Preparation of Novel Poly(aryleneamine)s by Palladium Complex Catalyzed Polycondensation of Dibromobenzenes with Diamines

Takaki Kanbara,* Akira Honma, and Kiyoshi Hasegawa
Department of Chemical and Biochemical Engineering, Faculty of Engineering, Toyama University, 3190 Gofuku, Toyama 930

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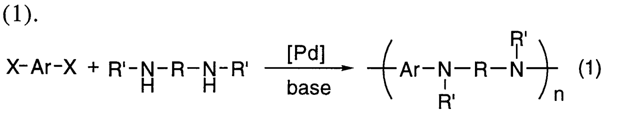
The reaction of aryl dibromides with secondary diamines proceeds smoothly in the presence of a stoichiometric base such as NaO*t*Bu and a catalytic amount of palladium complex, $PdCl_2(P(o\text{-tolyl})_3)_2$ ($P(o\text{-tolyl})_3$ = tri-*o*-tolylphosphine), in toluene to give the corresponding new poly(aryleneamine)s.

Polymer syntheses using organotransition metal complexes as catalysts are the subject of recent interest.[1] In particular, various bond formation processes involving the reaction of two kinds of functional groups catalyzed by the organometallic complexes have been applied to the polymerization reactions of bifunctional organic compounds to give novel poly(arylene)s,[2] polyesters,[3] polyamides,[4] and the related polymers. However, preparation of polyamines using organometallic processes has been limited.[5]

Recently, both of Buchwald et al. and Hartwig et al. have reported that Pd complexes catalyzed condensation of arylhalides with secondary amines gives arylamines under mild conditions.[6] This reaction provides a convenient method for aryl amination without the necessity for using aminotin compounds and the subsequent disposal of tin halides.[7,8] The Pd-catalyzed reaction of aromatic dihalides with secondary diamines would afford poly(aryleneamine)s through polycondensation according to Eq. (1).



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

On these bases, we report the results of a Pd complex catalyzed polycondensation of dibromobenzenes with secondary diamines to give new poly(aryleneamine)s.

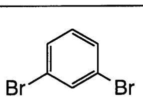
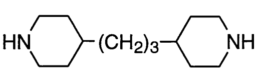
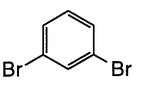
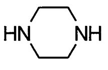
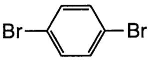
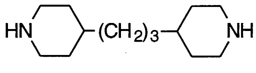
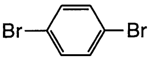
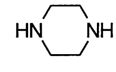
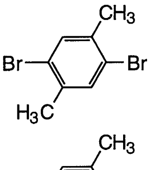
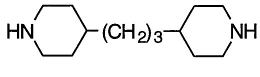
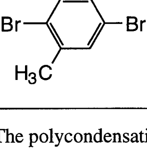
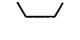
A mixture of 1,3-dibromobenzene (471 mg, 2 mmol) and 4,4'-trimethylenedipiperidine (421 mg, 2 mmol) was dissolved in toluene (15 cm^3). NaO*t*Bu (577 mg, 6 mmol) and $PdCl_2(P(o\text{-tolyl})_3)_2$ (79 mg, 0.1 mmol) were added to the solution at room temperature. The reaction mixture was stirred at 100 °C for 16 h under nitrogen. After cooling to room temperature, the mixture was quenched by adding aqueous ammonia (15-20 cm^3) and the product was extracted with $CHCl_3$ (30-40 cm^3). The organic fraction was concentrated, and reprecipitation from $CHCl_3$/hexane and $CHCl_3$/ether gave a pale-yellow powder of poly[1,1'-(4,4'-trimethylene)bispiperidinediyl-1,3-phenylene] (288 mg, 51% yield). Anal. Found: C, 78.9; H, 9.8; N, 9.5; Hal., 1.8%. Calcd for $(C_{19}H_{28}N_2)_n$: C, 80.2; H, 9.9; N, 9.8%. Other poly(aryleneamine)s were prepared analogously. The $CHCl_3$ insoluble fraction of the polymers was purified by washing with hexane and ether followed by reprecipitation from HCOOH/aqueous ammonia.

Table 1. Polycondensation of 1,3-dibromobenzene with 4,4'-trimethylenedipiperidine[a]

Run	Catalyst	Base	Temp /°C	Yield[b] /%	M_n[c] x 10^{-3}	M_w[c] x 10^{-3}
1	$PdCl_2[P(o\text{-tolyl})_3]_2$	NaO*t*Bu	100	51	4.5	5.9
2	$PdCl_2[P(o\text{-tolyl})_3]_2$	NaO*t*Bu	65	3	0.9	1.0
3	$PdCl_2[P(o\text{-tolyl})_3]_2$	KO*t*Bu	100	58	4.2	5.3
4	$PdCl_2[P(o\text{-tolyl})_3]_2$	$LiN(SiMe_3)_2$	100	55	5.1	6.3
5	$Pd(PPh_3)_4$	NaO*t*Bu	100	5	0.9	1.0
6	$NiBr_2(PPh_3)_2$	NaO*t*Bu	100	0	-	-
7	none	NaO*t*Bu	100	0	-	-

[a] In toluene (1 mmol of each monomer in 7.5 cm^3); catalyst (5 mol% for monomer); base (3 equiv. for monomer); for 16 h. [b] Insoluble fraction in ether. [c] Soluble fraction in $CHCl_3$; determined by GPC with polystyrene standards.

Table 2. Polycondensation of aryl dibromides and diamines[a]

Run	aryl dibromides	diamines	Yield[b] /%	M_n[c] x 10^{-3}	M_w[c] 10^{-3}
1			51 (0)	4.5	5.9
2			60 (17)	1.7	1.8
3			60 (2)	1.4	1.7
4			79 (66)	0.9	1.0
5			19 (0)	5.3	5.9
6			37 (2)	1.6	1.8

[a] The polycondensation of aryl dibromides (2 mmol) and diamines (2 mmol) was carried out in the presence of NaO*t*Bu (6 mmol) and $PdCl_2[P(o\text{-tolyl})_3]_2$ (0.1 mmol) in toluene (15 cm^3) at 100 °C for 16 h. [b] Total yield; the number in the parentheses is the yield of $CHCl_3$ insoluble fraction. [c] Soluble fraction in $CHCl_3$; determined by GPC with polystyrene standards.

Table 1 summarizes the results of the Pd-catalyzed polycondensation of 1,3-dibromobenzene with 4,4'-trimethylenedipiperidine under various conditions. Their molecular weights have been estimated by GPC. In the present study, $PdCl_2(P(o\text{-tolyl})_3)_2$ is the most effective catalyst to give the polymers. $Pd(PPh_3)_4$ is a less effective catalyst, and $NiBr_2(PPh_3)_2$ showed no catalytic activity. Ligands such as PPh_3, 1,3-bis(diphenyl-

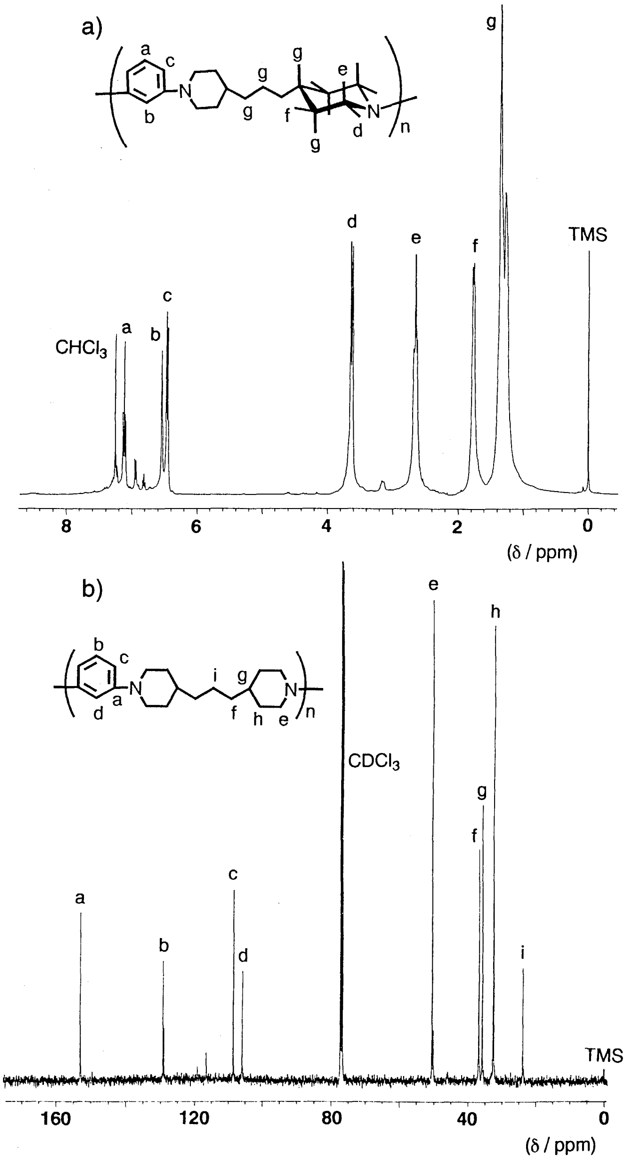


Figure 1. ^1H (a) and ^{13}C (b) NMR spectra of poly[1,1'-(4,4'-trimethylene)bispiperidinediyl-1,3-phenylene] in $CDCl_3$.

phosphino)propane, and 1,1'-bis(diphenylphosphino)ferrocene have been found to be inefficient for the Pd-catalyzed aryl amination.[6a,8] Yields of the polymers are independent of the Pd-catalyst concentration (5-20 mol%). The polycondensation does not proceed in the absence of Pd-catalyst. Although it has been reported that the Pd-catalyzed aryl amination is sensitive to the nature of the base,[6a,b] bases such as NaO*t*Bu, KO*t*Bu, and $LiN(SiMe_3)_2$ were effective for the polycondensation. At 100 °C, the polycondensation proceeds smoothly, while the reaction proceeds slowly at 65 °C. A trace amount of water inhibited the polycondensation.

The results of the Pd-catalyzed polycondensation of various aryl dibromides with secondary amines using the same conditions as that of Run 1 in Table 1 are summarized in Table 2. The structures of the polymers were confirmed by IR and NMR spectroscopy. Elemental analysis data of the polymers are reasonable for the calculated values for the corresponding structures. The poly(aryleneamine)s contain a $CHCl_3$ insoluble fraction with high molecular weights, however, it is soluble in acidic solvents such as formic acid. IR spectrum of the insoluble fraction is identical to that of the $CHCl_3$ soluble fraction.

Figure 1 shows the ^1H and ^{13}C NMR spectra of poly[1,1'-(4,4'-trimethylene)bispiperidinediyl-1,3-phenylene] (Table 1, Run 1) in $CDCl_3$. The peaks were assigned by comparing the position of the observed peaks with those of monomers. In Figure 1(a), the peak area ratios agree with the structure, although the aromatic protons show a somewhat complex pattern. The peaks due to the carbons of the terminal benzene ring are observed as weak signals in the ^{13}C NMR spectrum of the polymer (Figure 1(b)). The complicated patterns of the phenyl proton and carbon signals in the NMR spectra are attributed to a side reaction involving β-hydrogen elimination reaction of the Pd intermediate. A mechanism for the Pd-catalyzed aryl amination has been proposed,[6a,8] and according to the mechanism, formation of a reduced arene is considered to occur in part. This undesirable reaction may prevent propagation of the poly(aryleneamine)s and result in low yields of the polymers in some cases.

As described above, several new poly(aryleneamine)s are easily obtained by the Pd-catalyzed polycondensation. Although yields and molecular weights of the polymers are not high in the present study, the polycondensation could provide a variety of poly(aryleneamine)s by changing the structure of aryl dihalides and diamines. Further studies for obtaining the appropriate conditions for polymerization as well as preparation of other poly(aryleneamine)s are now in progress.

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