Use of Chiraphos as a Highly Efficient Ligand in the Nickel(II)-catalyzed Cross-coupling Polymerization for the synthesis of Poly(1,4-arylene)s

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(Citation)
Chemistry Letters,52(2):116-119

(Issue Date)
2023-02

(Resource Type)
journal article

(Version)
Accepted Manuscript

(URL)
https://hdl.handle.net/20.500.14094/0100482633

Use of Chiraphos as a Highly Efficient Ligand in the Nickel(II)-Catalyzed Cross-Coupling Polymerization for Poly(1,4-arylene)s

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Chiraphos (2,3-diphenylphosphinobutane) serves as a highly effective ligand for nickel catalyst in the cross-coupling polymerization reaction. Nickel(II) catalyst efficiently promotes the cross-coupling polymerization of 2,5-differently substituted 1,4-dihalobenzene particularly bearing a sterically congested substituent at the side chain affording the corresponding poly(1,4-phenylene). Such a highly active catalyst allowed the polymerization with diverse degree of polymerization with controlled molecular weight.

Keywords: Chiraphos, poly(1,4-phenylene), Nickel(II) catalyst.

Studies on ligand design in transition metal catalysis have attracted considerable attention in synthetic chemistry. The effective design plays a key role in unrevealed challenges into improved reactivities, selectivities, specificities, etc. in a wide range of catalytic synthetic reactions.[1,2] By using highly electron-donating ligands such as bulky alkylphosphines and N-heterocyclic carbenes, catalysis has led to a paradigm shift in cross-coupling chemistry that not only allows for smooth reactions with high turnover numbers/frequencies at sterically demanding reaction sites, but also allows for reactions to less active bonds to be catalytically activated.[3–6] In contrast, the effect of ligand design has remained rooms to be improved in polymer synthesis employing cross coupling strategies[7–13] and there exist limitations in their catalytic activities to achieve polymerization with controlled amount of degree of polymerization etc. Synthesis of π-conjugated poly[(hetero)arylene]s representative as poly(1,4-phenylene)s **1** and poly(3-substituted-thiophene)s **2** shown in Figure 1 has been of great interest in materials science since such polymers show remarkable characteristics as electronic materials.[14–17] The development of efficient preparative protocols is therefore a major concern in organic/polymer synthesis. Cross-coupling polymerization of (hetero)arylenes employing metalated haloarene **3** as an organometallic monomer has been a practical tool for the preparation of highly conjugated polymers.[18–21] In particular, polymerization that proceeds in a catalyst-transfer manner results in giving the well-defined polymer structure with controlled molecular weight based on the ratio of monomer feed/catalyst loading.[22–26] Bidentate phosphine DPPE[27] (**4**: 1,2-diphenylphosphinoethane) or DPPP[28] (**5**: 1,3-diphenylphosphinopropane) has been shown to serve as an effective ligand for the nickel(II) complex that undergoes polymerization smoothly in a catalyst-transfer manner and the use of which has allowed to give the corresponding polymers **1** and **2** with controllable molecular weight under living conditions.[29–32] However, *the catalysis still remains hitherto unremarked limitations in such polymer syntheses.* A sterically larger side chain in a monomer, for example, is critically inferior to their reactivities. If a smooth polymerization is successfully achieved in such steric demand, the diversity in the structural design can be dramatically extended in the synthesis of conjugated polymers.[33,34]

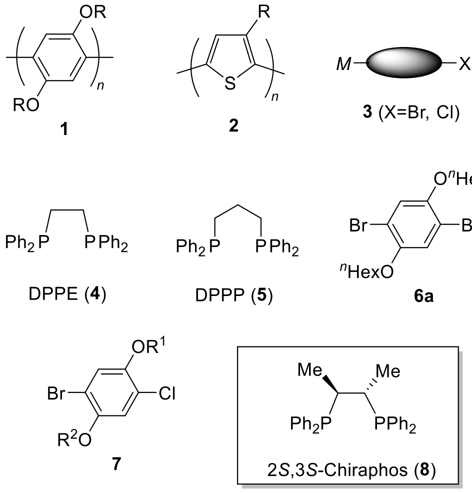


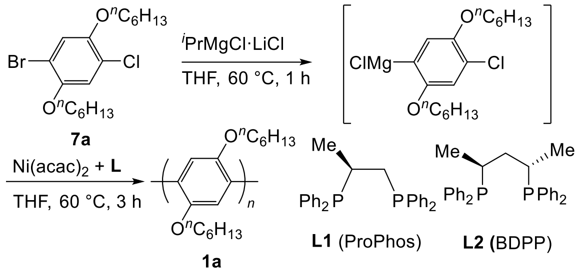
Figure 1. Poly(hetero)arenes with extended π-conjugation, monomer structures, and ligands for metal catalyst

Extensive studies for the synthesis of polythiophenes **2** have been pursued to date and highly regioregular polymers are obtained with controlled molecular weight and the molecular weight distribution employing the cross-coupling polymerization. In contrast, preparation methods of poly(1,4-phenylene)s **1**, in particular, in a scope of the side-chain structure have been less remarked. Synthetic studies for poly(1,4-phenylene) have only been examined employing a representative model substrate 2,5-dihexyloxy-1,4-dibromobenzene (**6a**) as a monomer precursor, which is converted into the organometallic monomer **3** (X = Br) by bromine-metal exchange and the cross-coupling polymerization follows by the addition of a metal catalyst.[35–37] Little case employing a more sterically demanding analog has been remarked so far in spite that the use of such a polymer extends significant potential in the structure design for advanced materials. Synthetic limitations have not been focused also on the use of organometallic (hetero)aryl chloride **3** (X = Cl) as a monomer because of less efficient activation of the carbon–chlorine bond,[38–40] accordingly, majority of poly(arylene) synthesis has been studied with related bromide or iodide derivatives.

We have recently reported polymerization of bromo(chloro)arene **7** bearing different OR and OR' substituents, which appeared the regioregularity issue in the obtained poly(1,4-arylene)[41] and it was found that the use of bidentate phosphine **4** or **5** as a ligand for nickel[42,43] afforded the polymer albeit insufficient catalyst transfer behavior suggesting living polymerization. We subsequently focused our concern to the preparation of regioregular poly(1,4-phenylene)s, in which development of highly active catalyst to afford the corresponding polymer with a controllable molecular weight based on the amount of catalyst loading. We herein report our findings that the use of Chiraphos (**8**) chiral 2*S*,3*S*-diphenylphosphinobutane a kind of bidentate phosphine ligand bearing a chiral carbon center[44–51] as a ligand for nickel realizes the highly effective polymerization of several organometallic monomers **3**, which has not been achieved successfully employing the conventional diphosphine ligands **4** and **5**.

In contrast that polymerization of dibromobenzene **6a** (OR^1, OR^2 = *n*-hexyl) with nickel catalyst bearing DPPE (**4**) or DPPP (**5**) has been shown to proceed in a living manner and the degree of polymerization agrees with the ratio of monomer feed and the catalyst loading,[35] our previous study shows that the related reaction with bromo(chloro)benzene **7a** (OR^1, OR^2 = *n*-hexyl) results in insufficient polymerization to afford the corresponding poly(1,4-phenylene) **1a** with much lower molecular weight when 1 mol% of $NiCl_2L$ (L = DPPE or DPPP) catalyst is employed.[41] (M_n = 13000–15000) Although slight improvement was found in the use of $Ni(acac)_2$ (acac: acetylacetonato) + ligand,[52–54] the degree of polymerization has been insufficient compared with the theoretical molecular weight based on the ratio of monomer feed/catalyst loading (M : 28000). We thus focused our attention on the development of a much more effective ligand for the efficient polymerization. Among a variety of ligands examined (See Supporting Information), it was found to show an enhanced reactivity when substituents are introduced on bridging carbon atoms in the bidentate phosphine ligand. In particular, Chiraphos[49] (**8**) bidentate phosphine bearing two methyl substituents on the ethylene bridge resulted in affording the highest molecular weight of polymer **1**. As summarized in Table 1, ProPhos **L1** and BDPP **L2** afforded polyphenylene **1a** with comparable or slightly superior M_n (entry 3 and 4) compared with DPPE or DPPP. When Chiraphs (**8**) was employed as a ligand, the molecular weight of **1a** was extremely high (entry 5, M_n = 25800), which was close to the theoretical M, along with the consumption of the most of the formed organometallic monomer.

Table 1. The effect of bidentate phosphine ligand of $Ni^{II}X_2$ to the result of the polymerization of bromo(chloro)benzene **7a**[a]

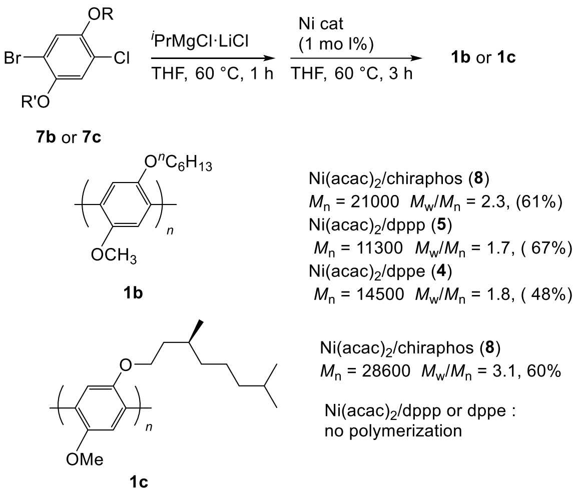


Entry	L	%Yield[b]	**1a** M_n (M_w/M_n)[c]
1	**4**	51	17900 (1.7)
2	**5**	51	15000 (1.9)
3	**L1** (ProPhos)	75	18700 (1.9)
4	**L2** (BDPP)	57	19200 (1.9)
5	Chiraphos (**8**)	56	25800 (1.7)

[a] The reaction was carried out with an equimolar amount of $Ni(acac)_2$ and ligand L. The formation of nickel complex was carried out by the reaction of the ligand (0.003 mmol) and $Ni(acac)_2$ (0.003 mmol) at room temperature for 1 h in THF. The polymerization reaction was carried out with **7a** (0.3 mmol) in 0.3 mL of THF. [b] Isolated yield. [c] Molecular weight and the molecular weight distribution of isolated **1a** based on SEC analysis.

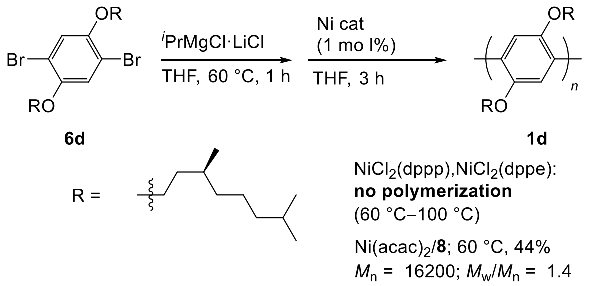
The distinguished catalytic activity of the nickel(II) Chiraphos complex is also remarkable as shown in Scheme 1 in the polymerization reaction of bromo(chloro)benzene bearing *n*-hexyl and methyl groups at the 2 and 5-positions (**7b**), respectively. When the reaction was carried out by the reaction of **7b** with ^{i}PrMgCl·LiCl in THF at 60 °C for 1 h to undergo halogen-metal exchange preferentially at the bromine atom followed by the nickel-catalyzed polymerization of the obtained organometallic monomer for 3 h, polymer **1b** was obtained with remarkably high molecular weight (M_n = 21000; M_w/M_n = 2.3) in 61% isolated yield. The obtained polymer was also regioregular as confirmed by ^{13}C NMR spectrum (see supporting information) similar to the case reported previously.[41] The M_n value was rather close to that of the theoretical one based on the ratio of catalyst loading and monomer feed (1.0 mol%, theoretical M = 21000 at complete consumption of the monomer) whereas the molecular weight distribution was still broader. In contrast, the polymerization of **7b** under similar conditions using nickel(II)–dppp (**5**) complex resulted to afford polymer **1b** with much lower molecular weight of M_n = 11300 with M_w/M_n = 1.7 in 67% yield. The result indicated that the molecular weight of the obtained polymer **1b** was marginal to the theoretical one. When the related bidentate phosphine DPPE (**4**) was employed in a similar manner to the case of DPPP (**5**), the molecular weight of **1b** was M_n = 14500 and M_w/M_n = 1.8 with the yield of 48%, which M_n was also much smaller. In addition, the marked difference in the reactivity of the polymerization catalyst was found in the reaction of bromo(chloro)benzene **7c** bearing a terpene-derived chiral substituent. The reaction with nickel catalyst bearing Chiraphos (**8**) as a ligand smoothly proceeded at 60 °C to afford poly(1,4-phenylene) **1c** with M_n=28600 and M_w/M_n=3.1 in 60%, while no polymerization took place at all in the use of conventional ligands DPPE (**4**) and DPPP (**5**) under similar conditions. (The reaction temperature at 100 °C has been the requirement to afford polymer **1c**).[41]

These results clearly show that the catalytic activity of nickel(II) complex bearing DPPE (**4**) and DPPP (**5**) is revealed to be much inferior particularly when a sterically larger substituent is introduced into the alkoxy group at the 2- or 5-position, while the use of Chiraphos (**8**) shows remarkably improved polymerization performance.



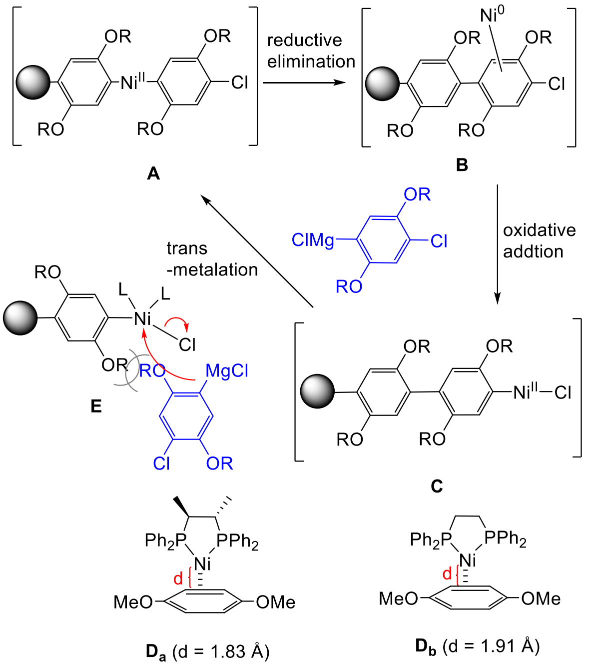
Scheme 1. Nickel(II)-catalyzed polymerization of bromo(chloro)arene **7**

The effect of Chiraphos as a ligand was also shown to be remarkable in the reaction of dibromoarene **6d**, in which the terpene derived chiral branched substituents were introduced at both 2- and 5-positions of the benzene ring.[55] When the reaction of **6d** was carried out with Ni(acac)$_2$/Chiraphos (**8**), the reaction proceeded at 60 °C for 3 h to afford the corresponding polymer **1d** with M_n =16200 and M_w/M_n = 1.43 in 44% yield. In a sharp contrast, no reaction was found to take place at all in the use of DPPP (**5**) and DPPE (**4**) during the temperature range of 60–100 °C as shown in Scheme 2.



Scheme 2. Polymerization of dibromo arene **6d** bearing chiral substituents

It has been recognized that cross-coupling polymerization of metalated (hetero)haloarenes **3** with nickel as a catalyst proceeds in a catalyst transfer manner as depicted in Scheme 3, where reductive elimination of intermediate **A** occurs through the C–C bond formation to give **B** and oxidative addition of the π-coordinated nickel(0) in the polymer chain into the terminal carbon–halogen follows leading to **C**.[7,31] The sequence is considered to proceed through the migration of the catalyst species along the π-interaction of the catalyst metal with the π-bond of the conjugating polymer main chain, which is illustrative as intermediate **B**. The stronger electron donation of the ligand to nickel would favor the following oxidative addition leading to **C**, which is particularly desired for the slow reaction to C–Cl bond. The use of Chiraphos (**8**) suggesting the electron-donating characteristics induced by the branched structure in the bridging methylene of **8**,[56] would be likely in oxidative addition to afford **C**. Otherwise, unexpected dissociation of catalyst species from polyphenylene **B** brings about undesired termination of the polymerization. However, too much electron-donating effect disturbs π-coordination from the polymer chain in **B**. In addition, transmetalation would also be retarded by the steric effect of OR groups shown as **E** particularly when a bulky R group is introduced.



Scheme 3. Mechanistic aspect of catalyst transfer polymerization to afford poly(1,4-phenylene) **1**

The key for the successful cross-coupling polymerization would be the well-balanced electronic ligand effect of nickel catalyst in preferable π-interaction as well as oxidative addition to terminal carbon–halogen bond, accordingly. DFT calculation of a model compound as nickel complex of 1,4-dimethoxybenzene $\mathbf{D_a}$ employing Chiraphos (**8**) showed the bond length of d to be 1.83 Å, while that of DPPE (**4**) shown as $\mathbf{D_b}$ was much longer (1.91 Å) suggesting easier dessociation.[57] The result shows that the intermediate **B** bearing Chiraphos as a ligand is more stabilized than that bearing DPPE (**4**) despite superior electron donation from Chiraphos to nickel because of the effect of the branched bridging structure and thus the stabilized **B** avoids the dissociation of nickel(0) efficiently from the polymer chain. As a result, the improved stability of **B** with Chiraphos would compensate inferior oxidative addition to the carbon–chlorine bond to result in successful polymerization.

In summary, we have shown that Chiraphos (**8**) serves as a remarkably efficient ligand for the nickel catalyst toward the catalyst-transfer-type cross-coupling polymerization of (hetero)arylenes such as poly(1,4-phenylene)s. The use of Chiraphos as a ligand improved the catalytic activity and thus allowed to overwhelm hitherto less remarked limitation in the steric demand for the synthesis of conjugated polymers whereas further improvement in the control of molecular weight as well as higher catalytic activity is necessary. Accordingly, Chiraphos (**8**) would extend the scope of structural diversity of conjugated polymers toward intelligent material design.

This work was supported by Kakenhi B by the MEXT (JP19182273).

Supporting Information is available on http://dx.doi.org/10.1246/cl.******.

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