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Preparation of Poly(diphenylamine-4,4′-diyl) and Related Random Copolymers by Organometallic Polycondensation. Electrical, Electrochemical, and Optical Properties

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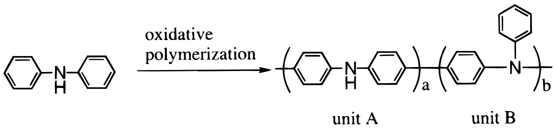
ABSTRACT: Preparation and properties of poly(arylamine)s prepared by organometallic polycondensation are described. Dehalogenative polycondensation of 4,4′-dibromodiphenylamine, Br−PhNHPh−Br, with a zerovalent nickel complex affords soluble poly(diphenylamine-4,4′-diyl), P(DPA) (nBr−PhNHPh−Br + nNi$^{(0)}$Lm → P(DPA)), with M_n and M_w values of 6.4×10^3 and 2.0×10^4 and an $[\eta]$ value of 0.66 dL g^{-1} in high yield. P(DPA) has a well-regulated structure and been characterized by IR, NMR, and UV−visible spectroscopy, as well as by cyclic voltammetry. The polymer shows a $\pi-\pi^*$ absorption band and photoluminescence band at 379 and 417 nm, respectively, in NMP. P(DPA) shows two reversible and stable redox cycles at $E° = 0.20$ and 0.60 V vs Ag/ Ag$^+$. Dehalogenative copolymerization of Br−PhNHPh−Br with 3,5-dibromotoluene, TolBr$_2$, with the zerovalent nickel complex gives random copolymers, P(DPA-*ran*-Tol), and they behave analogously in the electrochemical measurement. Films of P(DPA) and P(DPA-*ran*-Tol) exhibit electrochromism during their electrochemical oxidation, and the P(DPA) film reversibly changes its color stepwise from light brown to purple through red. P(DPA) shows electrical conductivity of 5 S cm^{-1} when treated with iodine.

Introduction

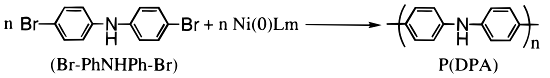
Polyaniline has attracted great interest of chemists[1] and has been prepared by electrochemical or chemical oxidation of aniline.[1−5] Polyanilines with various substituents on the aromatic ring[2a,6,7] and nitrogen[8−13] have also been prepared by oxidative polymerization. Similar polymerization of arylamines with fused rings (e.g., 1-naphthylamine) has also been the subject of recent many papers.[14]

Despite the numerous reports on the oxidative polymerization of ArNH$_2$ and ArAr′NH to yield (ArNH)$_n$ and (ArAr′N)$_n$,[15] there seems to exist some ambiguity concerning microstructures of the polymers. For example, even polyaniline may contain an *o*- or *m*-phenylene unit in a small quantity. When the monomer arylamine has a larger aryl group, there will be more ways for the aryl unit to be bonded to another monomer unit in the produced polymer. Actually, two kinds of poly(diphenylamine) (or poly(4-aminobiphenyl)) prepared by oxidation polymerization of C$_6$H$_5$NHC$_6$H$_5$[16] and C$_6$H$_5$C$_6$H$_4$NH$_2$[16a,b] present essentially the same IR spectrum[16b] and are considered to consist of the following two units.



(1)[16c]

To give a basis for structural analysis of poly(arylamine), we have carried out Ni-promoted dehalogenation polycondensation[17] of bis(4-bromophenyl)amine (Br−PhNHPh−Br) to yield the corresponding polymer poly(diphenylamine-4,4′-diyl) (P(DPA)).



(2)

Such polycondensation is considered to proceed selectively at the C−Br bond and the polymer obtained is considered to have a well-defined structure; however, application of the polycondensation to the synthesis of poly(arylamine) has not been reported to our knowledge. A part of the results has been reported in a communication.[18] In addition to the homopolymerization, we have carried out copolymerization of Br−PhNHPh−Br with 3,5-dibromotoluene, TolBr$_2$, and its results will be also reported.

Experimental Section

Materials. Commercially available diphenylamine, tetrabutylammonium tribromide (TBABr$_3$), 3,5-dibromotoluene, and 2,2′-bipyridyl (bpy) were purchased from Tokyo Chemical Industry Co., Ltd., and used without further purification. Solvents were dried, distilled, and stored under N$_2$. Bis(1,5-cyclooctadiene) nickel(0), Ni(cod)$_2$,[19] and 4,4′-dibromodiphenylamine, Br−PhNHPh−Br,[20] were prepared as previously reported; Br−PhNHPh−Br: mp 106−107 °C. ^{1}H NMR (CDCl$_3$, ppm): 5.45 (br, N−*H*, 1H), 6.8−7.5 (m, aromatic, 8H). UV−vis (NMP): $\lambda_{max} = 294$ nm. IR (cm^{-1}): 3412, 1600, 1470, 1320, 1069, 817, 749. Anal. Found: C, 44.1; H, 2.8; N, 4.3; Br, 48.9. Calcd for C$_{12}$H$_9$NBr$_2$: C, 44.1; H, 2.8; N, 4.3; Br, 48.9.

PLM type polyaniline was prepared according to a method given in the literature.[3]

Polymerization. The dehalogenation polycondensation using the zerovalent nickel complexes was carried out in a manner similar to those previously reported.[17] Copolymers have been prepared in an analogous way.

Poly(diphenylamine-4,4′-diyl). To a dry DMF (20 mL) solution containing Ni(cod)$_2$ (403 mg, 1.46 mmol), 1,5-cyclo-

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Table 1. Results of the Polymerization[a]

run	monomer[b]	conditions time (h)	yield (%)	M_n[c]	M_w[c]	$[\eta]$[d] (dL g^{-1})	λ_{max} (nm)[e]	PL (nm)[e]
1	Br−PhNHPh−Br	16	97	6400	20000	0.66	380	417, 440
2	Br−PhNHPh−Br	8	97	3600	5500		372	415
3	Br−PhNHPh−Br	4	97	2600	4000	0.32	369	414
4	Br−PhNHPh−Br:$TolBr_2$ = 4:1	16	99	4200	8600	0.45	375	416
5	Br−PhNHPh−Br:$TolBr_2$ = 8:1	16	99	4400	8300	1.0	377	417
6	Br−PhNHPh−Br:$TolBr_2$ = 12:1	16	99	9200	10400	1.57	377	416
7	Br−PhNHPh−Br:$TolBr_2$ = 16:1	16	99	4800	7500	0.98	370	417

[a] Carried out in DMFat 60 °C. [b] Br−PhNHPh−Br = 4,4′-dibromodiphenylamine, $TolBr_2$ = 3,5-dibromotoluene. [c] Determined by GPC (polystyrene standard; 0.01 M LiBr/DMF solution as eluent). [d] Instrinsic viscosity measured in NMP at 30 °C. [e] In NMP.

octadiene (0.5 mL), and bpy (229 mg, 1.46 mmol) was added Br−PhNHPh−Br (400 mg, 1.22 mmol).

After being stirred for 16 h at 60 °C, the reaction mixture was poured into an aqueous ammonia. The light green powder was collected by filtration and washed with dilute hydrochloric acid, warm aqueous solution of disodium ethylenediaminetetraacetate, Na_2EDTA, dilute aqueous ammonia, water, and methanol repeatedly. Drying the remaining powder under vacuum for 24 h gave P(DPA) in 97% yield. Removal of byproducts (e.g., Ni compounds) by the washing was accomplished rather easily, and ash-free polymer was obtained. Anal. Found: C, 84.7; H, 5.5; N, 8.4; Br, 0; ash, 0. Calcd for $[C_{12}H_9N(H_2O)_{0.1}]_n$: C, 85.3; H, 5.5; N, 8.3. The difference between the found and calculated carbon contents may be due to high thermal stability of the polymer. ^1H NMR (DMSO-d_6, 399.65 MHz, ppm): 8.32 (1H, N−*H*), 7.14 (d, 6.5 Hz, 4H, aromatic), 7.53 (d, 6.5 Hz, 4H, aromatic). $^{13}C\{^1H\}$-NMR (NMP-d_9, 100.40 MHz, ppm): 117.7, 127.0, 132.5, 143.0. UV−vis (NMP): λ_{max} = 380 nm. IR (cm^{-1}): 3388, 1600, 1490, 1310, 813, 748.

Copolymer (Poly(DPA-*ran*-Tol) (8:1)). To a dry DMF (40 mL) solution containing $Ni(cod)_2$ (2.16 mmol), 1,5-cyclooctadiene (0.5 mL), and bpy (2.16 mmol) were added Br−PhNHPh−Br (1.6 mmol) and $TolBr_2$ (0.2 mmol).

After being stirred for 16 h at 60 °C, the mixture was poured into aqueous ammonia to obtain a light green precipitate. After filtration, the light green powder was washed with dilute hydrochloric acid, a warm aqueous solution of Na_2EDTA, dilute aqueous ammonia, water, and methanol repeatedly and dried under vacuum for 24 h to obtain P(DPA-*ran*-Tol) (8:1) in 99% yield. Anal. Found: C, 85.3; H, 5.6; N, 7.8; Br, 0; ash, 0. Calcd for $[(C_{12}H_9N\cdot 0.1H_2O)_8(C_7H_6)]_n$: C, 85.7; H, 5.6; N, 7.8. ^1H NMR (CF_3COOD, 399.65 MHz, ppm): 7.5−7.8 (m, aromatic), 2.4−2.5 (m,CH_3); peak areas agreed. $^{13}C\{^1H\}$-NMR (NMP-d_9, 100.40 MHz) showed additional small two peaks of the Tol unit at 128.1 and 129.6 ppm besides the peaks observed for P(DPA). However, other peaks including the CH_3 signal were not detected clearly. UV−vis (NMP): λ_{max} = 377 nm. IR (cm^{-1}): 3386, 3024, 2916, 1601, 1494, 1311, 924, 814, 748. Other copolymerizations were carried out analogously.

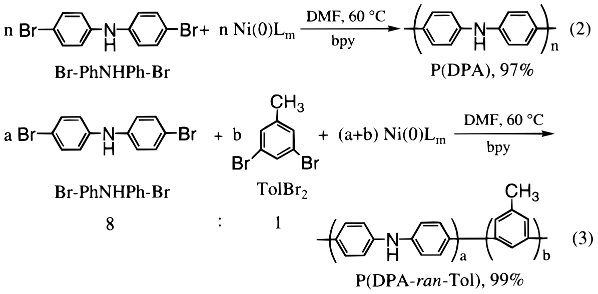
Measurement. IR spectra and ^1H and ^{13}C NMR spectra were recorded on a JASCO IR-810 spectrometer and a JEOL FX-100 or EX-400 spectrometer, respectively. UV−visible spectra and photoluminescence spectra were measured with a JASCO Ubest-35 spectrometer and a Hitachi F4010 spectrometer, respectively.

Elemental analysis was carried out by Mrs. Tanaka of our laboratory with a Yamagimoto CHN Autocorder Type MT-2 and a Mitamura Riken Kogyo Micro Elementary Analyzer. Molecular weight measurement was carried out with a Toso HLC-810 gel permeation chromatograph (GPC) (eluent = DMF; polystyrene standards). The instrinsic viscosity was measured in NMP or trifluoroacetic acid with an Ubbelohde viscometer at 30 °C.

Cyclic voltammetry was carried out with a Hokuto Denko HA-501 galvanostat/potentiostat and a Hokuto Denko KB-104 function generator. Conductivity measurement was carried out by a two-probe method using a Sanwa CDS-820 digital multimeter. Iodine doping was carried out by exposure of the polymer powder to the vapor of iodine in a vacuum line. Excess iodine was removed under vacuum. Doping with HCl was performed by stirring the polymer powder dispersed in an aqueous solution of HCl (0.1 M) for 1 day at room temperature, and the powder was collected by filtration and dried under vacuum. These doped samples were pressed into pellets at about 2×10^8 Pa. From the pellet a bar was obtained by cutting the pellet, and carbon paste was put at both the ends of the bar to measure the electrical conductivity. A film of P(DPA) was prepared by casting a NMP solution and immersed in an aqueous H_2SO_4 solution to measure the electrical conductivity. The thermal properties of the polymers were measured on Shimadzu TG-30 thermal analyzer under nitrogen at a constant heating rate of 10 °C min^{-1}.

Result and Discussion

Preparation. Dehalogenation polycondensation of the 4,4′-dibromodiphenylamine by using the zerovalent nickel complex gives the corresponding P(DPA) in high yield.



$Ni^{(0)}L_m$:a = 1:1 mixture of $Ni(cod)_2$ and bpy

Use of reaction conditions (employment of mixture of $Ni(cod)_2$ and bpy as $Ni^{(0)}L_m$ in DMF at 60 °C) applied to the previously reported analogous polycondensation is also effective in the present polycondensation, and the polymers are obtained in high yields (88−97%). In cases of chemical and electrochemical oxidative polymerizations of arylamines, the polymer is obtained as doped polymer. However, in the present polycondensation, the polymer obtained is in a neutral state.

Table 1 summarizes results of the polycondensation, molecular weights, and optical data of the polymers. P(DPA) gives an $[\eta]$ value of 0.66 dL g^{-1} (dL = 100 mL) in NMP at 30 °C and shows M_n and M_w values of 6400 and 20 000, respectively, as determined by its unimodal GPC trace (eluent = DMF; polystyrene standards). The relatively large $[\eta]$ value for the M_n value is attributed to a stiff structure of the polymer. At shorter polymerization time, e.g., 4 h (run 3 in Table 1), the polymer shows a smaller $[\eta]$ value of 0.32 dL g^{-1} and a lower M_w value of 4000. The previously reported poly(diphenylamine)s prepared by the oxidation polymerization of diphenylamine or 1-aminobiphenyl (eq 1)[16] seem not to have good solubility in solvents according to the literature. The copolymers P(DPA-*ran*-Tol) are also obtained in high yields (97−99%; runs 4−7 in Table 1).

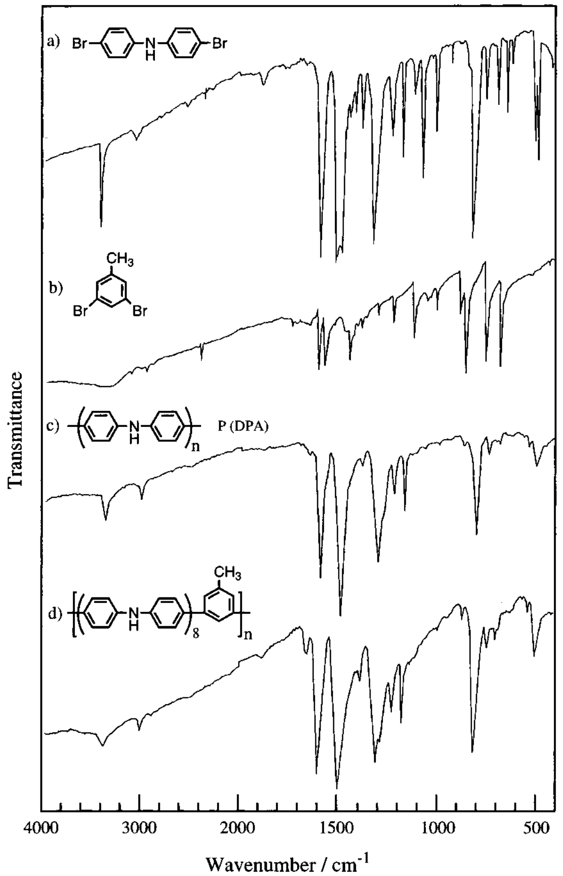


Figure 1. IR spectra of (a) Br–PhNHPh–Br, (b) $TolBr_2$, (c) P(DPA), and (d) P(DPA-*ran*-Tol) (8:1).

In the case of a 8:1 copolymer, it gives a [η] value of 1.0 dL g^{-1} (dL = 100 mL) in NMP at 30 °C and shows M_n and M_w values of 4400 and 8300, respectively, as determined by GPC. Other copolymers give the [η] value of 0.45–1.57 dL g^{-1} and the M_n value of 4200–9200 (runs 4, 6, and 7 in Table 1).

Both the homopolymer and copolymers are soluble in *N*-methyl-2-pyrrolidone (NMP) and trifluoroacetic acid and partly soluble in DMF, THF, and DMSO. The polymer is insoluble in other organic solvents. Solubility of the polymers is shown in the Supporting Information.

For both the homopolymer and copolymers, the weight loss starts at about 500 °C with 73 and 60% residual weight at 900 °C under N_2.

IR and NMR. Figure 1 shows the IR spectra of the polymers. The IR spectrum of P(DPA) resembles those of the corresponding polymers prepared by the oxidation polymerization (eq 1).[16] However, the IR spectrum of P(DPA) (spectrum c in Figure 1) exhibits a simpler absorption pattern and shows some differences from those of the previously reported polymers. For example, the ν(N–H) band of P(DPA) is considerably sharper than that[16c] of the previously reported poly(diphenylamine) obtained by the oxidative polymerization.

The present P(DPA) and its HCl adduct[18] give rise to one sharp out-of-plane vibration δ(CH) band at 803 cm^{-1} characteristic of the *p*-phenylene unit.[17a] On the other hand, the previously reported samples give multiple (two or three (e.g., at 812, 749, and about 690 cm^{-1},[16c] or 808 and 694 cm^{-1} [16d])) strong absorption bands in this region,[16c] presumably due to the presence of the aromatic units such as the unit B shown in eq 1 besides the unit A. The copolymers give additional peaks originating from the toluene-3,5-diyl unit (e.g., aliphatic ν(C–H) peak at 2900 cm^{-1} and δ(CH) peaks of 1,3,5-trisubstituted bezene in a range of 900–1200 cm^{-1}). The ν(C–Br) absorption band of the monomers is not observable in the IR spectra.

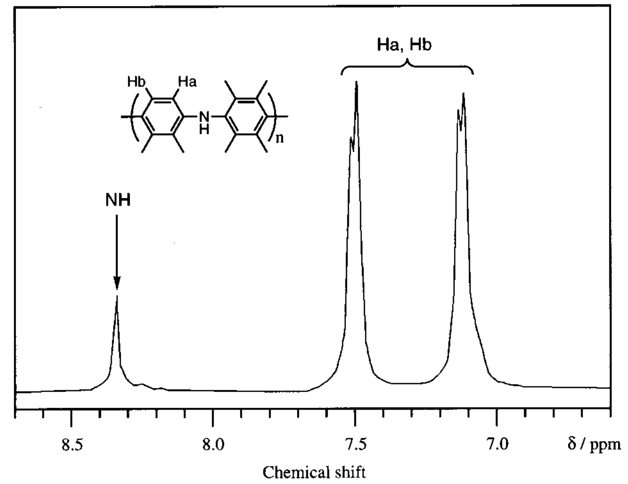


Figure 2. ^1H NMR spectrum of P(DPA) in DMSO-d_6.

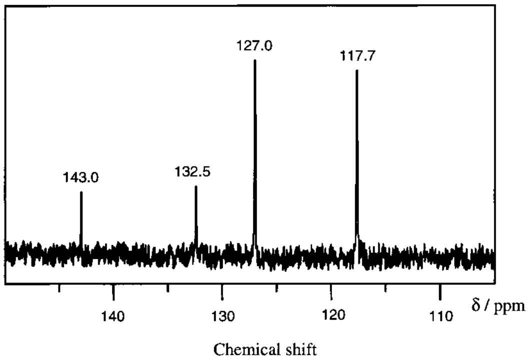


Figure 3. $^{13}C\{^1H\}$-NMR spectrum of P(DPA) in NMP-d_9.

For both P(DPA) and P(DPA-*ran*-Tol), a ν(N–H) absorption band appears around 3390 cm^{-1}. The absorption bands at 1600 to 1490 cm^{-1} are assigned to the ring-stretching modes of the phenyl groups in the polymers, respectively. These bands are also observed in the IR spectrum of polyaniline and have received the same assignment.[1–5]

NMR data of the polymers are also reasonable for their structures. Figure 2 shows the ^1H NMR spectrum of P(DPA) in DMSO-d_6. As shown in Figure 2, P(DPA) exhibits an AB quartet pattern (δ 7.14 and 7.53 ppm with J = 6.5 Hz) characteristic of the *p*-phenylene unit and gives a peak of N–H at δ 8.32 ppm, the position being comparable to that of the N–H peak of polyaniline.[21] The peak area ratio between the aromatic-H signals and the N–H signal agrees well with the structure of P(DPA). The copolymers in a CF_3COOD solution give rise to additional multiple peaks of the CH_3 group in a range from δ 2.4 to 2.6 ppm. The peak area ratio between the aromatic-H and methyl-H agrees with the feeding ratio of the two monomers.

The $^{13}C\{^1H\}$-NMR spectrum of P(DPA) shows sharp four clean peaks at δ 117.7, 127.0, 132.5 and 143.0 ppm in NMP-d_9 (Figure 3). All the IR and NMR data indicate that P(DPA) has a well-regulated structure.

UV–Visible and Photoluminescence. UV–visible spectrum of P(DPA) in NMP (Figure 4) shows a π–π*

Table 2. Conductivities of Polymers

polymer	conductivity σ (S cm^{-1}) HCl doped[a]	I$_2$ doped[a]	in 10% H$_2$SO$_4$[b,c]	in 30% H$_2$SO$_4$[b,c]	nondoped[a]
P(DPA) (run 1 in Table I)	1.14×10^{-5}	5	1.57×10^{-2}	5.69×10^{-1}	$<10^{-9}$
copolymer 4:1		6×10^{-1}			
8:1	1.97×10^{-5}	1.4			
12:1		2.9			
16:1		5×10^{-1}			

[a] Measured with compresed powder. [b] Measured with cast film. [c] The cast film was immersed in the H$_2$SO$_4$–adicic aqueous solution.

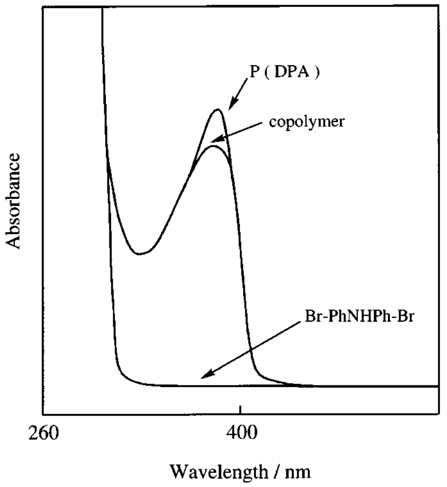


Figure 4. UV–visible spectra of (a) monomer, (b) P(DPA) and (c) P(DPA-*ran*-Tol) (8:1) in NMP.

absorption peak at 380 nm, which is somewhat shifted to a longer wavelength from that of the leucoemeraldine type polyaniline PLM $C_6H_4NH_n$ at 325 nm.[14] The monomer Br–PhNHPh–Br shows a $\pi-\pi^*$ absorption peak at 295 nm and the bathochromic shift (85 nm or 7600 cm^{-1}) for P(DPA) reveals expansion of the π-conjugation system by forming the polymer. Oxidized polyaniline, emeraldine type polyaniline PEM $(C_6H_4NHC_6H_4NH)_m(C_6H_4N{=}C_6H_4{=}N)_n$, gives a characteristic absorption band at 630 nm;[14] however, P(DPA) shows no absorption band in the region even in the NMP solution under air. These data indicate that P(DPA) is inert against oxidation by O_2 in air, in contrast to facile oxidation of PLM to PEM under air,[14b] and the results are consistent with higher oxidation potential of P(DPA) than that of PLM (vide infra).

UV–visible spectra of the copolymers in NMP show the $\pi-\pi^*$ absorption peak at almost the same position (second last column in Table 1). These data suggest expansion of the π-conjugation system even through the 1,3,5-trisubstituted benzene unit or stacking[22] of the copolymer in the solution. Cast films on a quartz glass plate essentially give the same UV–visible spectrum.

P(DPA) and the 8:1 copolymer show strong photoluminescence with a quantum yield of about 20 and 35% in NMP, respectively (Figure 5). The peak position of the photoluminescence (417 nm for both P(DPA) and the 8:1 copolymer) agrees with the onset position of the $\pi-\pi^*$ absorption band, as usually observed with photoluminescent aromatic compounds.

Conductivities. P(DPA) and the copolymers themselves are insulating materials; however, they are converted into semiconducting materials by treatment with acids or iodine. Table 2 summarizes the electrical conductivity of P(DPA) and the copolymers. P(DPA) and the 8:1 copolymer treated with 0.1 M HCl(aq) have electrical conductivities of 1.14×10^{-5} and 1.97×10^{-5} S cm^{-1}, respectively, as measured with compressed powders.

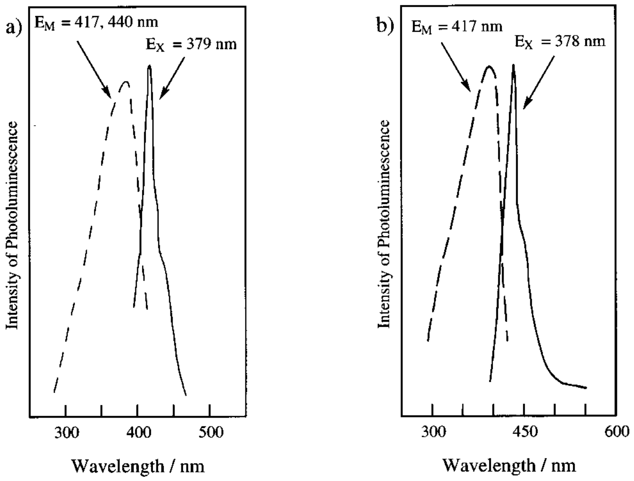


Figure 5. Photoluminescence spectra (solid line) of (a) P(DPA) and (b) P(DPA-*ran*-Tol) (8:1) in NMP. The broken line indicates the excitation spectrum. The wavelength of irradiated light E_X (for the photoluminescence spectrum) and the wavelength of monitering photoluminescence light E_M (for the excitation spectrum) are given in the figure. In Figure 5a, monitoring at the main (417 nm) and shoulder (440 nm) photoluminescence peaks gives essentially the same excitation spectrum.

A film of homopolymer prepared by casting from NMP is insulating with electrical conductivity of less than 10^{-9} S cm^{-1}; however, it shows electrical conductivity of 1.6×10^{-2} and 5.7×10^{-1} S cm^{-1} at room temperature when immersed in 10% and 30% H_2SO_4(aq), respectively. Due to the dependence of its conductivity on the concentration of H_2SO_4, the polymer may be usable as a sensor to measure the concentration of H_2SO_4 (e.g., in a lead battery).[23]

The homopolymer and the 8:1 copolymer show good conductivities with 5 and 1.4 S cm^{-1}, respectively, when treated with I_2. The treatment with I_2 is considered to bring about oxidation of P(DPA) and doping with HI, similar to the oxidation of PLM-type polyaniline to HX-doped PEM type polyaniline by abstraction of the NH hydrogen with halogene (X_2).[24] Although the π-conjugation system in the copolymer seems to be disturbed by the 3,5-Tol group, the copolymer is still considered to contain blocks constituted of the recurring *p*-biphenylenamine units which contribute to the electrical conduction.

Electrochemical Behavior. Figure 6 shows the cyclic voltammogram (CV) of a cast film of P(DPA) in a CH_3CN solution of $[Et_4N]BF_4$ (1.0 M). For comparison, a CV chart of PLM type polyaniline obtained by chemical oxidation polymerization was also recorded under similar conditions and is shown in part b in Figure 6. Both the CV charts exhibit two reversible redox cycles. As for P(DPA) the first and second electrochemical oxidation proceeds at E_{pa} of 0.27 and 0.65 V vs Ag/Ag$^+$,

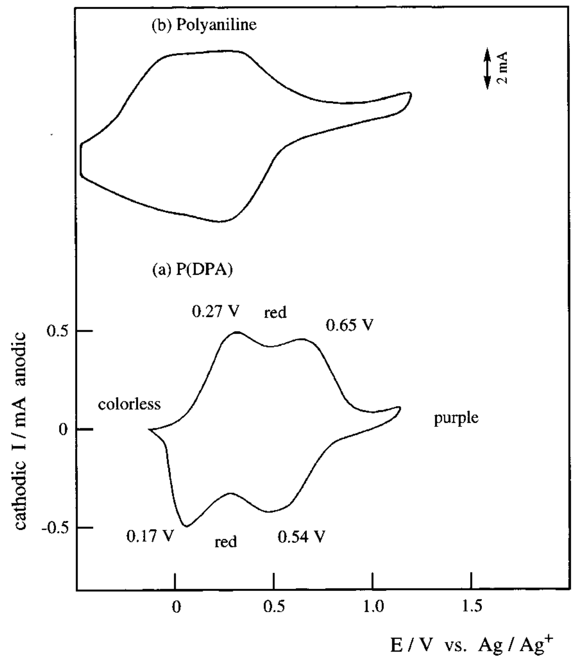
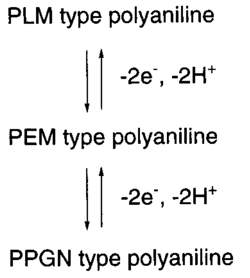


Figure 6. Cyclic voltammograms of (a) P(DPA) film and (b) polyaniline (neutral) film[27] on a Pt electrode (1 cm × 1 cm) in a CH_3CN solution of $[Et_4N]BF_4$ (1.0 M). Sweep rate = 20 mV s^{-1} for P(DPA).

Scheme 1. Oxidation of Poly(aniline)[1,25]



PLM: polyleucoemeraldine

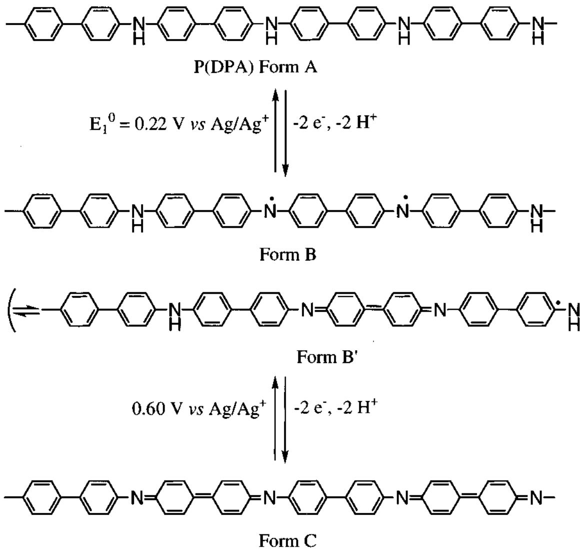
PEM: polyemeraldine

PPGN: polypernigraniline

respectively, and these two oxidation processes are coupled with the corresponding reduction processes with E_{pc} values of 0.12 and 0.54 V vs Ag/Ag$^+$, respectively. During the first oxidation step, the almost colorless film becomes red, whereas during the second oxidation step the color changes to purple. The color change is reversible, and the electrochemical redox reactions can be repeated more than 10 times without observable change in the CV curve. A film of poly(diphenylamine) prepared by the oxidative polymerization also shows similar two-step oxidation in a range of about 0.2–1.2 V vs Ag/Ag$^+$.[16d] However, the oxidation of the film of the present P(DPA) seems to take place at somewhat lower potential, and the color changes observed during the electrochemical oxidation also show differences.

The film of polyaniline shows similar two-step electrochemical processes,[25,26] and the redox potentials of P(DPA) are somewhat higher than those of polyaniline observed in organic solvents.[26] The two-step oxidation

Scheme 2. Oxidation of P(DPA)



of polyaniline is considered to be expressed by Scheme 1.[1,25]

If similar oxidation proceeds with P(DPA), it can be expressed by Scheme 2, and the oxidation of P(DPA) will request the formation of a planar quinoid type biphenyl unit in the polymer chain as depicted in form B′ and form C in the above shown scheme. The quinoid type biphenyl unit will receive steric repulsion due to the *o*-hydrogens, and this seems to be the reason for the higher oxidation potentials of P(DPA) than those of polyaniline. However, the oxidation potentials of P(DPA) are lower than that (ca. 1.1 V vs Ag/Ag$^+$) of poly(*p*-phenylene).[28]

Conclusions

Dehalogenation polycondensation of the corresponding dihalogenated monomers based on organonickel chemistry gives poly(biphenylamine) and its copolymer. Obtaining well-characterized poly(arylamine) is expected to contribute to comprehension of chemical properties of poly(arylamine)s. The polymers have strong photolumunescence with a quantum yield of about 20–35%. They are oxidized chemically and electrochemically to give semiconducting materials with color changes.

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Supporting Information Available: Solubility of polymers and TGA data of polymers (2 pages). Ordering information is given on any current masthead page.

References and Notes

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