Preparation of Poly(imino-1,3-phenylene) and Its Related Polymer by Palladium-catalyzed Polycondensation

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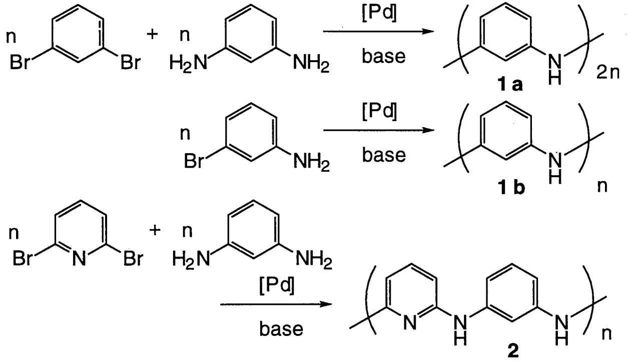
Palladium-catalyzed polycondensation reactions of 1,3-dibromobenzene with 1,3-phenylenediamine and 3-bromoaniline afforded soluble poly(imino-1,3-phenylene) in moderate to good yields. Poly(imino-2,6-pyridinediylimino-1,3-phenylene) was also prepared in an analogous way.

Recent developments in the palladium-catalyzed amination of aryl halides offer advantages over the classical methods which require either activated substrates or severe reaction conditions.[1] We have examined utility of the Pd-catalyzed amination in the polycondensation of aryl dibromides with secondary diamines to afford poly(arylenediamine)s.[2]

On the other hand, molecular design and syntheses of organic ferromagnets are one of the most challenging themes in synthetic metals. Recently, poly(imino-1,3-phenylene) (so-called poly(*m*-aniline)) has been prepared by the Ullmann condensation reaction of 3-halogenated aniline or 1,3-dibromobenzene with 1,3-phenylenediamine.[3] The polymer exhibited ferromagnetic interaction after oxidation.[3b,c,4] However, the polymer showed low solubility presumably due to a partial cross-linked structure.[3c,d] Preparation of regioregular and soluble polymer would be crucial for study of ferromagnetic polymers. In the course of our investigation on the Pd-catalyzed polycondensation, we have found that the polycondensation of 1,3-dibromobenzene with 1,3-phenylenediamine or 3-bromoaniline gives soluble poly(imino-1,3-phenylene) (**1a**,**b**). We here report results of preparation of poly(imino-1,3-phenylene) and its related poly(iminoarylene).



A mixture of 1,3-dibromobenzene (472 mg, 2 mmol) and 1,3-phenylenediamine (216 mg, 2 mmol) was dissolved in toluene (15 cm^3). NaO-*t*-Bu (577 mg, 6 mmol), tris(dibenzylideneacetone)dipalladium ($Pd_2(dba)_3$) (458 mg, 0.05 mmol), and 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl (BINAP) (93 mg, 0.15 mmol) were added to the solution at room temperature. The reaction mixture was stirred at 100 °C for 16 h under nitrogen to yield a reddish brown precipitate. After cooling to room temperature, the mixture was poured into methanol, and the precipitate was separated by filtration. A reddish brown powder of **1a** was purified by reprecipitation from formic acid/aqueous ammonia followed by washing thoroughly with methanol (313 mg, 86% yield). Anal. Found: C, 78.8; H, 5.6; N, 14.4; Br, 0.0%. Calcd for $(C_6H_5N)_n$: C, 79.1, H, 5.5, N, 15.4%. Other reactions were carried out analogously.

Table 1. Pd-catalyzed polycondensation of 1,3-dibromobenzene with 1,3-phenylenediamine using various ligands[a]

Run	Ligand[b]	Yield[c] /%	M_n[d]	M_w[d]
1	BINAP	86	20100	42400
2	DPPP	13	—[f]	—[f]
3	P(*o*-tolyl)$_3$	30	20400	35200
4	P(*t*-butyl)$_3$	48	10500	17500
5[e]	none	0	—	—

[a] The polycondensation of 1,3-dibromobenzene (2 mmol) and 1,3-phenylenediamine (2 mmol) was carried out in the presence of $Pd_2(dba)_3$ (0.05 mmol), ligand (P/Pd ratio = 3/1), and NaO-*t*-Bu (6 mmol) in toluene at 100 °C. [b] DPPP = 1,3-bis(diphenylphosphino)propane; P(*o*-tolyl)$_3$ = tri-*o*-tolylphosphine; P(*t*-butyl)$_3$ = tri-*t*-butylphosphine. [c] Insoluble fraction in methanol. [d] Calibrated by GPC (LiCl/DMF (0.01 M), polystyrene standards). [e] No catalyst was added. [f] Oligomeric product.

Table 1 summarizes the results of the Pd-catalyzed polycondensation of 1,3-dibromobenzene with 1,3-phenylenediamine under various conditions. In the present study, a combination of $Pd_2(dba)_3$ and BINAP is the most effective catalyst to give the polymer with high molecular weight. Use of other phosphine ligands gave the polymer in lower yields. BINAP has been found to be effective ligand for the Pd-catalyzed aryl amination of aryl bromides with primary amines.[1c] Use of 1,3-phenylenediamine as monomer would prevent the undesired side reaction involving β-hydrogen elimination reaction of Pd intermediate.[1a,b]

IR spectrum of **1a** is almost identical to that of the previously reported polymer,[3] showing absorption bands of skeletal in-plane ring vibration (1585, 1487 cm^{-1}), C-H out-of-plane bending (840, 768, 688 cm^{-1}), and N-H stretching (3384 cm^{-1}). Polymer **1a** is soluble in DMF, DMSO, NMP, and formic acid. Figure 1 shows the ^1H and ^{13}C NMR spectra of **1a** in DMSO-d_6. In Figure 1(a), the ratios of the peak area agree with the suggested assignment. The ^{13}C NMR spectrum shows 4 peaks. The peaks were confirmed by DEPT spectra. The IR and NMR data and high solubility of **1a** indicate that the polycondensation provides no or scarcely cross-linked poly(imino-1,3-phenylene). The Pd-catalyzed aryl amination of aryl bromide with primary amine would be much faster than that with secondary amine. Low solubility of **1a** in toluene might suppress the cross-linking reaction.

Table 2 summarizes the results of the Pd-catalyzed polycondensation reactions of 3-halogenated anilines and 2,6-dibromopyridine with 1,3-phenylenediamine using the same conditions as those of Run 1 in Table 1. Use of 3-bromoaniline as monomer also gave **1b** in a moderate yield. On the other hand,

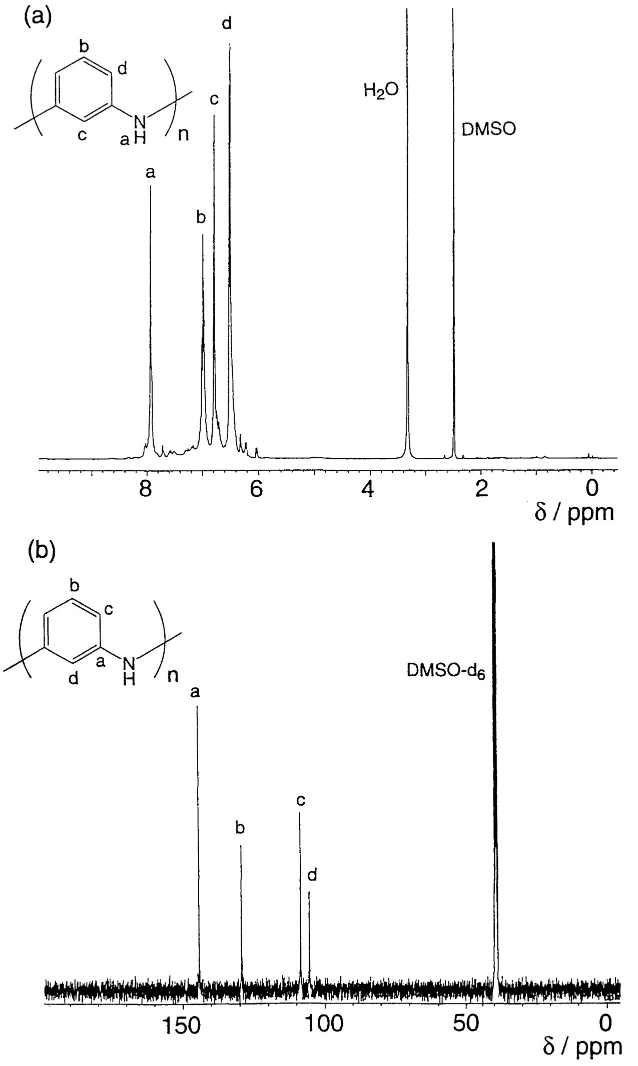
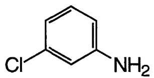
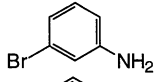
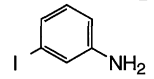
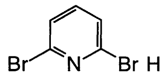
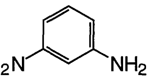


Figure 1. ${}^{1}H$ (a) and ${}^{13}C$ (b) NMR spectra of **1a** in DMSO-d_6.

the reaction employing 3-iodoaniline afforded lower yield of the polymer, and use of 3-chloroaniline did not give the product. In relation to the preparation of poly(imino-1,3-phenylene), polycondensation of 2,6-dibromopyridine with 1,3-phenylenediamine afforded poly(imino-2,6-pyridinediylimino-1,3-phenylene) (**2**) in a good yield.[5] Polymer **2** is soluble in formic acid and partially soluble in DMF, DMSO, and NMP.

As described above, soluble poly(imino-1,3-phenylene) with high molecular weight has been easily obtained by the Pd-catalyzed polycondensation. Since the polycondensation could afford various poly(iminoarylene)s constituted of same or alternating aromatic units by changing the structure of aryl dibromides and aryl diamines, the polycondensation may provide new high-spin polymers. Further studies for obtaining the appropriate conditions for polymerization as well as preparation of other poly(iminoarylene)s are now in progress.

Table 2. Pd-catalyzed polycondensation of 3-halogenated anilines and 2,6-dibromopyridine with 1,3-phenylenediamine[a]

Run	Monomer	Yield[b]/%	M_n[c]	M_w[c]
1		0	—	—
2		46	12300	23100
3		20	12900	16800
4	 	77	21800[d]	34700[d]

[a]The reactions of 3-halogenated anilines (4 mmol) (Run 1-3) and 2,6-dibromopyridine (2 mmol) with 1,3-phenylenediamine (2 mmol) (Run 4) were conducted similarly to that of Run 1 in Table 1. [b]Insoluble fraction in methanol. [c]Calibrated by GPC (LiCl/DMF (0.01 M), polystyrene standards). [d]Soluble fraction in DMF.

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References and Notes

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5 Anal. Found: C, 72.9; H, 5.1; N, 21.2; Br, 0.7%. Calcd for $(C_{11}H_9N_3)_n$: C, 72.1, H, 5.0, N, 22.9%. Spectral data: IR (KBr, cm^{-1}): 3042, 1578, 1442, 1290, 1151, 773, 693; ${}^{1}H$ NMR (DMSO-d_6, ppm): δ 6.1 (3H, br), 6.9-7.4 (4H, br), 8.4 (2H, br); ${}^{13}C$ NMR (CF_3COOD, ppm): δ 100.6, 122.3, 125.3, 134.4, 139.6, 149.1, 152.0.