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Synthesis of New Poly(arylamine)s (Aryl = Oligo-*p*-phenyl or Pyridyl) by Organometallic Polycondensation and Chemical Properties of the Polymers

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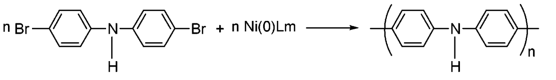
ABSTRACT: A series of poly(arylamine)s formulated as $[-(\mathrm{Ar})_m\mathrm{NR}-]_n$ (Ar = *p*-phenylene or pyridine-2,5-diyl; $m = 2-4$; R = H or alkyl) were prepared. Ni- or Pd-promoted dehalogenative polycondensation of the corresponding BOC- (*tert*-butoxycarbonyl-) substituted dibromo monomers afforded poly(oligo-*p*-phenylene-amine)s, $[-(p\text{-}\mathrm{C_6H_4})_m\mathrm{N(BOC)}-]_n$ ($m = 2-4$). Deprotection of the BOC group of the polymer at 200 °C gave $[-(p\text{-}\mathrm{C_6H_4})_m\mathrm{NH}-]_n$ ($m = 2-4$). The polymer behaved as an intermediate polymer between poly(aniline) **PAn** and poly(*p*-phenylene) **PPP**. For example, $[-(p\text{-}\mathrm{C_6H_4})_2\mathrm{NH}-]_n$, **P(DPA)**, showed two oxidation peaks at around 0.3 and 0.65 V vs $\mathrm{Ag^+/Ag}$ with equal intensity in its CV (cyclic voltammetry) chart, similar to **PAn**; in contrast, the CV chart of $[-(p\text{-}\mathrm{C_6H_4})_4\mathrm{NH}-]_n$ exhibited a main oxidation peak at 0.60 V vs $\mathrm{Ag^+/Ag}$, similar to **PPP**. ESR data of iodine-doped polymers supported the formation of radical species in oxidation of the polymer. The polymers were photoluminescent and gave quantum yields of 12−46%. Polymers with the pyridine unit formed metal complexes with $\mathrm{MX_2}$ (M = Cu, Ni, Co), and CD (circular dichroism) spectra of the metal complexes of the pyridine polymer having chiral side chains suggested formation of a helical structure by the metal complexation.

Introduction

Polyanilines[1−14] have been attracting great interest because of their electronic and optical functionalities, and industrial applications[11−14] of the polymers have been achieved. For example, a water-soluble polyaniline derivative[12] with $-\mathrm{SO_3H}$ substituents is industrially used to prepare an electrically conducting PET film coated with the polyaniline derivative.[12d]

Polyanilines have usually been prepared by chemical or electrochemical oxidation of anilines.[1−14] However, it has also been reported that some polyanilines such as poly(diphenylamine-4,4′-diyl), **P(DPA)**, can be prepared by organometallic polycondensation;[3,15] e.g.[15]



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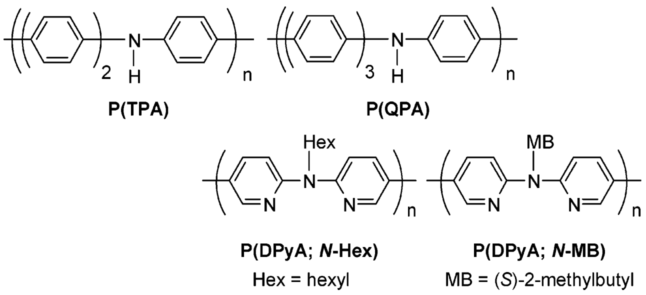
poly(diphenylamine-4,4'-diyl), **P(PDA)**

Ni(0)Lm: a mixture of bis(1,5-cyclooctadiene)nickel(0), $\mathrm{Ni(cod)_2}$, and 2,2'-bipyridyl, bpy

The obtained **P(DPA)** and its copolymers are photoluminescent and give electrochemical responses which are different from those of usual polyanilines due to existence of the 4,4′-biphenylene unit in the main chain. We have expanded the organometallic polycondensations and synthesized *p*-terphenylene, *p*-quaterphenylene, and bipyridyl analogues of **P(DPA)**: Synthesis of π-conjugated polymers by Ni-[2,15,16] and Pd-promoted[2,17,18] organometallic polycondensations have actively been carried out.

Herein we report synthetic results and chemical properties of the polymers. Studies on chemical properties of the *p*-phenylene type polymers, **P(TPA)** and **P(QPA)**, were focused on doping behavior of the polymers, whereas those of the pyridine polymers were focused on their optical properties and metal-complex-forming reactions. Di(2-pyridyl)amine, **DPyA**, which corresponds to the repeating unit of the pyridine polymers, is a typical chelating ligand and various metal complexes of the ligand have been reported.[19,20] **DPyA** behaves a bidentate chelating ligand via the two pyridyl-N atoms and forms a 1:1 complex with copper.[19a] However, the presence of the NH hydrogen in **DPyA** sometimes causes additional reaction with transition metal compounds.[19b,c] Consequently the alkyl group was introduced at the amino group in the pyridine polymers to avoid the complexity of the reaction with transition metal compounds. As described later, the N-alkylated pyridine polymer formed a 1:1 complex with copper.



Results and Discussion

Synthesis of Polymers. Scheme 1 indicates synthetic methods of the polymers. Precursor polymers of **P(TPA)** and **P(QPA)** with a BOC (*t*-butoxycarbonyl) protecting group, **P(TPA; *N*-BOC)** and **P(QPA; *N*-BOC)**, respectively, were prepared according to eq 2. Without the BOC group, the desired **P(TPA)** and **P(QPA)** were insoluble in organic solvents as described later. By introducing the BOC group, the precursor polymers became soluble, which made characterization and preparation of polymer films easy.

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Scheme 1. Preparation of Poly(arylamine)s

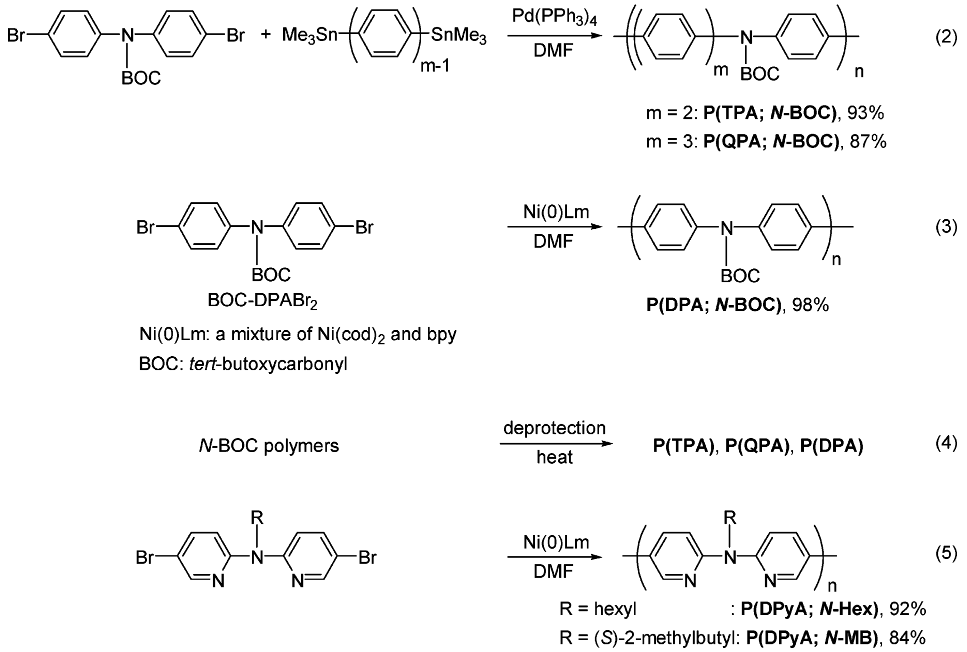


Table 1. Synthetic Results and Optical Data of the Polymers

				UV−vis, λ_{max}, nm		photoluminescence (PL), λ_{EM}, nm		
no.	polymer[a]	yield, %	molecular weight[b]	in $CHCl_3$ ($\epsilon \times 10^{-4}$/M^{-1} cm^{-1})[c]	film	in $CHCl_3$ (λ_{EX})[d]	Φ[e], %	film (λ_{EX})[d]
1	P(An; *N*-BOC)[f]			317 (in NMP)	310			
2	P(DPA; *N*-BOC)	98	5200 (M_n, GPC)	300 (2.2)	305	359 (302)	12	381 (295)
3	P(TPA; *N*-BOC)	93	7400 (M_n, GPC)	310 (3.0)	318	385 (313)	44	426 (312)
4	P(QPA; *N*-BOC)	97	9200 (M_n, GPC)	319 (4.2)	327	396 (319)	46	430 (323)
5	PAn[g]			325 (in NMP)	335			394[h]
6	P(DPA)[i]			380 (in DMF)	368	379 (440)	20	
7	P(TPA)				375			431 (375)
8	P(QPA)				375			469 (371)
9	PPP[j]				370−380			448
10	P(DPyA; *N*-Hex)	92	49000 (M_w, LS) 6400 (M_n, GPC)	380 (2.5)	380	415 (375)	9	
11	P(DPyA; *N*-MB)	84	44000 (M_w, LS) [η] = 0.52 dLg^{-1}	380 (2.1)	380	416 (375)	9	

[a] P(AN; *N*-BOC) = polyaniline with the BOC group at N. PAn = leucoemeraldine type polyaniline. PPP = poly(*p*-phenylene). [b] Number-average molecular weight M_n determined by GPC (gel permeation chromatography) or weight-average molecular weight M_w determined by LS (light scattering analysis). [c] The value in the parentheses indicates molar absorption coefficient. Molarity is based on the repeating unit. [d] The value in the parentheses indicates the peak position (λ_{EX} in nm) of the excitation spectrum. [e] PL quantum yield calculated by comparison with the standard of quinine sulfate (ca. 10^{-5} M solution in 0.5 M H_2SO_4, having a quantum yield of 54.6%; cf. ref 21). [f] From refs 3 and 8 for *N*-BOC polyaniline. [g] Data from refs 3, 5b, and 22. [h] Data from ref 23a. [i] Data from ref 15b. [j] Data from refs 2 and 24a for vacuum deposited PPP.

P(DPA; *N*-BOC) was also prepared by the method exhibited in eq 3. Deprotection of the BOC polymers by thermal treatment gave the corresponding *p*-phenylene polymers, **P(TPA)**, **P(QPA)**, and **P(DPA)**, as shown in eq 4. IR, UV−vis, and ^{1}H NMR data of **P(DPA)** thus obtained agreed with those of the previously reported **P(DPA)**, which had been prepared according to the aforementioned eq 1. **P(DPyA; *N*-Hex)** and **P(DPyA; *N*-MB)** were prepared similarly, as expressed in eq 5, by using the Ni(0) complex as a condensing agent. The organometallic polycondensations expressed by eqs 2, 3, and 5 gave the polymers in high yields (87−98%), and Table 1 summarizes results of the polymerization.

P(DPA; *N*-BOC), **P(TPA; *N*-BOC)**, and **P(QPA; *N*-BOC)** gave respective number-average molecular weights (M_n's) of 5200, 7400, and 9200 in GPC analysis (vs polystyrene standards); the M_n values corresponded to the degree of polymerization of 19−22. **P(DPyA; *N*-Hex)** showed M_n and M_w (weight-average molecular weight) of 6400 and 16400, respectively, in GPC analysis. **P(DPyA; *N*-Hex)** and **P(DPyA; *N*-MB)** exhibited M_w values of 49000 and 44000, respectively, in light scattering analysis[25] of chloroform solutions of the polymers, and **P(DPyA; *N*-MB)** gave an intrinsic viscosity of 0.52 dL g^{-1}. The larger M_w value of **P(DPyA; *N*-Hex)** estimated by the light scattering method as compared with that estimated by the GPC method suggests the presence of interaction of the polymer with the GPC column and/or partial aggregation of the polymer in the static solution used for the light scattering analysis. The light scattering analysis by the scattered light intensity gives an M_w of aggregated molecules in the solution.[25] The light scattering analysis gave a small ρ_v (degree of depolarization)[25] value of 0.041, which indicated that the polymer had essentially a random coil structure in the solution. IR spectra of the polymers resembled those of the monomers. However, the ν(C−Br) absorption peak of the monomers near 1100 cm^{-1} was not observed after the polymerization.

P(TPA; *N*-BOC), **P(QPA; *N*-BOC)**, **P(DPA; *N*-BOC)**, **P(DPyA; *N*-MB)**, and **P(DPyA; *N*-Hex)** were soluble in organic solvents such as DMF, THF, DMSO, and chloroform, and ^{1}H

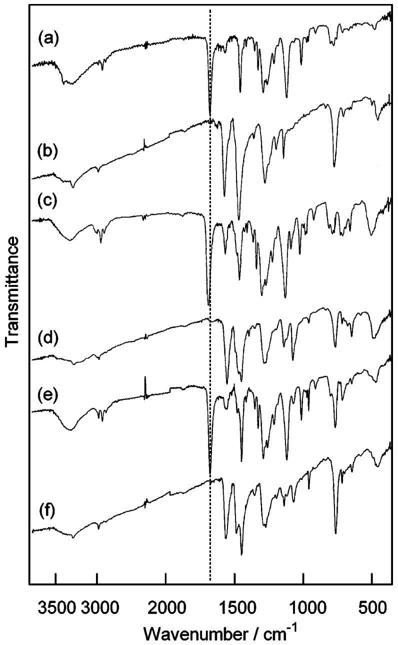
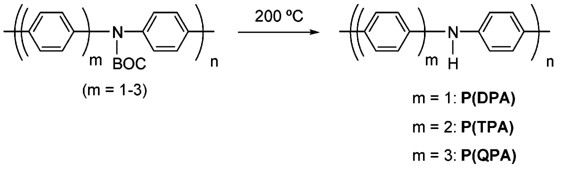


Figure 1. IR spectra of (a) **P(DPA; *N*-BOC)**, (b) **P(DPA)** prepared by deprotection of **P(DPA; *N*-BOC)**, (c) **P(TPA; *N*-BOC)**, (d) **P(TPA)**, (e) **P(QPA; *N*-BOC)**, and (f) **P(QPA)**.

Scheme 2. Deprotection of the BOC Group



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and ^{13}C NMR data given in the Supporting Information (Figures S1 and S3, and the synthetic part) agreed with the polymer structures. The BOC signal of the polymers appears at about δ 1.5 in the ^{1}H NMR spectrum, and its intensity indicates that the BOC protecting group remains intact during the organometallic polycondensation using the Pd and Ni complexes, similar to the cases of previously reported analogous organometallic polycondensations.[3,26]

Deprotection of the BOC Group. Deprotection of the BOC group of the polymers was completed by heating the polymer at 200 °C for 30 min under vacuum as expressed in Scheme 2. It has been reported that clear deprotection of the *N*-BOC group proceeds thermally with low-molecular-weight and polymeric compounds at about 200 °C.[3,26] CO_2 and *i*-butene are considered to be evolved.

Figure 1 shows changes of the IR spectra of the polymers after the deprotection of the BOC group. The IR spectrum after the thermal treatment exhibits clear disappearance of the ν(C=O) peak of the BOC group at 1700 cm^{-1}. The ν(N−H) peak appears as a weak peak at about 3500 cm^{-1}, similar to the case of leucoemeraldine base type poly(aniline), **PAn**.[1−6] The IR spectrum of **P(DPA)** thus obtained is identical with that of **P(DPA)** directly prepared by dehalogenative polycondensation of bis(4-bromophenyl)amine (Br−PhNHPh−Br) with the zerovalent nickel complex.[15b] The IR spectra of **P(DPA)**, **P(TPA)**, and **P(QPA)** show ring vibration peaks of the phenylene group at about 1590 and 1470 cm^{-1}, similar to those of **PAn**[1−6] and **PPP**;[2] however, the relative intensity of the peak at 1590 cm^{-1} is stronger, compared with that observed with **PAn**. After the deprotection, the obtained **P(TPA)** and **P(QPA)** became insoluble in organic solvents. However, films of **P(TPA)** and **P(QPA)** suited to optical and electrochemical measurements were obtained by thermal treatment of cast films of **P(TPA; *N*-BOC)** and **P(QPA; *N*-BOC)**, respectively. **P(DPA)** showed solubility in DMF and *N*-methyl-2-pyrrolidone.[15b] Solubility of the polymers is summarized in Table S1 in the Supporting Information.

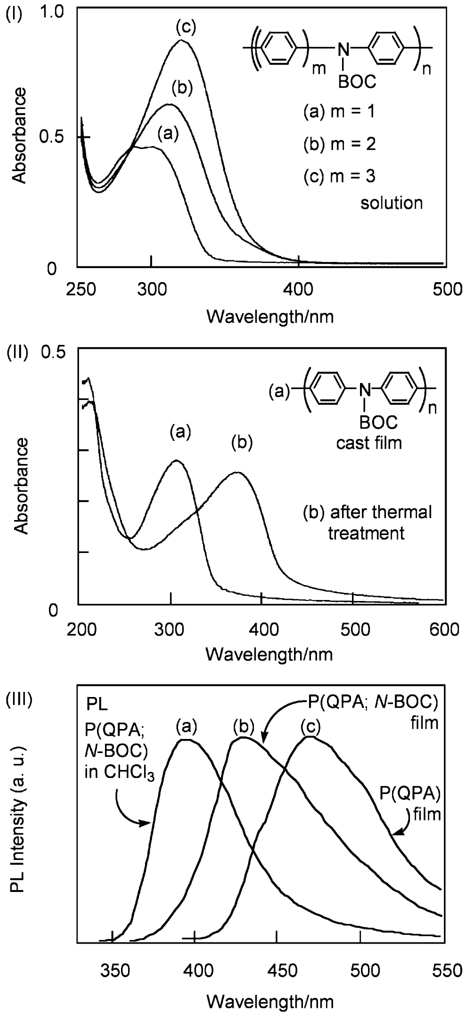
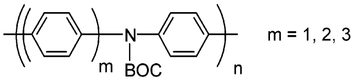


Figure 2. UV−vis and PL spectra. (I) UV−vis spectra of the BOC polymers (2.0 × 10^{-5} M monomer unit) in chloroform. (II) Change of the UV−vis spectrum of the cast film of **P(DPA; *N*-BOC)** on thermal treatment. (III) Examples of the PL spectra: (a) **P(QPA; *N*-BOC)** in chloroform; (b): cast film of **P(QPA; *N*-BOC)**; (c) film of **P(QPA)** prepared by thermal treatment of the cast film of **P(QPA; *N*-BOC)**.

UV−Vis and Photoluminescence (PL) Data. Figure 2 exhibits examples of UV−vis and PL spectra of the BOC polymers. The optical data of the polymers are included in Table 1. The data shown in Figure 2 and Table 1 reveal the following features, i−vii, of optical properties of the polymers.

(i) As seen from the top panel in Figure 2, the UV−vis absorption peak (λ_{max}) of the BOC polymers in chloroform shifts to a longer wavelength on increasing the number (*m*) of the phenylene rings.



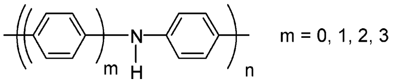
λ_{max}: 300 nm (m = 1) < 310 nm (m = 2) < 319 nm (m = 3)

The molar absorption coefficient calculated based on the repeating unit, ϵ in Table 1, roughly linearly increases with the number ($m + 1$).

(ii) The cast film of the BOC polymers gives λ_{max} roughly agreeing with λ_{max} of the chloroform solution of the polymers, indicating that the BOC polymers do not have a strong intermolecular electronic interaction even in the solid.

(iii) According to deprotection of the BOC polymers by eq 6, λ_{max} is shifted to a longer wavelength by about 50−80 nm. In the case of **P(DPA)**, λ_{max} (380 nm in chloroform) is located at a considerably longer wavelength than that of biphenyl (λ_{max} = 247 nm), implying that the polymer has an expanded electron system even through the −N− two single bonds. It has been reported that N in diphenylamine has a strong electronic coupling with the phenyl group and diphenylamine gives λ_{max} (286 nm) at a longer wavelength than those of diphenyl ether (λ_{max} = 279 nm) and diphenylmethane (λ_{max} = 269 nm).[27] The relatively short λ_{max} value of the BOC polymers suggests that expansion of the electron system through the −N− two single bonds is suppressed by bonding the bulky BOC group to the bridging −N− atom.

(iv) When the number of the *p*-phenylene group increases to 3 or 4 in **P(TPA)** and **P(QPA)**, λ_{max} of the polymer reaches near λ_{max} of **PPP** (cf. nos. 5−9 in Table 1).



λ_{max} (film): 335 (m = 0), 368 (m = 1),
375 (m = 2, 3) ~ 370-380 nm (λ_{max} of **PPP**)

(v) The BOC polymers are photoluminescent both in chloroform and in cast films; **P(TPA; *N*-BOC)** and **P(QPA; *N*-BOC)** give a good quantum yield of about 45%. The excitation spectrum gives the peak, λ_{EX}, essentially agreeing with λ_{max}, as usually observed with π-conjugated polymers. In the film, the emission peak, λ_{EM}, shifts to a longer wavelength from that observed in chloroform, suggesting formation of an excimer-like adduct between the photoactivated polymer molecule and polymer molecule in the ground state in the solid. The BOC-deprotected polymers are also photoluminescent and **P(DPA)** showed 20% quantum yield in chloroform.

(vi) The pyridine polymers, **P(DPyA; *N*-Hex)** and **P(DPyA; *N*-MB)**, give λ_{max} at 380 nm both in the solution and in film. The λ_{max} position locates at a longer wavelength by 80 nm than that of **P(DPA; *N*-BOC)**, although benzene and pyridine give almost the same λ_{max} value (ca. 250 nm) and **PPP** and poly(pyridine-2,5-diyl)[28] show λ_{max} at almost the same position (ca. 375 nm). These data suggest that the R group at the bridging −N− atom does not suppress the expansion of the electron system through the −N− two single bonds, in contrast to the case of the bulky BOC group.

(vii) **P(DPyA; *N*-Hex)** and **P(DPyA; *N*-MB)** are also photoluminescent in chloroform at 20 °C and in a frozen chloroform matrix. **P(DPyA; *N*-MB)** shows main and shoulder PL peaks at 416 and 440 nm, respectively, as exhibited in Figure 3. The position of the main peak agrees with the onset position of the UV−vis absorption band, as usually observed with aromatic compounds and polymers, and indicates that the main peak is assigned to a usual singlet−singlet emission. The PL main peak is located at a longer wavelength than that of the previously reported oligomers (e.g., 409 nm for $n = 4$).[20]
The shoulder PL peak of **P(DPyA; *N*-MB)** was ascribed to a phosphorescence based on its considerably long lifetime of about 700 ms at 20 °C, which was comparable to that observed with the oligomer (682 ms for $n = 3$).[20] In contrast, the lifetime of the main peak was shorter than 1 ms (detection limit of the measuring system), supporting the assignment of the emission to the usual singlet−singlet emission. As seen from Figure 3, relative intensity of the shoulder emission peak becomes stronger at −196 °C than that at +20 °C. Phosphorescence often shows enhancement of its intensity at lower temperatures, and the data support the assignment of the shoulder peak to phosphorescence.[29] A possible explanation for the PL data is that the photoenergy captured by **P(DPyA; *N*-MB)** is mainly emitted at the main PL peak, however, it is partly transferred to a triplet state[29b] to give the triplet−singlet (phosphorescent) sub-emission. PL spectra of aromatic polymers often show multiple peaks, however, observation of both the usual PL and phosphorescence is rare. Total quantum yield $\Phi_p + \Phi_f$ of **P(DPyA; *N*-MB)** at 20 °C was 9%.

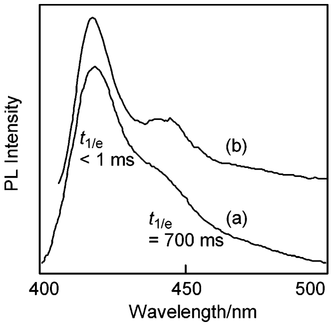
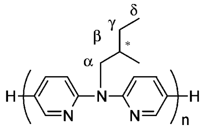


Figure 3. PL spectra of (a) the $CHCl_3$ solution of **P(DPyA; *N*-MB)** at 20 °C and (b) the frozen $CHCl_3$ solution of **P(DPyA; *N*-MB)** at −196 °C. $t_{1/e}$ indicates lifetime of the emission at 410 and 440 nm, respectively.



Oligo(DPyA; *N*-MB)
n = 2-4

λ_{max}: 350 (n = 2) – 369 nm (n = 4). λ_{EM}: 389 (n = 2) – 409 nm (n = 4).

Doping Behavior. Doping behavior of **P(DPA)**, **P(TPA)**, and **P(QPA)** was investigated by their electrochemical responses and reactions with iodine. Figure 4 shows cyclic voltammetry (CV) data of the films of the deprotected polymers. Results of the electrochemical data are summarized in Table 2. The film of **P(DPA)** exhibits two oxidation peaks at around 0.3 V vs Ag^+/Ag ($E_{pa}(1)$) and 0.65 V vs Ag^+/Ag ($E_{pa}(2)$), the two values agreeing with those previously reported for **P(DPA)** synthesized by the direct dehalogenative polymerization of $Br(C_6H_4NHC_6H_4)$-Br.[15b] Films of **P(TPA)** and **P(QPA)** also exhibit two oxidation peaks. Repeated scannings give essentially the same CV charts. It has been reported that polyaniline **PAn** also gives similar two oxidation peaks in aqueous media[1,2,30,31] and in acetonitrile.[15b] Because the CV chart of **P(DPA)** resembles that of **PAn** in CH_3CN,[15b] the electrochemical oxidation of **P(DPA)** is considered to involve the formation of polyemeraldines base type compound and polypernigraniline type compound, which may be formed by loss of H^+ from a $-NH^+$-species.

When the number of the *p*-phenylene unit is increased to 4 in **P(QPA)**, the CV chart differs considerably from those of **PAn** and **P(DPA)**. In the case of **P(QPA)**, the oxidized species may generate polaronic and bipolaronic states, similar to those proposed for **PPP**.[2]

The electrochemical oxidation of **P(QPA)** takes place at a lower potential (0.60 V vs Ag^+/Ag) than that of **PPP** (1.18 V[24b]), suggesting that the carbonium cation shown in Scheme 4, if it is formed, is stabilized by the −NH− group. It is known that

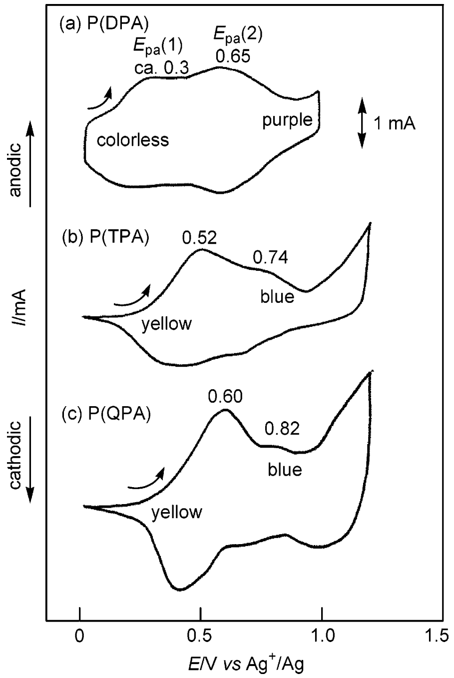


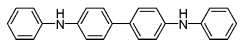
Figure 4. Cyclic voltammograms of the films of **P(DPA)**, **P(TPA)**, and **P(QPA)** on a Pt plate (1 cm × 1 cm). In an acetonitrile solution of 0.10 M $[NEt_4]BF_4$. Sweep rate = 20 mV s^{-1}.

Table 2. Electrochemical Data of the Polymers

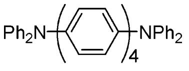
polymer	redox potential[a]/V vs Ag^+/Ag $E_{pa}(1)$[b]	$E_{pa}(2)$[c]	doping level[d]
PAn[e]	ca. 0	ca. 0.3	0.50
P(DPA)	ca. 0.3	0.65	0.24
P(TPA)	0.52	0.74	0.24
P(QPA)	0.60	0.82	0.31
PPP[f]	1.18		0.15
P(DPyA; *N*-Hex)	0.74[g]	0.83[g]	0.64

[a] Measured by cyclic voltammetry in an acetonitrile solution containing $[NEt_4]BF_4$ (0.10 M). Sweep rate: 20 mV s^{-1}. [b] The first anode peak current potential; cf. Figure 4. [c] The second anode peak current potential. [d] Positive charge stored per the repeating unit from the peak area in the CV chart. [e] Data from ref 15b. [f] Data from ref 24a. [g] Irreversible oxidation peak.

carbonium cation $C^+(X)(Y)(Z)$ is stabilized when an OR or NRR′ group is attached at the carbon atom. It has been reported that electrochemical oxidation of small molecules having a structure similar to that of the repeating unit of **P(DPA)**, e.g.



undergoes a two-step electrochemical oxidation with a fairly large peak separation between the two CV peaks (e.g., $E_{pa}(2) - E_{pa}(1) = 0.2$ V in CV).[32a] In contrast, for 4,4′-bis(diphenylamino)quaterphenyl[32b]



its CV chart shows only one oxidation peak, suggesting that there is only a weak electronic interaction between two radical cations separated by the longer quarterphenyl unit.

Electrochemical oxidation of **P(DPyA; *N*-Hex)** gave peaks at 0.74, 0.83, and 1.04 V (cf. Figure S8 in the Supporting Information). However, their corresponding reduction (or *p*-dedoping) peak was not observed, suggesting that the oxidized state was stabilized, possibly by coordination of the anion dopant (BF_4^-) to the −pyridyl−*N*-Hex−pyridyl− chelating units. Similar irreversible electrochemical oxidation peaks have often been observed for π-conjugated polymers composed of dialkoxy−phenylene units, and stabilization of the oxidized state by coordination of the anion dopant to the alkoxy group has been proposed.[33]

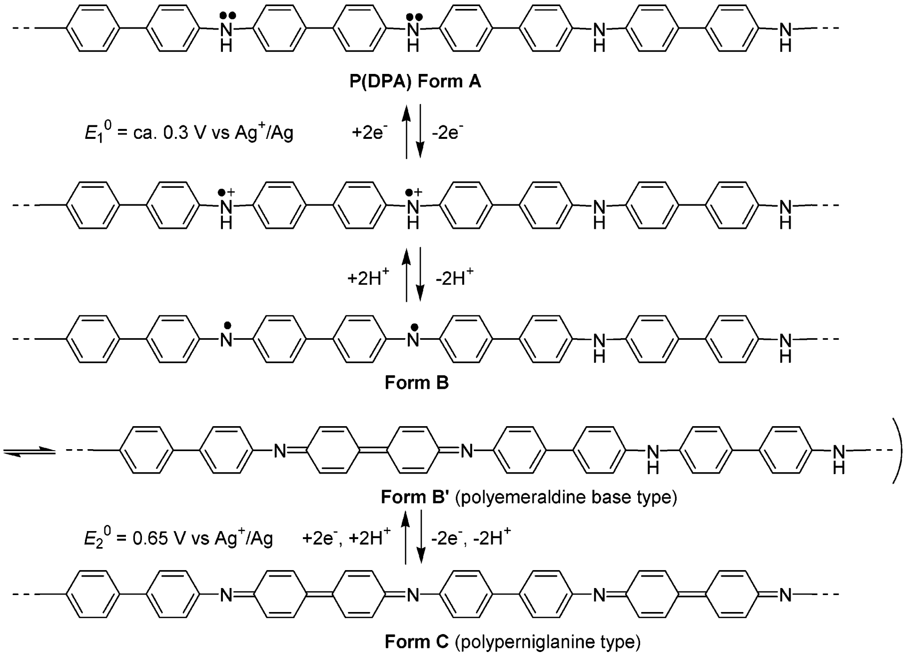
ESR Studies of Iodine Doped Samples. It was reported that **PAn**[34] and **P(DPA)**[15b] were oxidized with dihalogen (X_2) such as I_2. **P(TPA)** and **P(QPA)** also received oxidation with I_2, and the oxidation process was followed by ESR spectroscopy. Figure 5 exhibits ESR spectra of powdery polymers before and after exposure of the polymer sample to the vapor of I_2. Figure 6 discloses changes of the ESR parameters with time in the reaction of the polymer with I_2. As depicted in Figure 6a, **P(DPA)** has certain spin concentration even before treatment with I_2. This seems to be due to partial oxidation of **P(DPA)** under ambient conditions due to its relatively low oxidation potential; its oxidation starts at about 0.1 V vs Ag^+/Ag as depicted in Figure 4. It was reported that poly(pyrrole) with E_{pa} (anodic peak current potential) of about −0.3 V[2] vs Ag^+/Ag and poly(thiophene) also underwent partial oxidation under ambient conditions.[2,24a] However, further oxidation of **P(DPA)** with iodine does not seem to generate spins as depicted in Figure 6a; the oxidation seems to give HI-doped polyemeraldine type polymer without radical species (cf. Scheme 5).[15b,34]

The spin concentration of **P(TPA)** and **P(QPA)** is small before the iodine doping, which is consistent with the higher electrochemical oxidation potential of the polymer as shown in Figure 4 and Table 2. For these polymers, the ESR signal intensity increases according to the reaction with iodine as depicted in Figure 6, parts b and c. These data support the formation of the polaronic state depicted in Scheme 4, and the increase in the spin concentration in the reaction time range of 0−40 h implies that iodine does not have a strong oxidizing ability to form the extensively oxidized bipolaronic state depicted in Scheme 4. I_2 can oxidized (or p-dope) polyacetylene and polythiophenes, however, its oxidizing ability is not enough to p-dope PPP having a higher oxidation potential.[2]

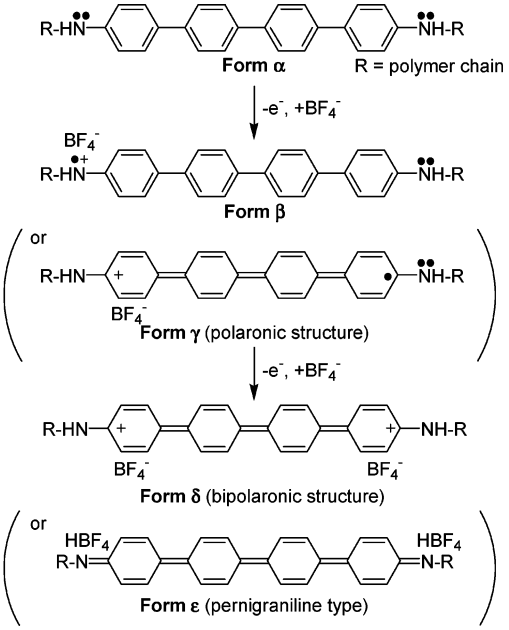
Metal Complexes. Reactions of **P(DPyA; *N*-Hex)** and **P(DPyA; *N*-MB)** with MCl_2 (M = Cu, Ni, and Co) gave 1:1 complexes of the metal ions with the polymer. The complexes became less soluble in organic solvents, and a **P(DPyA; *N*-Hex)**−$CuCl_2$ complex was characterized by IR and elemental analysis as described in the Experimental Section. Although the solubility of the metal complex was low, the complexation was able to be followed by UV−vis and CD (circular dichroism) spectroscopy.

Figure 7 depicts changes of UV−vis and CD spectrum of the $CHCl_3$ solution of **P(DPyA; *N*-MB)** on addition of MCl_2 (M = Cu, Ni, and Co). Addition of the methanol solution of MCl_2 into a chloroform solution of **P(DPyA; *N*-MB)** causes a shift of the absorption peak to a shorter wavelength, which suggests twisting of the polymer main chain caused by the coordination of MCl_2. However, the λ_{max} position still locates at a longer wavelength than that of 3,3′-bipyridyl ($\lambda_{max} = 274$ nm) which is the basic π-conjugated block in **P(DPyA; *N*-MB)**. For $NiCl_2$ and $CuCl_2$, the change of the UV−vis spectrum was almost saturated at the MCl_2/(chelating unit) ratio of 1 (cf. Figure S7), indicating that the complex forming reaction proceeded quantitatively. As seen from Figure 7, **P(DPyA; *N*-MB)** shows a CD signal with a Cotton effect corresponding to the UV−vis peak. The $CuCl_2$ and $NiCl_2$ complexes exhibit opposite CD signals to each other, revealing that the steric structure of the **P(DPyA; *N*-MB)** main chain is controlled by the coordination of MCl_2. The position of the Cotton effect is shifted to a shorter

Scheme 3. Oxidation of P(DPA)[15b]



Scheme 4. Oxidation of P(QPA)



wavelength in accord with the shift of the UV−vis peak. A 95:5 $CHCl_3-CH_3OH$ solution of **P(DPyA; *N*-MB)** containing $CuCl_2$ and $NiCl_2$ in a Cu:Ni:**P(DPyA; *N*-MB)** unit ratio of 1:1:1 showed a CD curve similar to the CD curve obtained with the solution made of **P(DPyA; *N*-MB)** and $CuCl_2$. These data indicate that $CuCl_2$ has a much higher coordinating ability toward **P(DPyA; *N*-MB)** than $NiCl_2$.

In contrast to the cases of $CuCl_2$ and $NiCl_2$, a solution made of **P(DPyA; *N*-MB)** and $CoCl_2$ gave only a very weak CD signal despite a UV−vis shift to 350 nm by coordination with $CoCl_2$, indicating that the complex formation with $CoCl_2$ did not bring about an ordered structure of the polymer main chain. A possible explanation about the CD data shown in Figure 7 is that **P(DPyA; *N*-MB)** has a helical structure induced by the side chain chirality and the coordination with $NiCl_2$ and $CuCl_2$ leads to reverse type of helical structures each other. It was reported that a helical structure of polythiophene with a chiral oxazole side chain, PTh−Oxz, was induced by metal complexation with Cu(II).[35] The peak θ value in the CD spectra of **P(DPyA; *N*-MB)** and its $CuCl_2$ and $NiCl_2$ complexes is comparable to that of the PTh−Oxz-Cu(II) system, supporting formation of the helical structures of MCl_2-**P(DPyA; *N*-MB)** (M = Cu and Ni) complexes in the solution. PL of the $CHCl_3$ solution of **P(DPyA; *N*-Hex)** and **P(DPyA; *N*-MB)** was quenched by addition of an equimolar amount of MCl_2 (for M = Cu, Ni, and Co; cf. Figure 8). The quenching of the PL is probably due to the existence of chloride ligands in MCl_2-**P(DPyA; *N*-Hex)** and MCl_2-**P(DPyA; *N*-MB)**, which are known to quench PL through heavy atom effects. Similar quenching effect of metal complexation on PL of derivatives of **DPyA** has been reported.[36] Light scattering analysis of the polymer−metal complex was not possible due to low solubility of the polymer−metal complex.

Conclusions

New polyaniline-type polymers containing the *p*-oligophenylene and pyridyl units in the main chain have been prepared. The polymers with the *p*-oligophenylene unit are photoluminescent and electrochemically active, and they behave as intermediate polymers between polyaniline and poly(*p*-phenylene). ESR data agree with this view. By choosing the number of the *p*-phenylene unit, m, the wavelength of the emitted light from $-[(p\text{-}C_6H_4)_m-NH]_n-$ and redox potential of the polyaniline-type polymer can be controlled. The polymer with the pyridyl unit form metal complexes with MCl_2. The obtained data will give bases not only for better understanding of polyaniline but also for designing new polyaniline-type polymers.

Experimental Section

Materials. Solvents were dried and stored under N_2. Bis(1,5-cyclooctadiene)nickel(0), $Ni(cod)_2$,[37] $Pd(PPh_4)_4$,[38] 4,4′-dibromodiphenylamine,[15] *N*-*tert*-butoxycarbonyl-4,4′-dibromodiphenylamine,[3] *N*-(*S*)-2-methylbutyl(5-bromo-2-pyridyl)amine,[20] 1,4-bis(trimethylstannyl)benzene,[39] and 4,4′-bis(trimethylstannyl)biphenyl[40] were prepared according to the literature.

Preparation of Polymers. P(TPA; *N*-BOC). To a 100 mL Schlenk tube charged with *N*-*tert*-butoxycarbonyl-4,4′-dibromo-

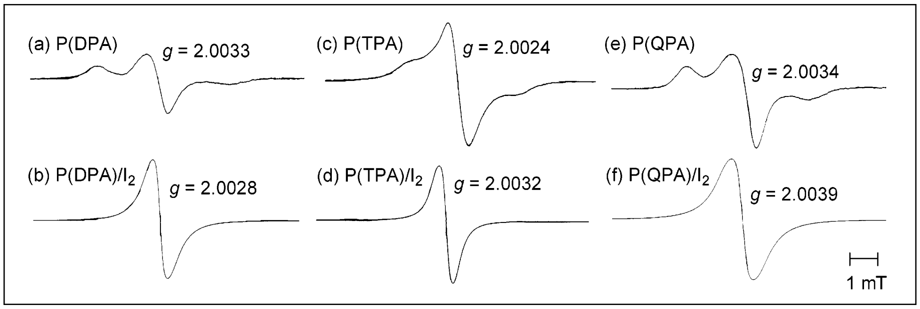


Figure 5. ESR spectra of (a) **P(DPA)**, (b) iodine-oxidized **P(DPA)**, (c) **P(TPA)**, (d) iodine oxidized **P(TPA)**, (e) **P(QPA)**, and (f) iodine-oxidized **P(QPA)**. Powdery samples. Procedures for the preparation of the iodine-doped sample are shown in Figure S5.

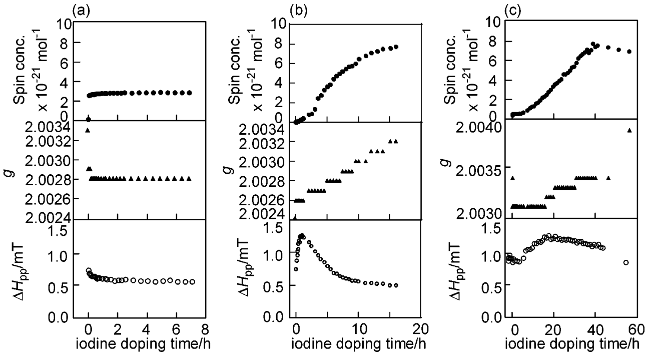
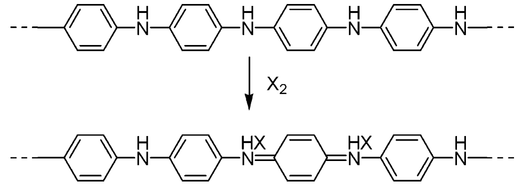


Figure 6. Changes of the ESR data with time in the reaction of the polymer with I_2. The powdery polymer sample was exposed to vapor of iodine in an ESR tube under vacuum: (a) **P(DPA)**; (b) **P(TPA)**; (c) **P(QPA)**.

Scheme 5. Oxidation of PAn by X_2



diphenylamine (854 mg, 2.00 mmol), 1,4-bis(trimethylstannyl)benzene (807 mg, 2.00 mmol), and $Pd(PPh_3)_4$ (60 mg, 0.052 mmol) was added 50 mL of degassed DMF, and the mixture was stirred for 48 h at 85 °C under N_2. After cooling to room temperature, the reaction mixture was poured into 200 mL of an aqueous solution containing 10% KF, and the precipitate of **P(TPA; *N*-BOC)** was separated by filtration. The filtrate was washed with an aqueous solution of 10% KF and methanol. After removal of the solvent by evaporation, the residue was dissolved in 5 mL of chloroform, and the solution was poured into 50 mL of hexane to give a polymer precipitate. Filtration and drying under vacuum gave **P(TPA; *N*-BOC)** as a light yellow powder (639 mg, 93%). M_n = 7400 (GPC, DMF); M_w = 9600. ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.76−7.71 (m, 8H), 7.33 (s, 4H), 1.43 (s, 9H). IR (KBr, cm^{-1}) 3054−2976, 1706, 1516−1482, 1322. Anal. Calcd for $(C_{23}H_{21}NO_2)_n$: C, 80.44; H, 6.16; N, 4.08. Found: C, 79.00; H, 5.82; N, 3.66; Br, 0.16. The ^{1}H NMR spectrum of the polymer is shown in Figure S1.

Synthesis of **P(QPA; *N*-BOC)** was carried out analogously. Characterization data of the polymer are shown below.

P(QPA; *N*-BOC) was obtained as a light yellow powder (93%). M_n = 9200 (GPC, DMF); M_w = 11 600. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74−7.12 (m, 16H, aromatic), 1.46 (s, 9H, $-CH_3$). IR (KBr, cm^{-1}): 3030−2974, 1709, 1485, 1328. The ^{1}H NMR spectrum of the polymer is shown in Figure S1.

P(DPA; *N*-BOC). $Ni(cod)_2$ (330 mg, 1.2 mmol), 1,5-cyclooctadiene (106 mg, 1.0 mmol), and bpy (187 mg, 1.2 mmol) were dissolved in 20 mL of DMF in a Schlenk tube under argon. To the solution was added *N-tert*-butoxycarbonyl-4,4′-dibromodiphenylamine (427 mg, 1.0 mmol) at room temperature, and the reaction mixture was stirred at 60 °C for 24 h. After cooling to room temperature, the reaction mixture was poured into an aqueous ammonia solution, and the precipitate was separated by filtration. The pecipitate was washed with aqueous ammonia, a hot aqueous solution of ethylenediaminetetraacetic acid (EDTA), and methanol. The solid was dissolved in 5 mL of chloroform, and the solution was poured into 50 mL of hexane to give a polymer precipitate. After filtration and drying under vacuum, **P(DPA; *N*-BOC)** was obtained as a light yellow powder (262 mg, 98%). M_n = 5200 (GPC, DMF); M_w = 7200. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, 4H), 7.27 (d, 4H), 1.44 (s, 9H). IR (KBr, cm^{-1}) 2974, 1712, 1495, 1330−

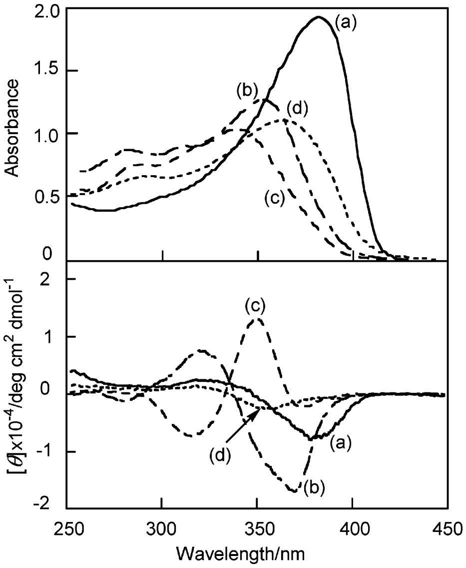


Figure 7. UV−vis absorption (top) and CD (bottom) spectra of the solution ($CHCl_3$: methanol = 95:5) of (a) **P(DPyA; *N*-MB)** and those obtained by addition of (b) $CuCl_2$, (c) $NiCl_2$, and (d) $CoCl_2$. The concentration of **P(DPyA; *N*-MB)** and that of M^{2+} in the solution are 0.60 mM, respectively. The molarity of **P(DPyA; *N*-MB)** is based on the repeating unit.

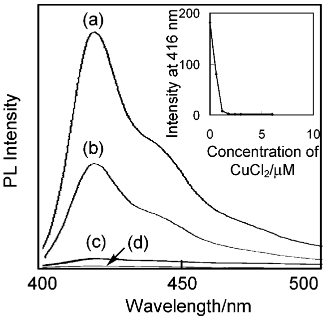


Figure 8. PL spectrum of the solution $CHCl_3$ of (a) **P(DPyA; *N*-Hex)** (2.0 μM) and those obtained by addition of $CuCl_2$ in (b) 0.60 μM (c) 1.20 μM, and (d) 2.0 μM. Relative intensity changes are shown in the inset.

1301. Anal. Calcd for $(C_{17}H_{17}NO_2)_n$: C, 76.38; H, 6.41; N, 5.24. Found: C, 74.04; H, 6.17; N, 5.34. The ^{1}H NMR spectrum of the polymer is shown in Figure S1.

BOC Deprotected Polymers. To a 100 mL Schlenk tube, a powder of **P(DPA; *N*-BOC)**, **P(TPA; *N*-BOC)**, or **P(QPA; *N*-BOC)** (100 mg for each) in a 8 mL sample tube or a cast film of the polymer on a quartz glass (for optical measurements) or platinum plate (for electrochemical measurements) was added, and the Schlenk tube was heated for 30 min at 200 °C under Ar gas.

P(DPyA; *N*-Nex). The monomer of the polymer was synthesized as follows. A DMSO solution (20 mL) of NaH (600 mg, 24 mmol) was stirred at 40 °C for 0.5 h and at 75 °C for 1 h. To the solution was added 2,2′-dipyridylamine (3.42 g, 20 mmol). After the reaction was stirred at 60 °C for 12 h, hexyl bromide (5.0 mL, 30 mmol) was added, and the solution was again stirred at 60 °C for 24 h. To the reaction mixture was added water, and the product was extracted with $CHCl_3$. After the organic layer was dried over Na_2SO_4, the solvent was removed by evaporation to give a yellow liquid, which was purified by silica gel column chromatography (eluent = first $CHCl_3$; second ethyl acetate). The solvent was removed by evaporation and the resulting liquid was dried under vacuum to give **DPyA**; ***N*-Hex** as a yellow liquid (2.3 g, 45%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.34 (d, 2H, 6-H of py), 7.50 (dd, 2H, 4-H of py), 7.07 (d, 2H, 5-H of py), 6.83 (dd, 2H, 3-H of py), 4.16 (t, 2H), 1.68 (tt, 2H), 1.29 (m, 6H), 0.86 (m, 3H).

To a chloroform solution (200 mL) of tetrabutylammonium tribromide (7.14 g, 14.8 mmol) was added dropwise a chloroform solution (50 mL) of **DPyA; *N*-Nex** (1.45 g, 7.4 mmol), and the mixture was stirred at 20 °C for 2 h. After an aqueous solution of sodium thiosulfate was added to the reaction mixture, the organic layer was separated and dried over Na_2SO_4. The solvent was removed by evaporation and the resulting yellow liquid was purified by silica gel column chromatography (eluent = $CHCl_3$) to give a yellow liquid of the monomer, **Br$_2$-DPyA; *N*-Hex** (1.07 g, 35%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.34 (d, 2H, H_a, $J = 2.1$ Hz), 7.60 (dd, 2H, $J = 8.8$ and 2.1 Hz), 7.00 (d, 2H, $J = 8.8$ Hz), 4.08 (t, 2H), 1.65 (m, 2H), 1.29 (m, 6H), 0.86 (m, 3H). IR (KBr, cm^{-1}): 2952−2854, 1584−1396, 1095. MS (EI) m/z 409.9890 (error: +5.6 ppm) for $C_{16}H_{18}N_3Br_2$ ($M - 1$). The ^{1}H NMR spectrum of the monomer is shown in Figure S2. From the monomer (330 mg, 1.0 mmol), Ni(cod)$_2$ (630 g, 2.2 mmol), and bpy (340 mg, 2.2 mmol) in DMF, **P(DPyA; *N*-Hex)** was prepared in a way similar to that applied for the synthesis of **P(DPA; *N*-BOC)**.

P(DPyA; *N*-Hex). A light yellow powder was obtained (235 mg, 92%). $M_n = 6400$, $M_w = 16\,400$ (GPC, THF). $M_w = 49\,000$ (light scattering in chloroform). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.34 (m, 2H), 7.76 (d, 2H, $J = 8.3$), 7.25 (d, 2H, $J = 8.8$), 4.25 (broad, 2H), 1.77 (br, 2H), 1.32 (m, 6H), 0.88 (m, 3H). IR (KBr, cm^{-1}) 2920−2850, 1589−1459. Anal. Calcd for $(C_{16}H_{19}N_3)_n$: C, 75.85; H, 7.56; N, 16.59. Found: C, 74.91; H, 7.43; N, 16.61. The ^{1}H NMR spectrum of the polymer is shown in Figure S3.

P(DPyA; *N*-MB). From Ni(cod)$_2$ (620 mg, 2.3 mmol), bpy (350 mg, 2.3 mmol), and *N*-(*S*)-2-methylbutylbis(5-bromo-2-pyridyl)-amine (330 mg, 1.0 mmol) was obtained **P(DPyA; *N*-MB)** as a light yellow powder (201 mg, 84%). $M_w = 44\,000$ (light scattering in chloroform). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.58 (d, 2H, $J = 2.4$ Hz), 7.75 (dd, 2H, $J = 8.3$ and 2.4 Hz) 7.23 (d, 2H, $J = 8.8$ Hz), 4.18 (m, 2H), 1.99 (m, 1H), 1.54 (m, 1H), 1.21 (m, 1H), 0.92 (m, 6H); ^{13}C NMR (100 MHz/$CDCl_3$): δ 156.9, 145.8, 135.0, 126.8, 115.0, 54.1, 34.1, 27.1, 17.0, 11.4. Anal. Calcd for $(C_{15}H_{17}N_3)_n$: C, 75.28; H, 7.16; N, 17.56. Found: C, 75.05; H, 7.37; N, 17.36. The ^{1}H and ^{13}C NMR spectra of the polymer are shown in Figure S3.

P(DPyA; *N*-Hex)—CuCl$_2$ Complex. P(DPyA; *N*-Hex) (30 mg, 0.12 mmol) was dissolved in 10 mL of $CHCl_3$ in a Schlenk tube under N_2. $CuCl_2$ (31 mg, 0.24 mmol) dissolved in 10 mL of methanol was added to the solution at room temperature, and the reaction mixture was stirred at room temperature for 12 h. After removal of the solvent by evaporation, the residue was washed with acetonitrile, and the dispersed powder in acetonitrile was separated by centrifugation (4000 rpm, 30 min). After drying under vacuum, **P(DPyA; *N*-Hex)**−$CuCl_2$ was obtained as a deep green powder. Anal. Calcd for $(C_{16}H_{19}N_3CuCl_2)_n$: C, 48.99; H, 4.88; N, 10.72; Cl, 18.08. Found: C, 48.49; H, 5.23; N, 10.70; Cl, 18.64.

Measurements. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on a JEOL EX-400 spectrometer. IR spectra were recorded on a Jasco IR-810 spectrometer. Elemental analyses were carried out with a Yanaco Mt-5 CHN autorecorder. Gel permeation chromatography (GPC; vs polystyrene standards) was performed using a Tosoh GPC-8020 device equipped with a differential refractometer detector and a variable-wavelength UV−vis detector, using DMF or THF as the eluent. For **P(DPyA; *N*-Hex)** and **P(DPyA; *N*-MB)** the molecular weight was determined by a light scattering method by using an Otsuka Electronics DLS-7000 super-dynamic light scattering spectrometer and a method described in our previous report[25] by using chloroform solutions. Viscosity was measured with a Ubbelohde viscometer. Thermogravimetric analysis (TGA) was carried out with a Shimadzu TGA-50 thermoanalyzer. UV−vis and photoluminescence spectra were obtained with Shimadzu UV-2100PC and Hitachi F-4010 spectrometers, respectively. Cyclic voltammetry (CV) of cast films of the polymers on platinum plates (1.0 × 1.0 cm) was carried out by using a CH_3CN solution containing 0.10 M $[NEt_4]BF_4$ and an electrochemical interface/gain-phase analyzer (Solartron Analytical IS 1287). Measurements were carried out under inert gas in a standard one-compartment cell equipped with a Ag^+/Ag reference electrode and a platinum-plate counter electrode (1.0 × 1.0 cm, respectively). ESR spectra were recorded on a JEOL EX-400 spectrometer. A powdery polymer sample in a glass capillary was placed in an ESR tube, and iodine vapor was introduced to the polymer sample under vacuum. The ESR tube was sealed, and the time-course of the ESR spectrum was measured, as depicted in Figure S5.

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Supporting Information Available: Tables giving the solubility data for the polymers and the ESR measurement parameters and figures showing the NMR spectra of the monomers and polymers, the preparation of the ESR samples, the changes in the UV−vis spectra of **P(DPyA; *N*-Hex)**, plots of absorbance for the **P(DPyA; *N*-Hex)**−metal systems, and the CV of the film of **P(DPyA; Hex)**. This material is available free of charge via the Internet at http://pubs.acs.org.

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