Synthesis and coordination behaviors of P-stereogenic polymers†

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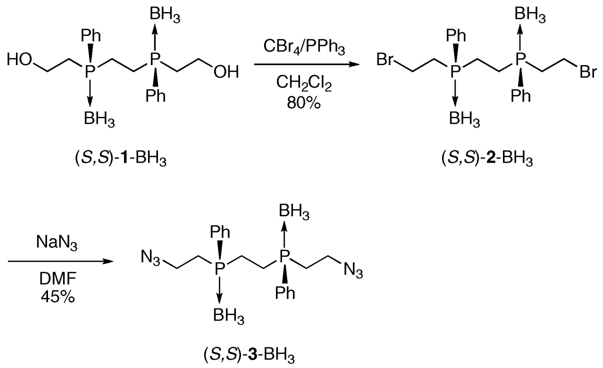
Optically active polymers containing P-stereogenic bisphosphine and 1,2,3-triazole units in the main chain were obtained by copper-catalyzed Huisgen cycloaddition. The repeating unit of the polymer adopted bidentate as well as tetradentate coordination, leading to the change in the conformations of the polymer *via* complexation with transition metals.

The functions of polymers are highly influenced by the higher-ordered structures of molecules and of the polymers themselves. Among the different higher-ordered structures, the one-handed helix, which is observed in naturally occurring macromolecules such as DNA molecules[1] (right-handed double helix) and polypeptides[2] (α-helix), is a representative example of a second-ordered structure. Their chiral higher-ordered structures are essential for maintaining biological activity in various organisms. The design and artificial construction of structurally analogous polymers[3] have attracted attention in polymer science; in particular, the control of the higher-ordered structures of polymers by external stimuli has been extensively investigated.[4] Yashima and coworkers found that optically inactive *cis*-transoid poly(phenylacetylene)s formed one-handed helix structures under the dynamic influence of chiral additives.[5] The chiral helix structure was maintained even after the replacement of chiral additives with achiral ones.[5c,d] It is reported that some foldamers enclosed chiral molecules within their cylindrical cavity through hydrophobic interactions to form one-handed helix structures.[6]

Metal ions can serve as a trigger for the conformational change in polymers possessing metal receptors such as crown ether[7] and bipyridine[8] moieties. Recently, we synthesized optically active polymers[9] and oligomers[10] containing phosphorus atoms, which can potentially capture transition metals, by using P-stereogenic bisphosphine compounds as monomers. The addition of transition metals to P-stereogenic polymers causes the polymers to undergo stimulus-induced conformation changes and thus form chiral higher-ordered structures. In this study, we investigate optically active polymers comprising P-stereogenic bisphosphine and 1,2,3-triazole units in the main chain, which exhibit drastic conformational changes in response to transition metal addition.

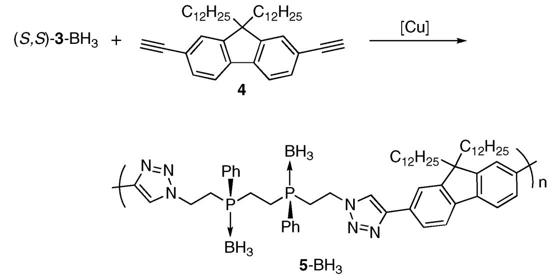


Scheme 1 Synthesis of monomer (*S*,*S*)-**3**–BH_3.

We incorporated the 1,2,3-triazole skeleton and P-stereogenic bisphosphine into a repeating unit of the polymer to ensure that the repeating unit adopts multidentate coordination when transition metals are added. We designed and synthesized monomer (*S*,*S*)-**3**–BH_3 from P-stereogenic bisphosphine (*S*,*S*)-**1**–BH_3,[11] as shown in Scheme 1.

It is noted that the P-stereocenters of bisphosphine retain their configuration during the reaction as well as during the next polymerization reaction. The Huisgen cycloaddition[12] polymerization of (*S*,*S*)-**3**–BH_3 with 9,9-didodecyl-2,7-diethynylfluorene **4** was carried out in the presence of a copper catalyst; this reaction is known as the click reaction.[13] The effect of the catalysts was examined (results listed in Table 1). For successful polymerization, it was important to use an appropriate catalyst combined with a solvent. The combination of the $Cu(MeCN)_4PF_6$ complex with $CHCl_3$ solvent was ineffective even in the presence of tridentate nitrogen ligands, and the low molecular weights of the obtained polymer resulted in the loss

Table 1 Results of the Huisgen cycloaddition polymerization[a]



Entry	Catalyst	Ligand	Solvent	Y[b] (%)	M_n[c]	M_w[c]
1	$Cu(MeCN)_4PF_6$	$(BimH)_3$[d]	$CHCl_3$	Trace	3300	3700
2	$Cu(MeCN)_4PF_6$	TBTA[e]	$CHCl_3$	21	2200	4300
3	$Cu(PPh_3)_3Br$	—	$CHCl_3$	45	6100	8000
4	$Cu(MeCN)_4PF_6$	—	DMF	69	7900	14 800
5[f]	$Cu(MeCN)_4PF_6$	—	DMF	75	16 500	42 000

[a] Condition: concentration of each monomer = 0.05 M, catalyst (10 mol%), ligand (10 mol%), 50 °C, 6 h. [b] Isolated yield. [c] Determined by GPC (polystyrene standards, $CHCl_3$ eluent). [d] Tris(2-benzimidazolylmethyl)amine. [e] Tris(benzyltriazolylmethyl)amine. [f] Concentration of each monomer = 0.20 M.

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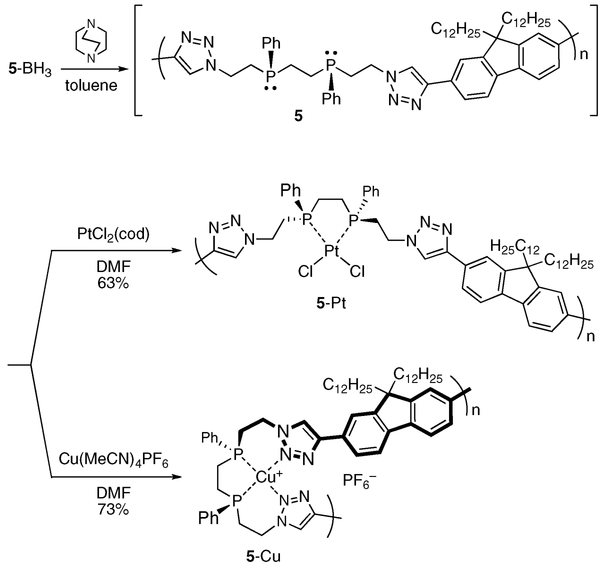

Scheme 2 Coordination behaviors of the P-stereogenic polymer.

of the polymer during the purification procedure (entries 1 and 2). The combination of $Cu(PPh_3)_3Br$ with $CHCl_3$ showed good catalytic activity (entry 3) to obtain polymer **5**–BH_3 with a yield of 45% and number-average molecular weight (M_n) of 6100 as estimated by gel permeation chromatography (GPC, polystyrene standards, $CHCl_3$ eluent). The $Cu(MeCN)_4PF_6$/DMF system enhanced the catalytic activity (entries 4 and 5), and a relatively concentrated solution (0.20 M) provided the best result (entry 5).

Coordinated boranes were completely removed by the reaction of **5**–BH_3 with 1,4-diazabicyclo[2.2.2]octane (DABCO) in toluene (Scheme 2). Successive treatment of **5** with $PtCl_2$(cod) (cod = 1,5-cyclooctadiene) and $Cu(MeCN)_4PF_6$ in DMF afforded the corresponding polymer complexes **5**–Pt and **5**–Cu with yields of 63% and 73%, respectively. The complexations of **5** with Pt and Cu were confirmed by ^{31}P and ^{1}H NMR spectra (Fig. 1). In the ^{31}P NMR spectra (Fig. 1a), the signal of the chiral phosphine in **5**–BH_3 appeared at +16.1 ppm. This signal was shifted downfield to +42.2 ppm by the complexation with $PtCl_2$, and the satellite peak assigned to phosphorus–platinum coupling ($J_{P–Pt}$ = 3577 Hz) was clearly observed. This $J_{P–Pt}$ value suggests the bidentate coordination of the bisphosphine unit to *cis*-Pt(II)Cl_2.[14] The broad signal in **5**–Cu was observed at −8.1 ppm. The upfield shift of the ^{31}P NMR signals by the coordination of phosphines to $Cu^+PF_6^-$ species was reported,[15] indicating the complexation of P-stereogenic phosphine units to $Cu^+PF_6^-$.

In the ^{1}H NMR spectra (Fig. 1b), the signal of the 1,2,3-triazole proton in **5**–BH_3 appeared at 7.66 ppm. This peak was slightly shifted to 7.78 ppm by the complexation with Pt, while the peak of **5**–Cu was observed at around 8.94 ppm.[16] The ^{1}H NMR chemical shift of the 1,2,3-triazole proton at around 9 ppm indicates the coordination of the 1,2,3-triazole moiety to Cu(I)$^+$.[17] Thus, the P-stereogenic phosphine unit of the polymer can undergo bidentate and tetradentate coordination depending on the metal ion used, *i.e.*, only bisphosphine coordinates to Pt(II)Cl_2 and both bisphosphine and 1,2,3-triazoles coordinate to Cu(I)$^+$. These NMR behaviors were also observed in the case of model compounds (Fig. S22 in ESI†).

Fig. 2 shows the circular dichroism (CD) and ultraviolet-visible (UV-vis) absorption spectra of **5**–BH_3, **5**–Pt, and **5**–Cu recorded in DMF (1.0×10^{-5} M) at room temperature. The UV-vis absorption spectra of **5**–BH_3, **5**–Pt, and **5**–Cu exhibited the same absorption band at 280–350 nm; this band was assigned to the π-conjugated triazolyl-fluorenylene-triazolyl unit in the polymer main chain. A relatively weak Cotton effect was observed in the CD spectrum of optically active **5**–BH_3 because of the flexible polymer backbone. In the CD spectrum of **5**–Pt, the coordination of the P-stereogenic bisphosphine units to Pt(II)Cl_2 resulted in the appearance of a strong Cotton effect in the range 280–350 nm. Coordination to Cu(I)$^+$ caused a drastic change in the chiroptical property, and the CD profile of **5**–Cu was distinct from those of **5**–BH_3 and **5**–Pt, as shown in Fig. 2. The coordination of the 1,2,3-triazole units in addition to the P-stereogenic centers is expected to contribute to the tetrahedral coordination, which triggers the chiral conformational change. The specific rotations of **5**–Pt ($[\alpha]^{25}_D$ 40.2, *c* 0.5 in $CHCl_3$) and **5**–Cu ($[\alpha]^{25}_D$ 8.4, *c* 0.5 in

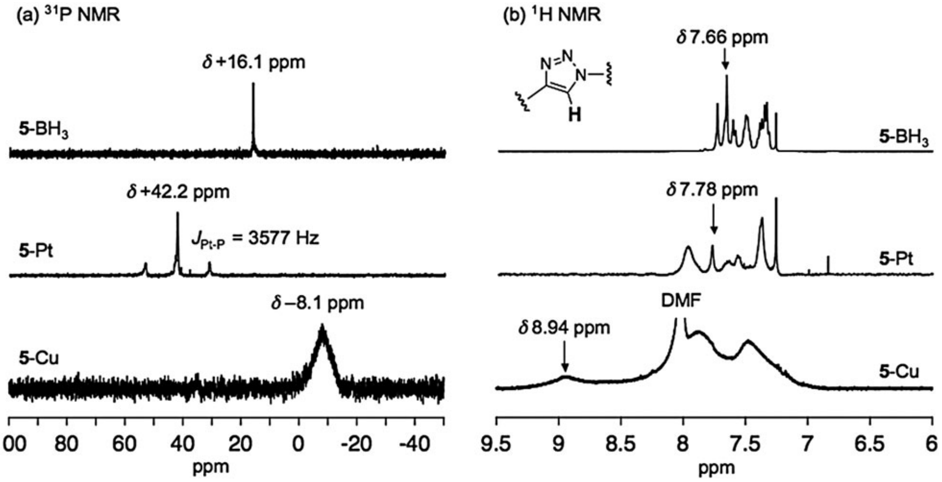

Fig. 1 (a) ^{31}P and (b) ^{1}H NMR spectra of **5**–BH_3 (in $CDCl_3$), **5**–Pt (in $CDCl_3$), and **5**–Cu (in DMF-d_7).

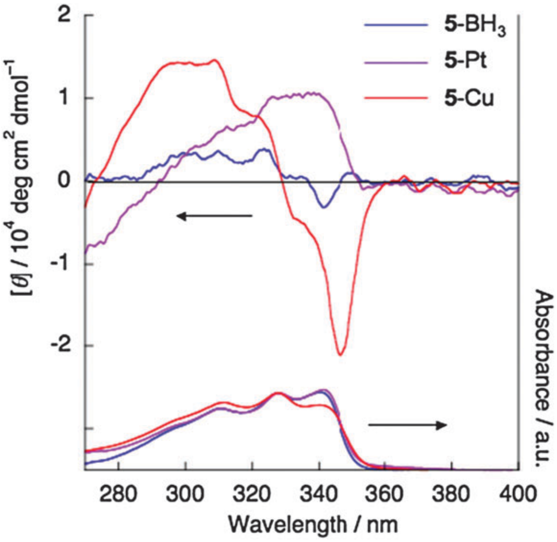

Fig. 2 CD (upper) and UV-vis absorption (lower) spectra of **5**–BH$_3$, **5**–Pt, and **5**–Cu in DMF (1.0×10^{-5} M) at room temperature.

CHCl$_3$) were relatively small, implying that the Cotton effect of the π-conjugated unit in the polymer arises from the chirality around the metal-complex moiety and the conformational change does not induce the chiral higher-ordered structure of the whole polymer chain due to the free rotation of the triazolyl-fluorenylene-triazolyl unit.

In summary, we synthesized optically active polymers containing P-stereogenic bisphosphine and 1,2,3-triazole moieties in the repeating unit by Huisgen cycloaddition polymerization. We demonstrated the drastic conformational change in the polymer *via* bidentate and tetradentate coordination to Pt(II) and Cu(I), respectively. Further investigations on the higher-ordered-structure changes of P-stereogenic polymers by the metal coordination that give rise to the colorimetric and/or fluorometric detection of metal ions are currently underway.

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