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Palladium-Catalyzed Polycondensation of Diiodobenzenes with 1,3-Bis(phenylphosphino)propane and Preparation of Polymer Transition-Metal Complexes

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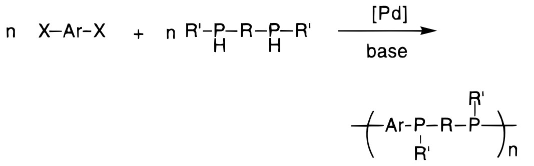
Polymer-bound transition-metal catalysts have attracted a great deal of interest for exploitation in industrial organic reactions.[1] Phosphine compounds are an important class of ligands for various transition metals; therefore, a large number of phosphinated polymers and polymer-anchored transition-metal complexes have been synthesized and characterized.[1,2] On the other hand, palladium and nickel complexes have been reported to catalyze reactions of aryl halides with (trimethylstannyl)diphenylphosphine,[3] (trimethylsilyl)diphenylphosphine,[3] chlorodiphenylphosphine,[4] and secondary diphenylphosphine[5] to give triarylphosphines. However, preparation of polyphosphines using organometallic processes has been limited.[2,6]

These observations described above prompted us to examine utility of the Pd-catalyzed carbon−phosphine cross-coupling reaction in a polycondensation of aryl dihalides with secondary diphosphine to afford new poly(arylenediphosphine)s.



$$n\ X{-}Ar{-}X + n\ R'{-}\underset{H}{P}{-}R{-}\underset{H}{P}{-}R' \xrightarrow[\text{base}]{[Pd]} \left(Ar{-}\underset{R'}{P}{-}R{-}\overset{R'}{P} \right)_n \qquad (1)$$

Because the obtained polymer has a bidentate bis(phosphine) ligand structure in the polymer backbone, the polycondensation is expected to provide new polymer-chelating ligands. In contrast to the recent active study of the chelating polymer complexes constituted of imine nitrogen-containing heterocycles in the polymer backbone,[7] to our knowledge, there is no report on the intramolecularly chelating polyphosphine with a phosphorus functional group on the polymer backbone. We here report the results of the Pd-catalyzed polycondensation of aryl diiodides with 1,3-bis(phenylphosphino)propane[8] (**1**) to give new poly(arylenediphosphine)s, and the preliminary coordinating properties of the polymers toward transition metals are also reported.

A typical reaction procedure is as follows. A mixture of 1,4-diiodobenzene (660 mg, 2 mmol) and **1** (521 mg, 2 mmol) was dissolved in *N*,*N*-dimethylacetamide (DMAc) (15 mL). Palladium(II) chloride (9 mg, 0.05 mmol) and potassium acetate (KOAc) (589 mg, 6 mmol) were added to the solution at room temperature. The reaction mixture was stirred at 130 °C for 24 h under nitrogen. After cooling to room temperature, the mixture was poured into a mixture of aqueous ammonia (50 mL) and methanol (200 mL). The precipitate was washed thoroughly with methanol, and reprecipitation from $CHCl_3$/ether gave a pale orange powder of poly[(phenylphosphinediyl)trimethylene(phenylphosphinediyl)-1,4-phenylene] (poly-**1**) (547 mg, 82% yield). Anal. Calcd for $(C_{21}H_{20}P_2)_n$: C, 75.4; H, 6.0. Found: C, 73.5; H, 5.8; I, 0.5.

Table 1. Palladium-Catalyzed Polycondensation of 1,4-Diiodobenzene with 1[a]

run	catalyst[b]	solvent	base	temp (°C)	yield[c] (%)	η_{inh}[d] (g dL^{-1})
1	$PdCl_2$	DMAc	KOAc	130	82	0.12
2	$Pd(OAc)_2$	DMAc	KOAc	130	74	0.12
3	$Pd(PPh_3)_4$	DMAc	KOAc	130	81	0.12
4	$NiCl_2DPPE$	DMAc	KOAc	130	trace	
5	none[e]	DMAc	KOAc	0		
6	$PdCl_2$	DMAc	KOAc	100	70	0.08
7	$PdCl_2$	DMAc	KOAc	65	0	
8	$PdCl_2$	toluene	KOAc	100	72	0.09
9	$PdCl_2$	dioxane	KOAc	100	40	0.04
10	$PdCl_2$	DMAc	K_2CO_3	130	73	0.09
11	$PdCl_2$	DMAc	NaO-*t*-Bu	130	0	
12[f]	$PdCl_2$	DMAc	KOAc	130	82	0.13

[a] Reactions were carried out in the presence of catalyst (2.5 mol % for monomer) and base (3 equiv for monomer) for 24 h under nitrogen. [b] $Pd(OAc)_2$ = palladium acetate, $Pd(PPh_3)_4$ = tetrakis(triphenylphosphine) palladium(0), $NiCl_2DPPE$ = dichloro(1,2-bis(diphenylphosphino)ethane) nickel(II). [c] Fraction insoluble in methanol and ether. [d] Measured at a concentration of 1.0 g dL^{-1} in $CHCl_3$ at 30 °C using Ubbelohde viscometer. [e] No catalyst was added. [f] Triphenylphosphine (4 equiv for $PdCl_2$) was added.

Table 1 summarizes the results of the Pd-catalyzed polycondensation of 1,4-diiodobenzene with **1** under various conditions. As shown in Table 1, the Pd-catalyzed polycondensation gave poly-**1** in good yields in DMAc over 100 °C for 24 h. The reaction did not proceed in the absence of the catalyst, and nickel complex would not be an effective catalyst for the polycondensation. The addition of phosphine ligands such as triphenylphosphine, 1,3-bis(diphenylphosphino)propane (DPPP), and 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl was scarcely effective for the polycondensation.

Poly-**1** exhibits good solubility in polar solvents such as DMAc, *N*,*N*-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), and chloroform. Poly-**1** (run 1 in Table 1) has a number-average molecular weight (M_n) of 5400 (degree of polymerization = ca. 16), as determined by VPO.[9]

The IR spectrum of poly-**1** is essentially similar to that of DPPP, which supports the proposed structure of the polymer. No absorbance of the ν(P−H) band (2280 cm^{-1} for **1**) was observed. Figure 1 shows ^1H, ^{13}C, and ^{31}P NMR spectra of poly-**1** in $CDCl_3$. The peaks were assigned by comparison of the peak positions of poly-**1** with those of monomers and DPPP. The ^{13}C NMR spectrum was also confirmed by DEPT spectrum. In Figure 1a, no peak assignable to P−H (δ 4.07 ppm for **1**) group is observed. The ratios of the peak area agree with the suggested assignment. Minor resonance in the spectra would be attributed to the presence of phosphine oxide, which would be formed concomitantly by the aqueous workup.[10] In the ^{31}P NMR spectrum, a major peak at δ −18.2 ppm is attributed to tertiary phosphine group of the recurring unit. A small peak assignable to phosphine oxide is observed at δ 31.5 ppm, and a small

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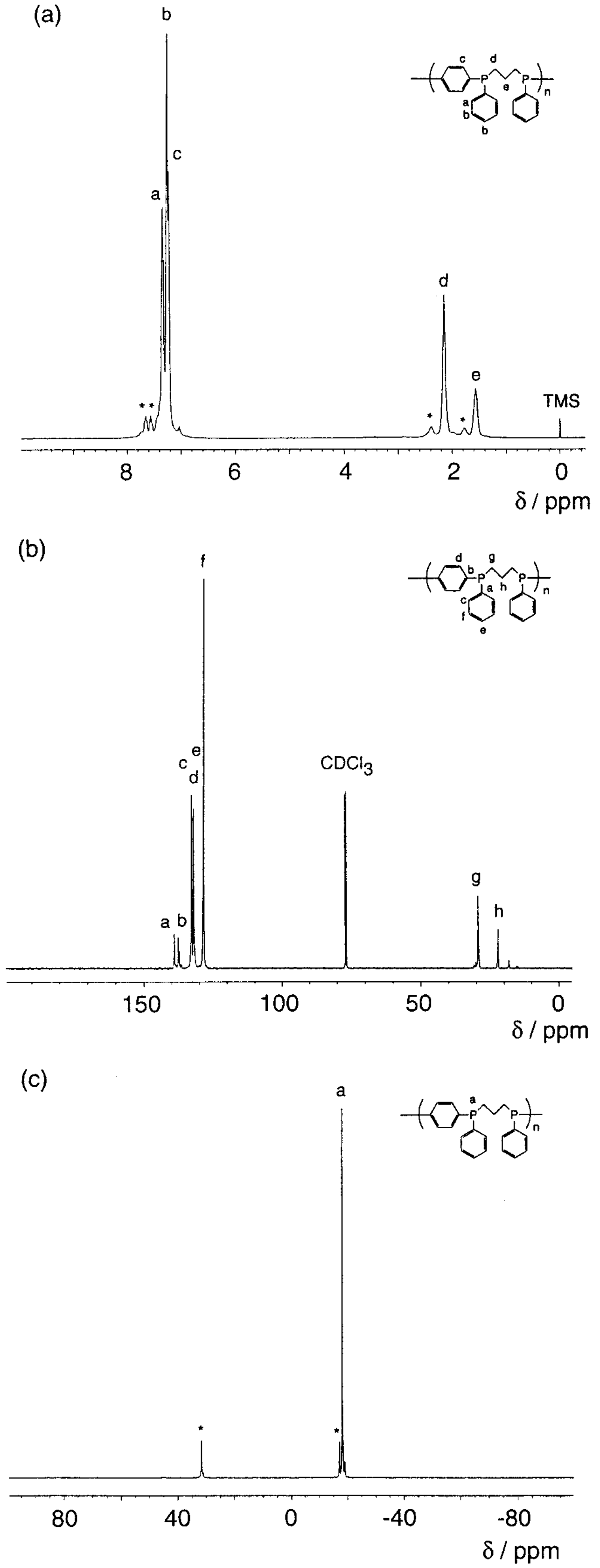
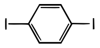
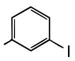
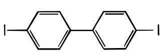
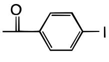
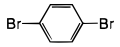


Figure 1. ^{1}H (a), ^{13}C (b), and ^{31}P (c) NMR spectra of poly-**1** in $CDCl_3$. Peaks with asterisks are correlated with oxidized phosphine unit.

peak at δ −17.2 ppm would be assigned to tertiary phosphine adjacent to phosphine oxide unit. No peak assignable to the P−H (δ −53.6 ppm for **1**) group is detected.

Table 2. Palladium-Catalyzed Polycondensation of Aryl Dihalides with 1[a]

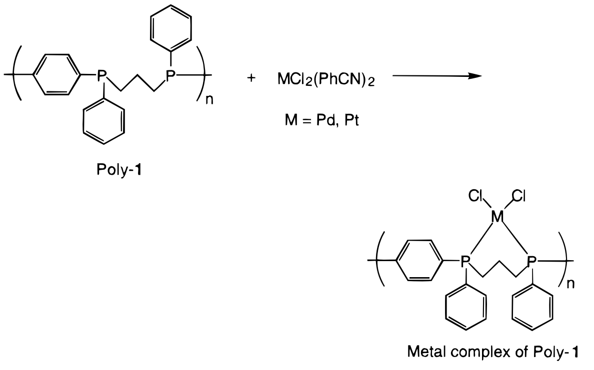
Run	Aryl Dihalide	Yield[b] / %	η_{inh}[c] / g dL^{-1}	M_n[d] x 10^{-3}
1		82	0.12	5.4
2		78	0.07	3.3
3		99	0.16	7.1
4		94	0.24	11.0
5		41	0.14	-[e]
6		23	0.04	-[e]

[a] The polycondensation of aryl dihalide (2 mmol) and **1** (2 mmol) was carried out in the presence of $PdCl_2$ (0.05 mmol) and KOAc (6 mmol) in DMAc (15 mL) at 130 °C for 24 h. [b] Fraction insoluble in methanol and ether. [c] Measured at a concentration of 1.0 g dL^{-1} in $CHCl_3$ at 30 °C using Ubbelohde viscometer. [d] Measured by VPO in $CHCl_3$ at 30 °C. [e] Not measured.

A powder of poly-**1** was fairly stable under air, whereas poly-**1** in chloroform solution was gradually oxidized under air. After being stirred vigorously, the ^{1}H NMR spectrum of the $CDCl_3$ solution of poly-**1** under air for 1 week exhibited an increase of the signal at δ 2.4 ppm attributed to the methylene protons neighboring on the phosphine oxide.

Table 2 summarizes the results of the Pd-catalyzed polycondensation of several aryl dihalides with **1** under the same conditions as that of run 1 in Table 1. The structures of the polymers were confirmed by IR and NMR spectroscopy. Some functional groups such as ether and ester are tolerated by the Pd-catalyzed polycondensation. The comparison of the yields and η_{inh} values implies that the reaction using aryl diiodides proceeds faster than that using the dibromide analogues and the electron-withdrawing property of ester moiety would decrease the reactivity of the monomer.

The poly(arylenediphosphine)s consist of repeating units analogous to DPPP, which is one of the most useful chelating phosphine ligand to form a variety of transition-metal complexes. To explore the metal coordination properties of the polymers, we reacted the polymers with dichlorobis(benzonitrile) palladium(II) ($PdCl_2(PhCN)_2$) and dichlorobis(benzonitrile) platinum-(II) ($PtCl_2(PhCN)_2$).[11]



(2)

A typical reaction procedure is as follows. Poly-**1** (117 mg, 0.35 mmol of monomer unit) was dissolved in DMF (10 mL). $PdCl_2(PhCN)_2$ (142 mg, 0.37 mmol) was added to the solution, and the solution was stirred at 100 °C for 1 h under nitrogen. After cooling to room temperature, the mixture was poured into acetone (100 mL). The precipitate was washed thoroughly with acetone and ether to give a yellow powder of polymer−palladium complex (168 mg, relative recovery of polymer 97%). Anal. Calcd for $[(C_{21}H_{20}Cl_2P_2Pd)_{0.90} + (C_{21}H_{20}O_2P_2)_{0.10}]_n$: C, 50.7; H, 4.1; Cl, 12.8. Found: C, 48.1; H, 4.1; N, 0.0; Cl, 11.8. IR (KBr, cm^{-1}): 3044, 2907, 1663, 1482, 1435, 1385, 1154, 1099, 790, 745, 691, 552. ^1H NMR (400 MHz, in DMSO-d_6, ppm): δ 1.6 (2H, br), 2.7 (4H, br), 7.2−8.2 (14H, br). ^{13}C NMR (100 MHz, in DMSO-d_6, ppm): δ 18.2, 23.7, 128.8, 130.4, 132.0, 133.1. ^{31}P NMR (160 MHz, in DMSO-d_6, ppm): δ 12.4, 27.5, 29.5.

Reactions of poly-**1** with $PdCl_2(PhCN)_2$ and $PtCl_2(PhCN)_2$ in DMF afforded brownish yellow and pale yellow precipitates, respectively. The Pd complex of poly-**1** is soluble in polar solvents such as DMF and DMSO but insoluble in toluene and chloroform, whereas the Pt complex of poly-**1** exhibits poor solubility in common organic solvents. In the ^{31}P NMR spectrum of the Pd complex of poly-**1**, a main peak is observed at δ 12.4 ppm, which is assignable to tertiary phosphine taking part in complex formation with Pd(II). The resonance correlated well with the spectrum of dichloro[1,3-bis(diphenylphosphino)propane] palladium(II) ($PdCl_2DPPP$) (δ_p 12.9 ppm).[11] A resonance peak at δ −18.2 ppm of uncoordinated tertiary phosphine is scarcely observed, and the presence of the peaks at δ 27.5 and 29.5 ppm implies that the uncoordinated phosphine was oxidized during the workup. In the ^{31}P NMR spectrum of DMSO-soluble fraction of the Pt complex of poly-**1**, the resonance peak of tertiary phosphine coordinated to Pt(II) is observed at δ −4.9 ppm with an associated pair of $^{195}Pt-^{31}P$ satellites (^1J ($^{195}Pt-^{31}P$) = 3387 Hz). The resonance also correlated well with the spectrum of dichloro[1,3-bis(diphenylphosphino)propane] platinum(II) ($PtCl_2DPPP$) (δ_p −5.6 ppm, ^1J ($^{195}Pt-^{31}P$) = 3420 Hz).[11c] The poly(arylenediphosphine) prepared from 1,6-bis(4-iodophenoxy)hexane and **1** (run 4 in Table 2, poly-**2**) also formed polymer complexes with Pd(II) and Pt(II). The ^{31}P NMR spectra of poly-**2** treated with $PdCl_2(PhCN)_2$ and $PtCl_2(PhCN)_2$ also exhibit a new signal of tertiary phosphine coordinated to the metals at δ 10.4 and −7.0 (^1J ($^{195}Pt-^{31}P$) = 3398 Hz) ppm, respectively.

The obtained polymer complexes are stable in air. The transition-metal contents of the polymer complexes were determined by inductively coupled plasma atomic emission spectrometry (ICP-AES).[12] The Pd(II) and Pt(II) complexes of poly-**1** contain 19 and 22 wt % of transition metal, which imply that approximately 90 and 55 mol % of repeating unit of poly-**1** form the complexes with Pd(II) and Pt(II), respectively. The values roughly agree with the degree of coordination of poly-**1** to Pd(II) and Pt(II) estimated from Cl contents of the samples determined by elemental analysis. The metal contents of the polymers may be affected by the solubility of the polymer metal complexes. These results indicate that the poly(arylenediphosphine)s have available bidentate ligand structure with coordinating ability toward transition metals.

As described above, new poly(arylenediphosphine)s were obtained by the Pd-catalyzed polycondensation. Although the present synthesis is limited and molecular weights of the products are not high in the present study, the polycondensation may provide a variety of poly(arylenediphosphine)s by changing the structure of aryl dihalides and secondary diphosphines. The obtained polymers contain chelating ligand structure in the polymer backbone that is able to form chelate complexes with Pd(II) and Pt(II). Thus, the polymers are possible polymeric supports for various transition metals and would be capable of forming polymer complexes. Further studies including preparation of other polyphosphines and properties of the polymer complexes are in progress.

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Supporting Information Available: The ^{31}P NMR spectra of the Pd complex of poly-**1** and the DMSO soluble fraction of Pt complex of poly-**1** in DMSO-d_6. This material is available free of charge via the Internet at http://pubs.acs.org.

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(8) Of the air-sensitive secondary diphosphines, only **1** is commercially available (Strem).

(9) Measurement of M_n was carried out with a Knauer VPO Type 11.00 in $CHCl_3$ at 30 °C. The poly(arylenediphosphine)s did not elute from a gel permeation chromatograph using $CHCl_3$ and DMF as the elution solvent.

(10) The coexistence of phosphine oxide unit in poly-**1** makes the assignment of the possible end group difficult.

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(12) The amount of transition metals incorporated in the polymers was determined by decomposing the weighted samples into aqua regia and measuring the concentration of the metals with a Perkin-Elmer Optima 3000XL.

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