overnight. The reaction mixture was concentrated *in vacuo* and poured into 40 mL of diethyl ether under Ar atmosphere. The white precipitate was collected by centrifugation and dried *in vacuo* to give polymer **7d** (0.48 g, 0.15 mmol, 49%) as a white powder: $^1$H NMR

($CDCl_3$) $\delta$ –0.30-3.10 (br, aliphatic protons), 6.00-8.40 (br, aromatic protons); $^{31}P\{^1H\}$NMR ($CDCl_3$) $\delta$ –32.8, –19.6 ppm.

## *Synthesis of polymer **8d**.*

A solution of polymer **7d** (430 mg, 0.13 mmol) and *cis*-$PtCl_2$(cod) (90 mg, 0.24 mmol) in dry $CH_2Cl_2$ (45 mL) was prepared under Ar atmosphere. The mixture was stirred at room temperature overnight. The solvent was removed *in vacuo*. After the purification using HPLC to remove the remained platinum species, polymer **8d** was obtained as a white powder (228 mg, 0.08 mmol, 58%): $^1H$ NMR ($CDCl_3$) $\delta$ -0.10-3.10 (br, aliphatic protons), 5.95-8.15 (br, aromatic protons); $^{31}P\{^1H\}$NMR ($CDCl_3$) $\delta$ +37.5 (s with $^{195}Pt$ satellites, $J_{Pt\text{-}P}$ = 3564 Hz), +45.1 ppm (s with $^{195}Pt$ satellites, $J_{Pt\text{-}P}$ = 3623 Hz).

# REFERENCES


1. J. D. Watson, F. H. C. Crick, Nature **171**, 737 (1953).
2. L. Pauling, R. B. Corey, H. R. Branson, Proc. Natl. Acad. Sci. U. S. A. **378**, 205 (1951).
3. G. E. Schulz, R. H. Schirmer, *Principles of Protein Structure* (Springer, New York, 1979).
4. W. Saenger, *Principles of Nucleic Acid Structure* (Springer, New York, 1984).
5. C. Branden, J. Tooze, *Introduction of Protein Structure, 2nd ed.* (Garlnad Publishing, New York, 1999).
6. Y. Okamoto, E. Yashima, Prog. Polym. Sci. **15**, 263 (1990).
7. Y. Okamoto, T. Nakano, Chem. Rev. **94**, 349 (1994).
8. Y. Okamoto, T. Nakano, Chem. Rev. **101**, 4013 (2001).
9. K. Nozaki, T. Hiyama, J. Organomet. Chem. **576**, 248 (1999).
10. S. Itsuno, Prog. Polym. Sci. **30**, 540 (2005).
11. Y. Suginome, Y. Ito, Adv. Polym. Sci. **171**, 77 (2004).
12. L. Pu, Acta Polym. **48**, 116 (1997).
13. L. Pu, Chem. Rev. **98**, 2405 (1998).
14. J. J. L. M. Cornelissen, A. E. Rowan, R. J. M. Nolte, N. A. J. M. Sommerdijk, Chem. Rev. **101**, 4039 (2001).
15. E. Yashima, Anal. Sci. **18**, 3 (2002).
16. E. Yashima, K. Maeda, Macromolecules **41**, 3 (2008).
17. M. Fujiki, Macromol. Rapid. Commun. **22**, 539 (2001).
18. M. Fujiki, J. R. Koe, K. Terao, T. Sato, A. Teramoto, J. Watanabe, Polym. J. **35**, 297 (2003).
19. T. Masuda, J. Polym. Sci. Part A: Polym. Chem. **45**, 165 (2007).
20. D. J. Hill, M. J. Mio, R. B. Prince, T. S. Hughes, J. S., Chem. Rev. **101**, 3893 (2001).
21. M. M. Green, J.-W. Park, T. Sato, A. Teramoto, S. Lifson, R. L. B. Selinger, J. V. Selinger, Angew. Chem., Int. Ed. **38**, 3138 (1999).
22. Y. Kawakami, K. Takeyama, K. Komuro, O. Ooi, Macromolecules **31**, 551 (1998).
23. Y. Kawakami, T. Takahashi, Y. Yada, I. Imae, Polym. J. **30**, 1001 (1998).
24. Y. Kawakami, K. Nakao, S. Shinke, I. Imae, Macromolecules **32**, 6874 (1999).
25. Y. Kawakami, M. Omote, I. Imae, E. Shirakawa, Macromolecules **36**, 7461 (2003).
26. K. Uenishi, I. Imae, E. Shirakawa, Y. Kawakami, Macromolecules **35**, 2455 (2002).
27. Y. Li, Y. Kawakami, Macromolecules **31**, 5592 (1998).
28. Y. Li, Y. Kawakami, Macromolecules **32**, 548 (1999).
29. Y. Li, Y. Kawakami, Macromolecules **33**, 1560 (2000).

30. M. Murano, Y. Li, Y. Kawakami, Macromolecules **33**, 3940 (2000).
31. A. Angeloni, M. Laus, D. Caretti, E. Chiellini, G. Galli, Makromol. Chem. **191**, 2787 (1990).
32. T. Oyama, Y. Chujo, Macromolecules **32**, 7732 (1999).
33. Y. Morisaki, Y. Ouchi, K. Tsurui, Y. Chujo, J. Polym. Sci., Part A: Polym. Chem. **45**, 866 (2007).
34. Y. Morisaki, Y. Ouchi, K. Tsurui, Y. Chujo, Polym. Bull. **58**, 665 (2007).
35. Y. Ouchi, Y. Morisaki, T. Ogoshi, Y. Chujo, Chem. Asian J. **2**, 397 (2007).
36. R. E. Weston, J. Am. Chem. Soc. **76**, 2645 (1954).
37. K. Milslow, Trans. N. Y. Acad. Sci. **35**, 227 (1973).
38. M. Ohff, J. Holz, M. Quirmbach, A. Börner, Synthesis 1391 (1998).
39. M. J. Johansson, N. C. Kann, Minirev. Org. Chem. **1**, 233 (2004).
40. Grabulosa, J. Granell, G. Muller, Coord. Chem. Rev. **1**, 25 (2004).
41. I. G. M. Campbell, J. K. J. Way, Chem. Soc. 5034 (1960).
42. L. Horner, H. Winkler, A. Rapp, A. Mentrup, Tetrahedron Lett. **5**, 161 (1961).
43. R. Noyori, *Asymmetric Catalyst in Organic Synthesis* (John Wiley & Sons, New York, 1994).
44. I. M. Pitrusiewicz, M. Zabloka, Chem. Rev. **94**, 1375 (1994).
45. I. Ojima, *Catalytic Asymmetric Synthesis* (John Wiley & Sons, New York, 2000).
46. I. Horner, H. Siegel, H. Buthe, Angew. Chem., Int. Ed. **7**, 942 (1968).
47. W. S. Knowles, M. J. Sabacky, J. Chem. Soc., Chem. Commun. 1445 (1968).
48. W. S. Knowles, M. J. Sabacky, B. D. Vineyard, J. Chem. Soc., Chem. Commun. 10 (1972).
49. W. S. Knowles, M. J. Sabacky, B. D. Vineyard, D. J. Weinkauff, J. Am. Chem. Soc. **97**, 2567 (1975).
50. B. D. Vineyard, W. S. Knowles, M. J. Sabacky, G. L. Bachman, D. J. Weinkauff, J. Am. Chem. Soc. **99**, 5946 (1977).
51. W. S. Knowles, Acc. Chem. Res. **16**, 106 (1983).
52. R. D. Baechler, K. Mislow, J. Am. Chem. Soc. **92**, 3090 (1970).
53. A. L. Airey, G. Swiegers, A. C. Willis, S. B. Wild, J. Chem. Soc., Chem. Commum. 695 (1995).
54. P. K. Bowyer, C. C. Vernon, G.-N. Nahid, P. A. Gugger, A. D. Rae, G. F. Swiegers, A. C. Willis, J. Zank, S. B. Wild, Proc. Natl. Acad. Sci. USA. **99**, 4877 (2002).
55. T. Imamoto, J. Watanabe, Y. Wada, H. Masuda, H. Yamada, H. Tsuruta, S. Matsukawa, K. Yamaguchi, J. Am. Chem. Soc. **120**, 1635 (1998).
56. I. V. L. Crépy, T. Imamoto, Top. Curr. Chem. **229**, 1 (2003).

57. I. V. L. Crépy, T. Imamoto, Adv. Synth. Catal. **345(1-2)**, 79 (2003).
58. Y. Morisaki, Y. Ouchi, T. Fukui, K. Naka, Y. Chujo, Tetrahedron Lett. **46**, 7011 (2005).
59. Y. Morisaki, Y. Ouchi, K. Naka, Y. Chujo, Tetrahedron Lett. **48**, 1451 (2007).
60. Y. Morisaki, Y. Ouchi, Y. Chujo, Chem. Asian J. **2**, 1166 (2007).
61. Y. Ouchi, Y. Morisaki, Y. Chujo, Polym. Bull. **59**, 339 (2007).
62. A. R. Muci, K. R. Campos, D. A. Evans, J. Am. Chem. Soc. **117**, 9075 (1995).
63. Yu. B. monakov, N. G. Marina, O. I. Kozlova, F. Ya. Kanzafarov, G. A. Tolstikov, Dokl, Akad. Nauk SSSR **292**, 405 (1987).
64. Y. Okamoto, K. Suzuki, K. Ohta, K. Hatada, H. Yuki, J. Am. Chem. Soc. **101**, 4763 (1979).
65. Y. Okamoto, K. Suzuki, H. Yuki, J. Polym. Sci., Polym. Chem. Ed. **18**, 3043 (1980).
66. Y. Okamoto, H. Shohi, H. Yuki, J. Polym. Sci., Polym. Lett. Ed. **21**, 601 (1983).
67. T. Nakano, Y. Okamoto, K. Hatada, J. Am. Chem. Soc. **114**, 1318 (1992).
68. T. Nakano, Y. Hidaka, Y. Okamoto, Polym. J. **30**, 596 (1998).
69. P. O'Brien, Chem. Commun. 655 (2008).
70. I. V. L. Crépy, T. Imamoto, Tetrahedron Lett. **43**, 7735 (2002).
71. F. Takei, K. Yanai, K. Onitsuka, S. Takahashi, Chem. Eur. J. **6**, 983 (2000).
72. I. Maeda, Y. Okamoto, Polym. J. **30**, 100 (1998).
73. T. Sanji, K. Takase, H. Sakurai, J. Am. Chem. Soc. **123**, 12690 (2001).
74. Y. Morisaki, H. Imoto, Y. Ouchi, Y. Nagata, Y. Chujo, Org. Lett. **10**, 1489 (2008).
75. I. McKinstry, T. Livinghouse, Tetrahedron Lett. **35**, 9319 (1994).
76. I. McKinstry, T. Livinghouse, Tetrahedron **50**, 6145 (1994).
77. T. Imamoto, T. Oshiki, T. Onozawa, T. Kusumoto, K. Sato, J. Am. Chem. Soc. **112**, 5244 (1990).
78. A. B. Pangborn, M. A. Giardello, R. H. Grubbs, R. K. Rosen, F. J. Timmers, Organometallics **15**, 1518 (1996).
79. J. P. Chen, J. P. Gao, Z. Y. Wang, J. Polym. Sci., Part A: Polym. Chem. **35**, 9 (1997).

**Table 1.** Results of polymerization and $[a]_D^{25}$ of the polymers

| run | polymer | initiator[a] | feed ratio initiator / TrMA | yield (%)[b] | $M_n$[c] | $M_w/M_n$[c] | DP | $[\alpha]_D^{25}$ [d] |
|---|---|---|---|---|---|---|---|---|
| 1 | **2a** | (*S,S*)-**1** | 1 / 5 | 66 | 1500 | 1.3 | 3.5 | +16.9 |
| 2 | **2b** | (*S,S*)-**1** | 1 / 10 | 87 | 2700 | 1.3 | 7 | +83.3 |
| 3 | **2c** | (*S,S*)-**1** | 1 / 15 | 80 | 4200 | 1.3 | 11 (11.5)[e] | +109.6 |
| 4 | **3** | (*R,R*)-**1** | 1 / 10 | 80 | 2300 | 1.2 | 6 | –74.8 |
| 5 | **4** | **1'** | 1 / 10 | 76 | 2400 | 1.2 | 6 | 0 |

[a] 1 equivalent of *s*-BuLi. [b] Isolated yield after reprecipitation. [c] Determined by GPC (DMF, 40 °C, polystyrene standards). [d] Degree of polymerization was calculated from the $^1$H NMR integral ratio. [d] THF solution (*c* 0.5). [e] Poly(TrMA) **2c** was converted to poly(MMA), and $M_n$ was calculated by GPC relative to poly(MMA) standards ($CHCl_3$ eluent).

**Table 2.** Results of polymerization by using (*S,S*)-**5** and $[a]_D^{25}$ of polymers **6a–d**

| run | polymer | feed ratio initiator[a] / TrMA | yield (%)[b] | $M_n$[c] | $M_w/M_n$[c] | DP | $[\alpha]_D^{25}$ [d] |
|---|---|---|---|---|---|---|---|
| 1 | **6a** | 1 / 5 | 70 | 2000 | 1.3 | 5 | +39.5 |
| 2 | **6b** | 1 / 10 | 74 | 2400 | 1.3 | 6 | +55.4 |
| 3 | **6c** | 1 / 15 | 54 | 2800 | 1.3 | 7 (8)[e] | +57.2 |
| 4 | **6d** | 1 / 20 | 51 | 3200 | 1.2 | 8 | +53.3 |

[a] 1 equivalent of *s*-BuLi. [b] Isolated yield after reprecipitation. [c] Determined by GPC (DMF, 40 °C, polystyrene standards). [d] THF solution (*c* 0.5). [e] Poly(TrMA)s **6c** was converted to poly(MMA), and $M_n$ was calculated by GPC relative to poly(MMA) standards ($CHCl_3$ eluent).

FIGURE CAPTIONs

**Fig. 1**. $^{31}P\{^{1}H\}$ NMR spectrum of polymer **2b** (161.9 MHz, $CDCl_3$).

**Fig. 2.** $^{1}H$ NMR spectrum of poly(MMA) **2c** prepared from poly(TrMA) **2c** in $CDCl_3$ (400 MHz).

**Fig. 3**. CD spectra of polymers **2b**, **3**, and **4**, and the absorption spectrum of polymer **2b** (THF solution, $1.0 \times 10^{-5}$ M).

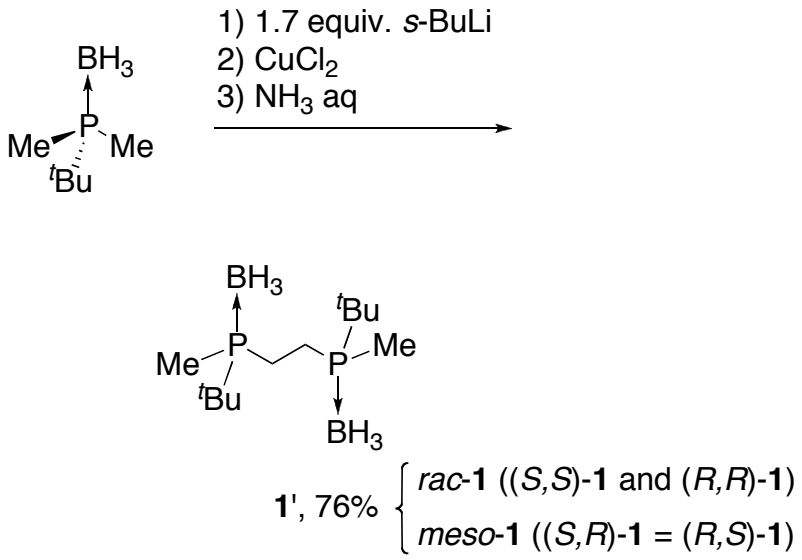
**Fig. 4**. CD and absorption spectra of polymers **6d** and **2b**, and those of the optically active initiator (*S,S*)-**5** (THF solution, $1.0 \times 10^{-5}$ M).

**Fig. 5**. $^{31}P\{^{1}H\}$ NMR spectra of polymers **6d**–**8d** (161.9 MHz, $CDCl_3$).

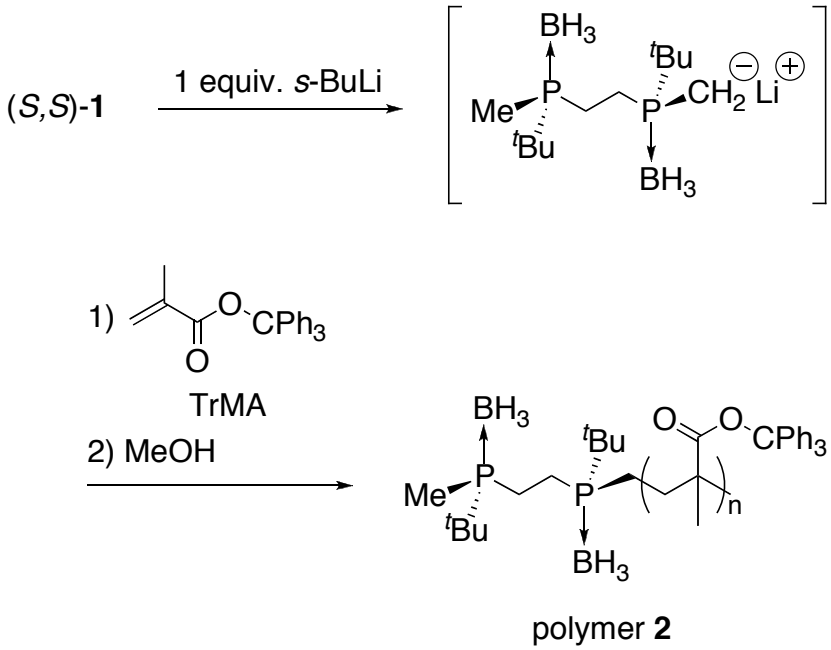
**Fig. 6**. GPC traces for polymers **6d** and **8d**; DMF containing 10 mM LiBr, 40 °C, polystyrene standards, TSK-GEL α-3000, 1.0 mL/min. Schematic structures of polymers **6d** and **8d** are also included.

**Fig. 7**. CD spectra of polymers **6d** and **8d** (THF solution, $1.0 \times 10^{-5}$ M). The specific rotations of the polymers (THF, *c* 0.5) are included.

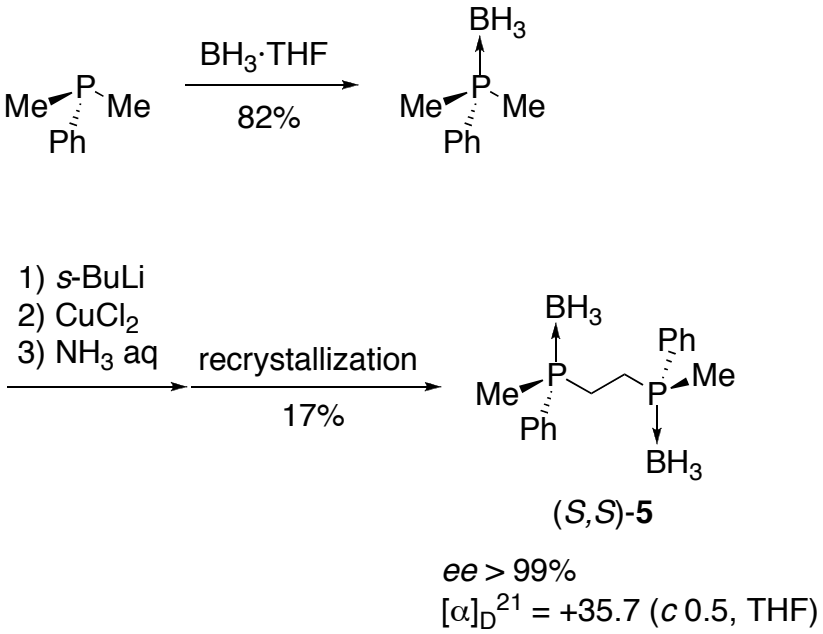
Scheme 1


1) 1.7 equiv. s-BuLi
2) CuCl2
3) NH3 aq
BH3
P
Me
Me
tBu
BH3
tBu
P
Me
Me
P
tBu
BH3
1', 76%
rac-1 ((S,S)-1 and (R,R)-1)
meso-1 ((S,R)-1 = (R,S)-1)

Scheme 2


(S,S)-1
1 equiv. s-BuLi
BH3
tBu
Me
P
P
CH2 Li
tBu
BH3
1)
O
CPh3
O
TrMA
2) MeOH
BH3
tBu
O
O
CPh3
Me
P
P
n
tBu
BH3
polymer 2

Scheme 3

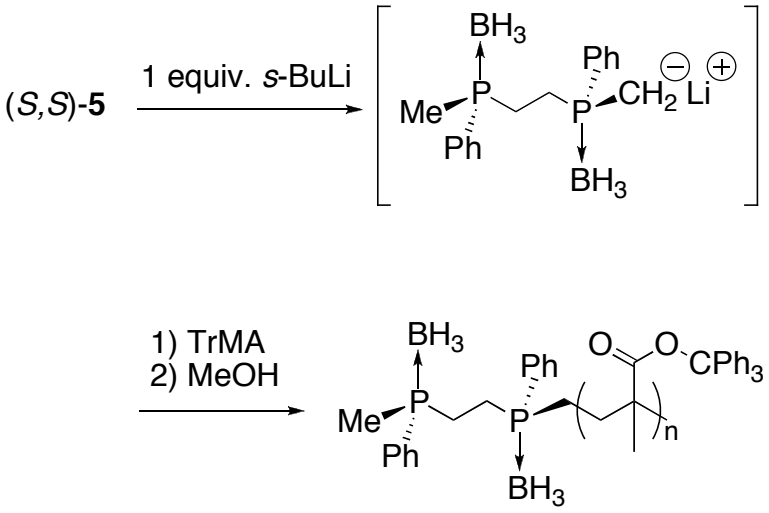



(*S,S*)-**5**

*ee* > 99%

$[\alpha]_D^{21}$ = +35.7 (*c* 0.5, THF)

Scheme 4




polymer **6**

Scheme 5

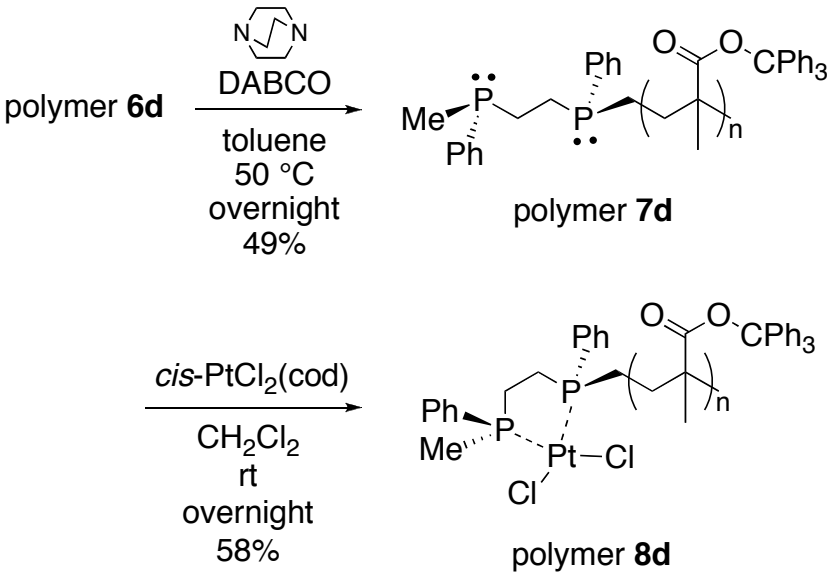

polymer 6d
DABCO
toluene
50 °C
overnight
49%
polymer 7d
cis-PtCl2(cod)
CH2Cl2
rt
overnight
58%
polymer 8d

Figure 1

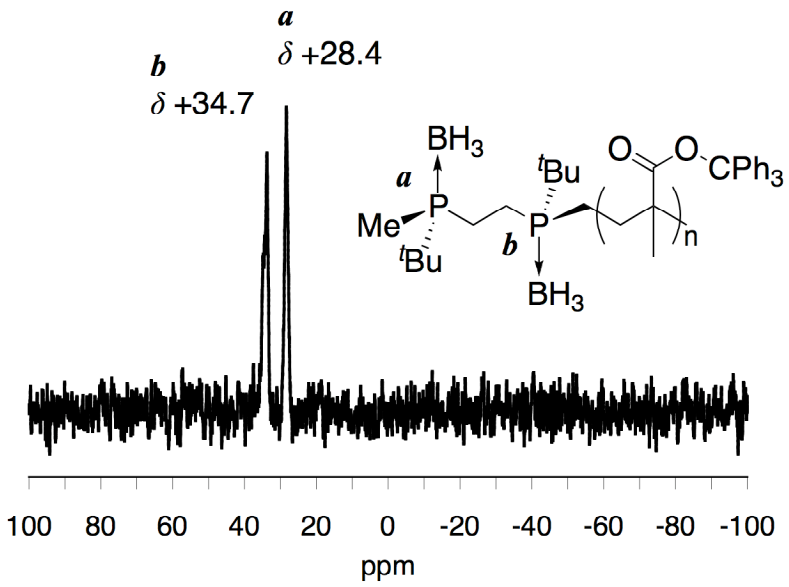



**Fig. 1**. $^{31}P\{^{1}H\}$ NMR spectrum of polymer **2b** (161.9 MHz, $CDCl_3$).

Figure 2

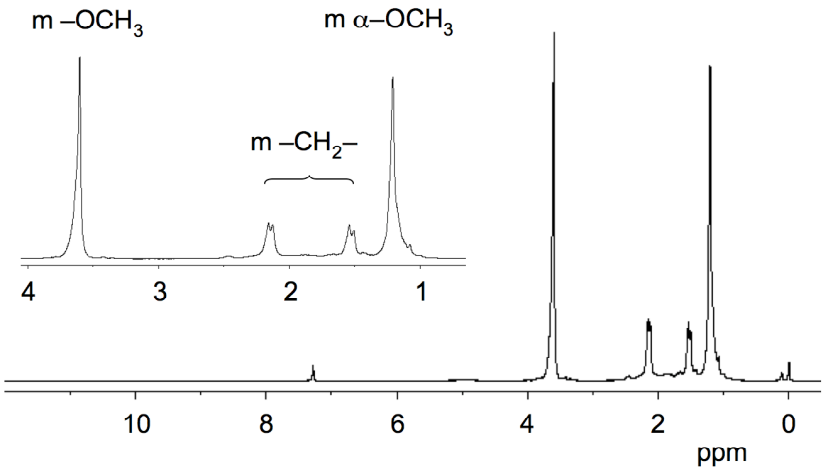



**Fig. 2.** $^{1}$H NMR spectrum of poly(MMA) **2c** prepared from poly(TrMA) **2c** in $CDCl_3$ (400 MHz).

Figure 3

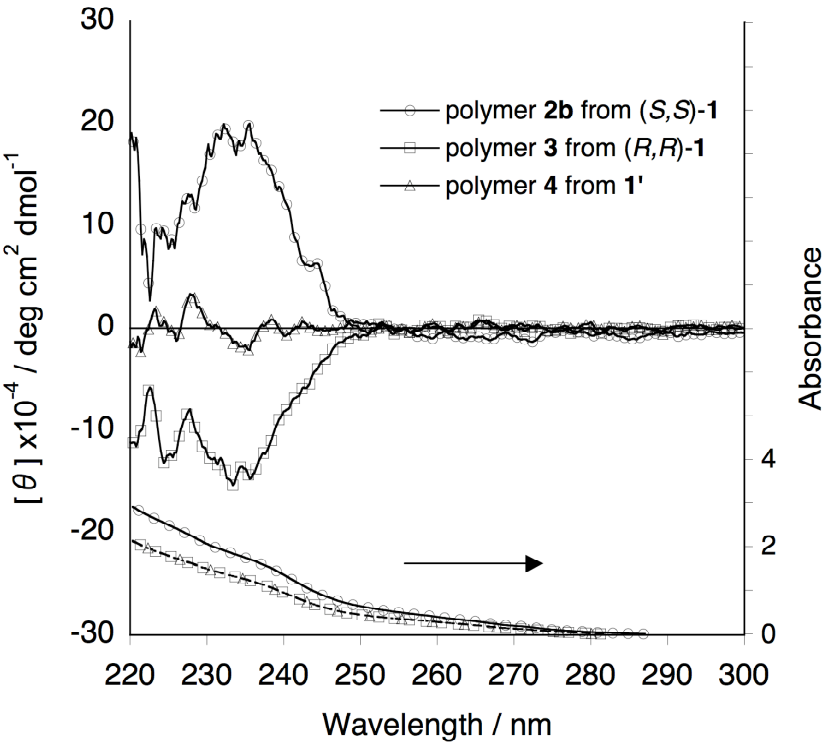



**Fig. 3**. CD spectra of polymers **2b**, **3**, and **4**, and the absorption spectrum of polymer **2b** (THF solution, $1.0 \times 10^{-5}$ M).

Figure 4

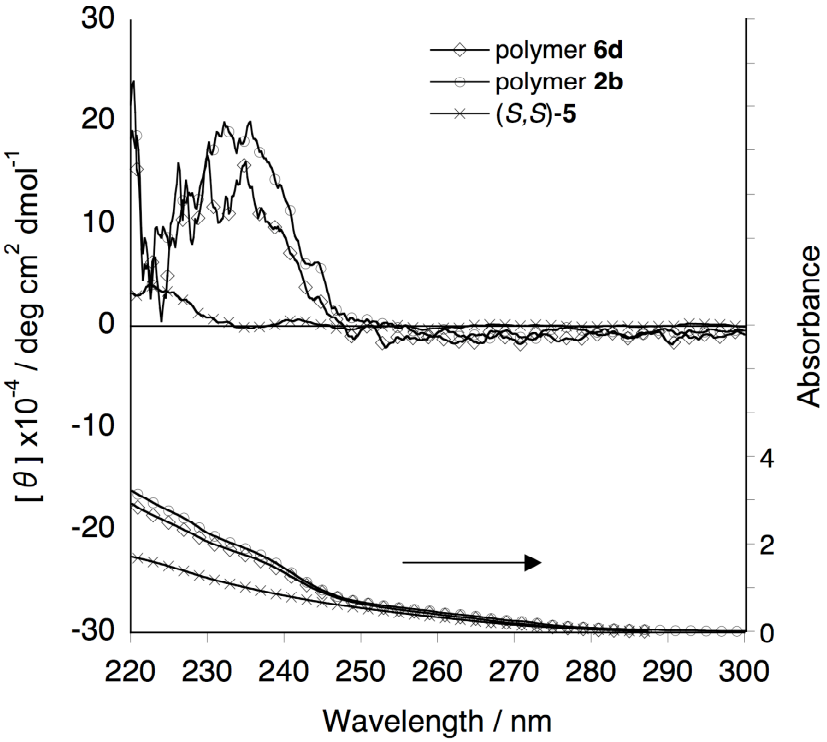



**Fig. 4**. CD and absorption spectra of polymers **6d** and **2b**, and those of the optically active initiator (*S,S*)-**5** (THF solution, $1.0 \times 10^{-5}$ M).

Figure 5

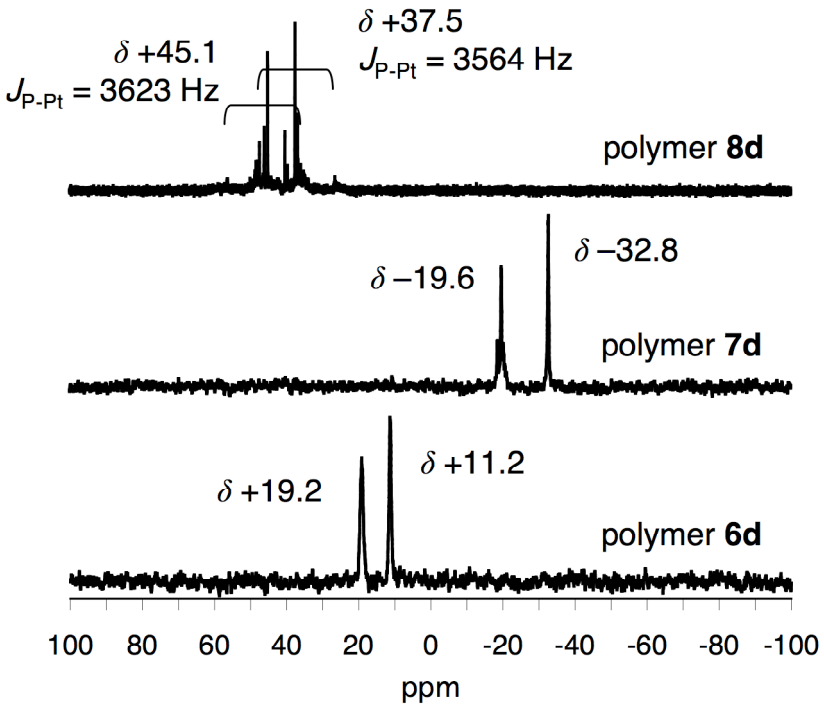



**Fig. 5**. $^{31}P\{^{1}H\}$ NMR spectra of polymers **6d**–**8d** (161.9 MHz, $CDCl_3$).

Figure 6

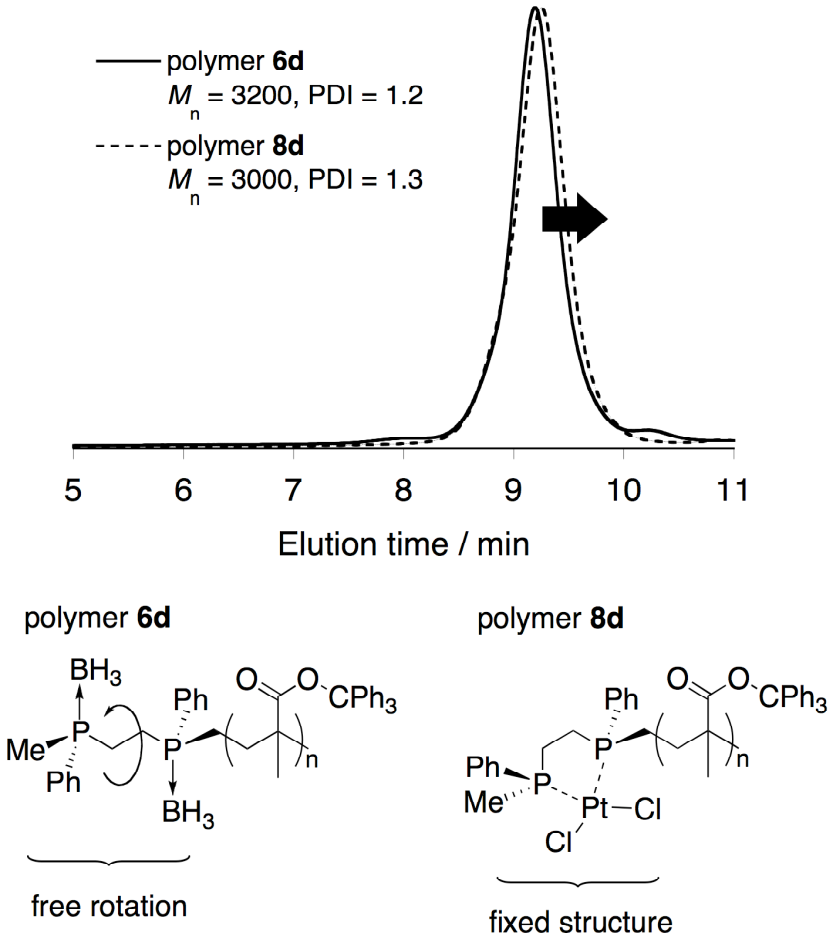



**Fig. 6**. GPC traces for polymers **6d** and **8d**; DMF containing 10 mM LiBr, 40 °C, polystyrene standards, TSK-GEL α-3000, 1.0 mL/min. Schematic structures of polymers **6d** and **8d** are also included.

Figure 7

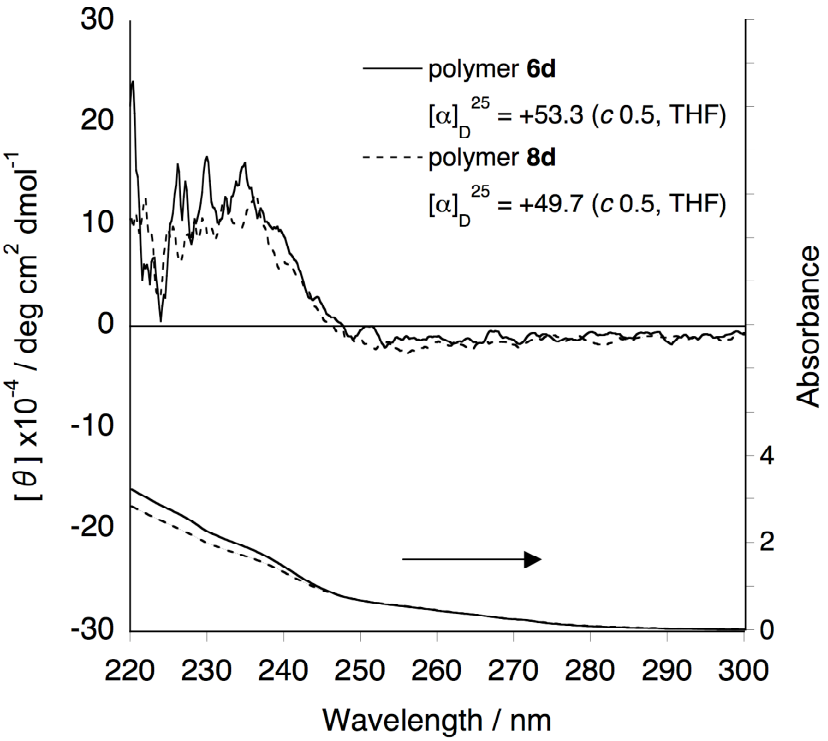
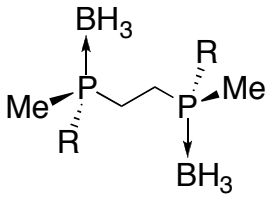


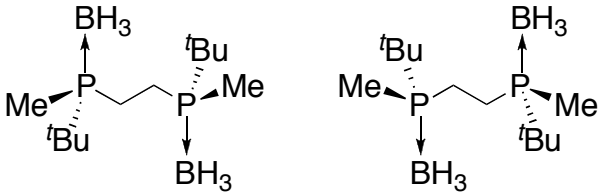

**Fig. 7**. CD spectra of polymers **6d** and **8d** (THF solution, $1.0 \times 10^{-5}$ M). The specific rotations of the polymers (THF, *c* 0.5) are included.

Structures of (*S,S*)-**1** and (*S,S*)-**5**



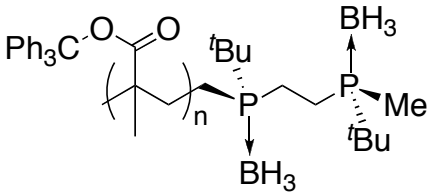

R = $^t$Bu, (*S,S*)-**1**
R = Ph, (*S,S*)-**5**

Structures of (*S,S*)-**1** and (*R,R*)-**1**

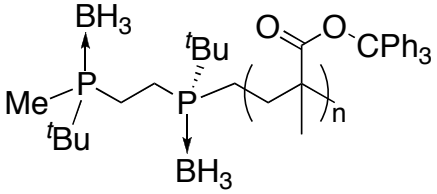



(*S,S*)-**1** (*R,R*)-**1**

Structures of polymers **3** and **4**




polymer **3**
from (*R,R*)-**1**




polymer **4**
from **1'**