Synthesis and Chiroptical Properties of Optically Active Poly(*N*-alkylanilines) Doped and Intertwined with Dextran Sulfate in Aqueous Solution

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ABSTRACT: Optically active and water-processable poly(*N*-alkylanilines) (*N*-PAAs), such as poly(*N*-methylaniline), poly(*N*-ethylaniline), and poly(*N*-*n*-propylaniline), were synthesized by chemical polymerization of the corresponding monomer in the presence of dextran sulfate (DSA). The resultant *N*-PAAs were doped and intertwined with DSA in complex form, *N*-PAAs−DSA, which was characterized by UV−vis, FTIR, cyclic voltammetry, and GPC. The induction of chiral structure on *N*-PAAs was confirmed by CD spectra. The size of alkyl groups had a great effect on the optical activity of final polymers. The detailed investigation of ionic strength effect on the optical activity in *N*-PAAs supported that excess one-handed helical structure was induced into *N*-PAAs by doping and intertwining them with DSA in a macromolecular complex. On the basis of titration of *N*-PAAs−DSA aqueous solution, the optical and chiroptical behaviors of *N*-PAAs−DSA were intensively investigated with varying pH. The studies on the conductivity of *N*-PAAs−DSA and the chiroptical properties of them in different redox states provide proof for them to be used as conductively and electroactively chiral materials.

Introduction

The field of inherently conducting polymers has attracted considerable attention due to their interestingly electrical and optical properties for many technological applications. Recently, chiral conjugated polymers have been synthesized for potential applications to circularly polarized electroluminesence[1] and chiral electrode.[2] In addition, some important concepts, such as cooperative response to chiral information,[3] memory of helicity,[4] and odd−even effect,[5] have been introduced and confirmed by studying the substituted derivatives of these polymers.

Polyanilines (PANIs) are some of the most extensively studied inherently conducting polymers because of their excellent stability and electronic properties. Helical PANI and its ring-substituted derivatives have been enantioselectively synthesized by using low molecular camphorsulfonic acid (CSA^-H^+) as chiral dopant.[6−9] However, few reports have prepared optically active N-substituted PANIs, which are distinguishable from ring-substituted PANIs.

Poly(*N*-alkylanilines) (*N*-PAAs) have been extensively studied. Compared with the low molecular weights obtained in ring-substituted poly(alkylaniline) with a long alkyl group,[10] *N*-PAAs have much higher degrees of polymerization.[11] The successful synthesis of conducting *N*-PAAs with alkyl groups ranging from methyl to *n*-butyl was first reported in 1989 via electrochemical polymerization of *N*-alkylanilines in H_2SO_4 aqueous solution.[12] Dao et al.[11] studied the synthesis and characterization of poly(*N*-alkylanilines) with alkyl groups ranging from methyl to *n*-dodecyl by chemical and electrochemical polymerization of the corresponding monomer in 1.0 M perchloric acid using ammonium persulfate (APS) as oxidant. These *N*-PAAs have high degrees of polymerization and show multiple and reversible optical transitions similar to those of PANI.

Kane-Maguire et al.[6] has suggested that a preferred one-screw in PANI is maintained by both the electrostatic bonding of CSA^- anions to PANI $HN^{\bullet+}$ centers and H bonding of CSA^- carbonyl groups to HN sites. Acid doping of emeraldine base (EB) form of poly(*o*-methylaniline) and poly(*o*-methoxyaniline) with (+)- or (−)-CSA in dimethyl sulfoxide (DMSO) also induced chirality.[7,13] However, it is much slower than that of the parent PANI (EB) because of steric hindrance to polymer rearrangement by methyl and methoxy ring substituents. Similarly, PEOA completely lost its optical activity in DMSO because the large steric hindrance of ethoxy ring substituents destroys the hydrogen bonding of CSA^- carbonyl groups to PEOA HN sites and therefore the preferred one-screw.[9] Because of the higher steric hindrance of N-substituted alkyl groups, it seems that it would be much more difficult to induce a helical structure on *N*-PAAs and maintain their preferred one-screw by protonating them with CSA^-H^+. Moreover, the classic scheme of *N*-PAAs[11] suggests that the yield of $NR^{\bullet+}$ in polymers is not protonation-dependent.

We recently reported that a preferred one-handed helical structure was induced into the main chain of parent and some ring-substituted PANIs by chemical polymerization of the corresponding monomers in the presence of a chiral polyanion, dextran sulfate (DSA), where the protonated monomers were aligned along the chain of DSA by electrostatic interaction prior to polymerization and the resultant PANI was proposed to predominantly adopt a one-handed helical screw while it was doped and intertwined with DSA through interpolymeric complexation.[14] Such an induced chirality on PANIs indicates that the macromolecular architecture of PANIs can be controlled at the molecular level by

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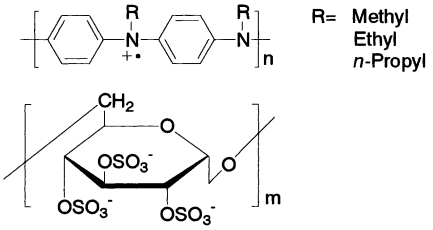
Scheme 1



intermacromolecular complex formation rather than by isolated incorporation of low molecular weight CSA along their chains. Also, it offers a preferable method to control the helical conformation of PANIs in aqueous solution since most important biological events with biomacromolecules occur in water.[15] In addition, incorporation of such a structure-ordered ionic polysaccharide into PANIs may also make the resultant PANI−DSA useful as electroactively chiral selector material.[16]

Herein, we report in-situ preparation of three optically active *N*-PAAs (Scheme 1) by chemical polymerization of the corresponding monomers in the presence of DSA using APS as oxidant. To our knowledge, this is the first example for successful preparation of optically active N-substituted PANIs. The synthesized *N*-PAAs were doped and intertwined with DSA to form macromolecular complexes, *N*-PAAs−DSA. Since DSA also imparts water solubility (or dispersibility) to the final molecular complex *N*-PAAs−DSA, it is possible to study the chiroptical properties of these *N*-PAAs in aqueous solution. The effect of substituents on the induction of chirality was investigated by adjusting N-substituted alkyl size.

Experimental Section

Materials and Methods. The sample of dextran sulfate sodium salt was the product of Meito (Japan); M_w 70 000, S 18% corresponding to three sulfate groups per one D-glucose unit. The Na^+ salt of dextran sulfate (DSA^-Na^+) (0.2 g of DSANa dissolved in 200 mL of deionized water) was first converted to H^+ form (DSA^-H^+) using ion-exchange resin (Tokyo Chemical, Na^+ exchanged into H^+ in advance), and DSAH was concentrated in 50 mL of aqueous solution by distilling under reduced pressure. The DSAH solution was dialyzed against deionized water using a dialysis membrane (Spectrum products) with a molecular weight cutoff at ca. 8000, and the average acid concentration in the solution (50 mL) was determined by titration to be 1.1 mmol with standard aqueous NaOH. As *N*-alkylanilines, the methylaniline, ethylaniline, *n*-propylaniline, and *n*-butylaniline were purchased from Tokyo Chemical Industry Co. Ltd. (Japan) as reagent grade. Ammonium persulfate (APS), LiBr, *N*,*N*-dimethylformamide (DMF), and all of other reagents were the products of Kanto Chemical (Japan) and used as received.

Preparation of Poly(*N*-alkylanilines)−DSA Complex. Poly(*N*-methylaniline) (*N*-PMeA), poly(*N*-ethylaniline) (*N*-PEtA), poly(*N*-*n*-propylaniline) (*N*-PPrA), and poly(*N*-*n*-butylaniline) (*N*-PBuA) were prepared by chemical polymerization of the corresponding monomer in the presence of dextran sulfate. Typically, *N*-methylaniline monomer (1 mmol) was added to DSAH aqueous solution (1.1 mmol in 50 mL) with vigorous stirring for 30 min. Then, chemical polymerization was initiated by dropwisely adding APS aqueous solution (1 mmol in 5 mL) to monomer solution at ca. 0 °C and carried out for 20 h. After dialysis of the final solution against deionized water by using dialysis membrane with the molecular weight cutoff at ca. 8000, a homogeneous dark green *N*-PMeA−DSA aqueous solution (ca. 50 mL) was obtained. Also, homogeneous green aqueous solutions were obtained for *N*-PEtA−DSA, *N*-PPrA−DSA, and *N*-PBuA−DSA after dialysis against deionized water. *N*-PAAs−DSA could be respectively precipitated from the corresponding solution by dipping it into excess acetone. After filtering, washing with 1:1 acetone/water solution, and drying sequentially, a green powder of *N*-PAAs−DSA was obtained: *N*-PMeA−DSA, 0.24 g; *N*-PEtA−DSA, 0.24 g; *N*-PPrA−DSA, 0.23 g; *N*-PBuA−DSA, 0.21 g.

FTIR data of *N*-PAAs−DSA (KBr pellet, cm^{-1}): *N*-PMeA−DSA, 2800−3000 (ν_{C-H} in CH_3), 1580 (quinoid), 1510 (benzenoid), 1380 (ν_{C-N}), 1120 and 1050 ($\nu_{O=S=O}$); *N*-PEtA−DSA, 2800−3100 (ν_{C-H}), 1580 (quinoid), 1500 (benzenoid), 1390 (ν_{C-N}), 1120 and 1050 ($\nu_{O=S=O}$); *N*-PPrA−DSA, 2800−3100 (ν_{C-H}), 1580 (quinoid), 1500 (benzenoid), 1400 (ν_{C-N}), 1120 and 1050 ($\nu_{O=S=O}$); *N*-PBuA−DSA, 2800−3100 (ν_{C-H}), 1580 (quinoid), 1500 (benzenoid), 1405 (ν_{C-N}), 1120 and 1050 ($\nu_{O=S=O}$). Anal. Found (%): *N*-PMeA−DSA, S 11.44, N 4.81; *N*-PEtA−DSA, S 11.38, N 4.25; *N*-PPrA−DSA, S 11.06, N 4.01; *N*-PBuA−DSA, S 10.75, N 3.79.

Spectroscopic Studies and Light Scattering Analysis. UV−vis and circular dichroism (CD) spectra of polymers were recorded on a JASCO V-570 UV−vis−NIR spectrophotometer and a JASCO V-720WI spectropolarimeter, respectively. The spectral measurement was performed in a 10 mm quartz cell for aqueous solution or on a glass substrate for coated films. FTIR spectra of dried sample in KBr pellet were recorded using a Fourier transform infrared spectrometer (HORIBA F-210). The data of particle size distribution were recorded on a HORIBA laser scattering particle size distribution analyzer LA-300 (0.1−600 μm) by the light scattering measurement of diluted *N*-PAAs−DSA aqueous solution in quartz cell, which was performed only while the light transmittance is over 90%.

Gel Permeation Chromatograms (GPC). *N*-PAAs−DSA samples were first treated with concentrated HCl solution to decompose the polymeric DSA into low weight molecules. To remove DSA from the *N*-PAAs, the treated *N*-PAAs−DSA were dedoped by respectively stirring them in 1 N NH_4OH aqueous solution. After filtering and drying, *N*-PAAs samples were obtained and dissolved in DMF. GPC was recorded on TOSOH HLC-8120GPC (column, TOSOH KD80M) at 25 °C using 0.01 mol L^{-1} LiBr/DMF as eluent. The weight-average (M_w) molecular weight was determined by standard procedures using polystyrene standards.

Preparation of Films and Measurement of Conductivity. After evaporation of water from dialyzed aqueous solution on a glass substrate at room temperature, continuous and smooth films were obtained for *N*-PMeA−DSA, *N*-PEtA−DSA, and *N*-PPrA−DSA. The film of *N*-PBuA−DSA is not as good as those three. After drying under vacuum, the conductivity of these films was measured using a standard four-probe method with a Loresta HP (MCP 410) (Mitsubishi Chemical Co.).

Cyclic Voltammetry. The electrochemical characterization of *N*-PAAs−DSA films coated on Pt electrode was performed using cyclic voltammetry. The cyclic voltammograms were obtained with a potentiostat/galvanostat (Hokuto Denko model HA-301) and a X−Y recorder. The potential was cycled between −0.2 and 1.0 V (vs Ag/AgCl) at a scan rate of 50 mV/s in aqueous 1.0 mol dm^{-3} HCl as supporting electrolyte and using Pt counter electrode.

Results and Discussion

Chiroptical Properties of *N*-PAAs−DSA. After dialyzing the final solutions against the deionized water as described above, green homogeneous solutions (or dispersions) were obtained without visual particles or precipitates for *N*-PMeA−DSA, *N*-PEtA−DSA, *N*-PPr−DSA, and *N*-PBuA−DSA. These aqueous polymer solutions remain stable for months; that is, polymer does not precipitate out of solution. The result of light-scattering analysis also confirms the yielded *N*-PAAs−DSA complexes are well dispersed (or dissolved) in aqueous solutions without particles observed (0.1−600 μm). DSA apparently imparted the water dispersibility

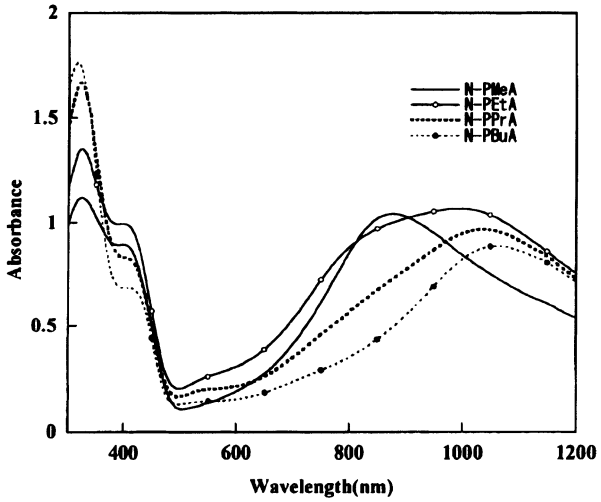


Figure 1. UV−vis spectra of *N*-PMeA−DSA, *N*-PEtA−DSA, *N*-PPrA−DSA, and *N*-PBuA−DSA in aqueous solutions (by diluting 0.1 mL of 50 mL of dialyzed *N*-PAAs−DSA aqueous solution to 4 mL with deionized water).

Table 1. Molecular Weights (M_w) and the Degree of Polymerization (D_p) of *N*-PAAs and Molar Ratio of S/N in Complexes

N-PAAs	M_w	D_p	S/N
N-PMeA	40 000	374	1.04
N-PEtA	44 000	363	1.17
N-PPrA	43 800	325	1.21
N-PBuA	45 700	307	1.24

of the final intermacromolecule complex. The UV−vis spectra (Figure 1) of these aqueous solutions show essentially the same pattern as that of PANI with the observed $\pi-\pi^*$ transition and polaron bands.[17] For instance, *N*-PMeA−DSA exhibits an intense $\pi-\pi^*$ transition at 325 nm, and the polaron bands at 410 and 877 nm are tentatively assigned as second and localized polaron bands, respectively. The spectrum is characteristic of *N*-PMeA in the conducting polaron form and is identical to that doped with ClO_4^-.[11] For other *N*-PAAs, besides the change in the relative intensity of bands at 325 and 410 nm, the localized polaron bands regularly shift to higher wavelength. Such a shift in localized polaron band is probably due to a change of conjugation length in these *N*-PAAs with different alkyl length, which may contribute to the conductivity of the final polymers.[18]

All of *N*-PAAs have a high degree of polymerization over 300 as shown in Table 1, which is comparable to that previously reported.[11] Although the molecular weight is not significantly improved in these cases, GPC fractions showed that the yield of oligomers was very little. It is proposed that DSA served as a template for the polymerization of *N*-PAAs; that is, the polymerization of monomers aligned on template was improved.[17] The molar ratio of S/N in these final polymers is also shown in Table 1, which indicates the ratio of dextran to *N*-alkyanilines unit in the final *N*-PAAs−DSA complex. Because half of the monomer units in *N*-PAAs were doped with DSA based on the classic scheme,[11] the free SO_3^- serves to impart the water solubility of the final complex. The S/N ratio shows a little increase with the size of alkyl group increasing, which may be effected by the yield of *N*-PAAs and size of alkyl group in.

The CD spectra (Figure 2) of *N*-PAAs−DSA aqueous solutions confirm that *N*-PMeA−DSA, *N*-PEtA−DSA,

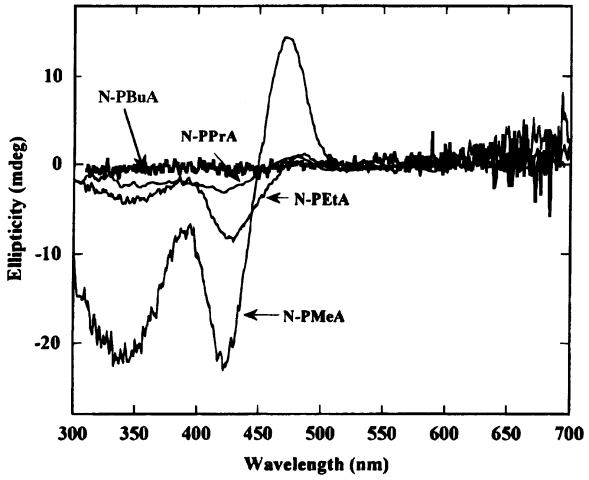


Figure 2. CD spectra of *N*-PMeA−DSA, *N*-PEtA−DSA, *N*-PPrA−DSA, and *N*-PBuA−DSA in aqueous solutions corresponding to Figure 1.

and *N*-PPrA−DSA were optically active. They share almost similar CD spectra pattern with well-defined CD bnads between 300 and 700 nm. For *N*-PMeA−DSA, the CD peaks at 470 and 420 nm are tentatively assigned as bisignate, exciton-coupled bands associated with the polaron band. The band at 340 nm is the only one of another probable pair of bisignate excition-coupled CD bands corresponding to the $\pi-\pi^*$ transition at 325 nm. Although the final data confirmed the yield of *N*-PBuA doped with DSA, the aqueous solution of it did not show clear CD bands in this region. It is presumed that the steric hindrance of the *n*-butyl group restricted the arrangement of polymer chain to adopt a chiral architecture. Such an effect of substituents on the chirality is also reflected in CD bands intensity of optically active *N*-PAAs. Although the UV spectra in Figure 1 indicate the similar concentration of these *N*-PAAs solutions, the CD band's intensity of *N*-PPrA−DSA is much weaker than that of *N*-PMeA−DSA. According to such a trend, it is reasonable to understand that the optical inactivity of *N*-PBuA is due to the large bulkiness of the *n*-butyl group.

The films of optically active *N*-PMeA−DSA and *N*-PEtA−DSA were prepared on a glass substrate by coating the corresponding aqueous solution on it. *N*-PMeA−DSA film (4 μm) shows an intensive CD band at ca. 465 nm and another possible band at lower wavelength (Figure 3A), which is obviously different from that of aqueous solution. A similar result is also observed in *N*-PEtA−DSA film (5 μm). The change in CD bands probably indicates that there is a change in the conformation of polymer chain while the condition was changed from aqueous solution to solid film.[8] Nevertheless, *N*-PMeA−DSA film shows an identical UV−vis spectrum (Figure 3B) with that of aqueous solution. Conversely, in the case of parent and ring-substituted PANIs, either the aqueous solutions or the films show almost similar CD spectra.[14]

Cyclic Voltammetry and Conductivity. The cyclic voltammogram (Figure 4) of the optically active *N*-PMeA−DSA film coated on a Pt electrode confirmed that the polymer was electroactive, with two redox couples at +0.38 and +0.51 V (vs Ag/AgCl) for anodic peaks termed as E_{pa1} and E_{pa2}, respectively. The positions of these redox couples were nearly identical to those reported *N*-PMeA doped with ClO_4^-.[11] The first (+0.38 V) anodic process is related to the oxidation of

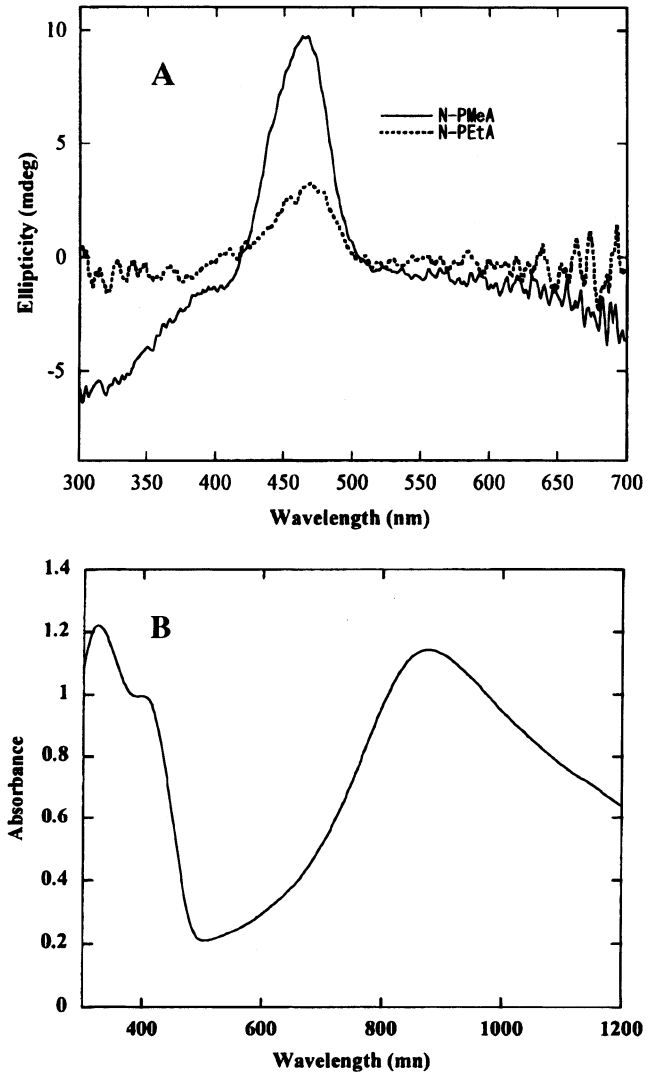


Figure 3. CD spectra of *N*-PMeA−DSA (4 μm) and *N*-PEtA−DSA (5 μm) films (A) and corresponding UV−vis spectra of *N*-PMeA−DSA film (B).

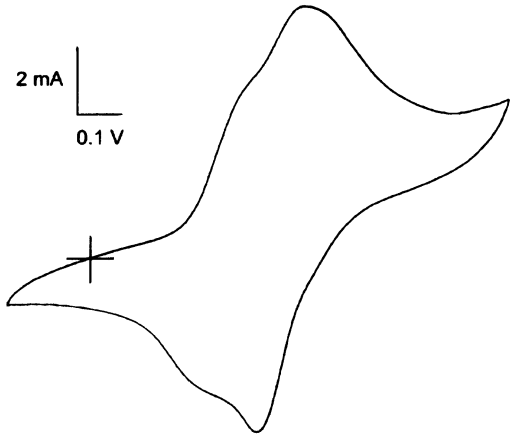


Figure 4. Cyclic voltammogram of *N*-PMeA−DSA in 1.0 mol dm^{-3} HCl; −0.2 to 1.0 V vs Ag/AgCl, Pt electrode, scan rate 50 mV/s.

reduced *N*-PMeA to polaronic form, while the second (+0.51 V) anodic process corresponds to the oxidation of polaronic form to bipolaronic form. The E_{pa} values of *N*-PEtA−DSA and *N*-PPrA−DSA are also shown in Table 2. The values show an increase from *N*-PMeA to *N*-PPrA. Such a trend has also been observed for the

Table 2. Conductivity[a] and Anodic Peaks[b] Observed for *N*-PPAs−DSA

N-PAAs−DSA	conductivity (S/cm)	anodic peaks (V vs Ag/AgCl) E_{pa1}	E_{pa2}
N-PMeA−DSA	6.8×10^{-2}	0.38	0.51
N-PEtA−DSA	5.3×10^{-4}	0.45	0.53
N-PPrA−DSA	2.1×10^{-4}	0.48	0.53

[a] The conductivity measured in the films cast from aqueous dispersions. [b] The cyclic voltammogram obtained in 0.5 M HCl at a scan rate of 50 V/s on a Pt electrode.

first anodic peaks in ring-substituted PANIs.[14] It has been suggested that the presence of increasingly bulky substituents induces additional deformation along the polymer backbone due to the steric hindrance.[10,11] Consequently, the degree of conjugated degree decreases and the oxidation potential increases, which is consistent with that reflected in electronic spectra.

As shown in Table 2, *N*-PAAs have a rather high conductivity comparable to that of ring-substituted PANIs.[14] The observed conductivity is ca. 1−3 orders of magnitude higher than that of *N*-PAAs doped with ClO_4^-,[11] which is proposed arising from ordered structure on *N*-PAAs chains induced by structure-ordered DSA. Similar appearances have also been reported for PANI while it was doped by chiral CSA.[19] At least, Liu et al. have found that polyelectrolyte served as template for the polymerization of aniline and helped to promote a more ordered para-directed polymerization and improve the degree of polymerization.[17,20]

Chiroptical Properties in Redox States. The chiroptical properties of *N*-PMeA were also studied in three different redox forms, tentatively termed as leucoemeraldine (reduced form), emeraldine salt (in-situ synthesized form), and pernigraniline (oxidized form) following those of the parent PANI. The as-synthesized *N*-PMeA was in the state of emeraldine salt. After addition of ammonium persulfate or phenylhydrazine to *N*-PMeA−DSA aqueous solution, *N*-PMeA was oxided to its pernigraniline state or reduced to its leucoemeraldine state, respectively. The color changes were similar to that of electrochemical oxidation or reduction of *N*-PMeA on an ITO glass electrode:[11] blue in the oxidized state and colorless in the reduced state. Oxidation to the pernigraniline form was confirmed by the characteristic absorption band at 640 nm (Figure 5A). The CD band (Figure 5B) at ca. 660 nm associated with this absorption band indicates the retention of chiral structure in fully oxidized *N*-PMeA. The reduction to leucoemeraldine was confirmed by the characteristic UV band at 320 nm due to $\pi-\pi^*$ transition and the disappearance of the initial visible region absorption bands. The CD bands at ca. 350 and 310 nm for its aqueous solution are tentatively assigned as the bisignate exciton-coupled bands associated with the 320 nm absorption band, which indicates that *N*-PMeA are still optically active at the fully reduced state in such an intertwined macromolecular complex. The stability for *N*-PMeA to keep its optical activity in different redox states is of significance for it to be used as a chiral electrode in electrochemically asymmetric synthesis and as an electroactively chiral membrane.[21]

Effect of Ionic Strength. *N*-Methylaniline was polymerized in the presence of different concentrations of additional NaCl. The CD bands intensity of resultant polymer decreased with increasing NaCl concentration, which is identical with that of preparing PANI−DSA

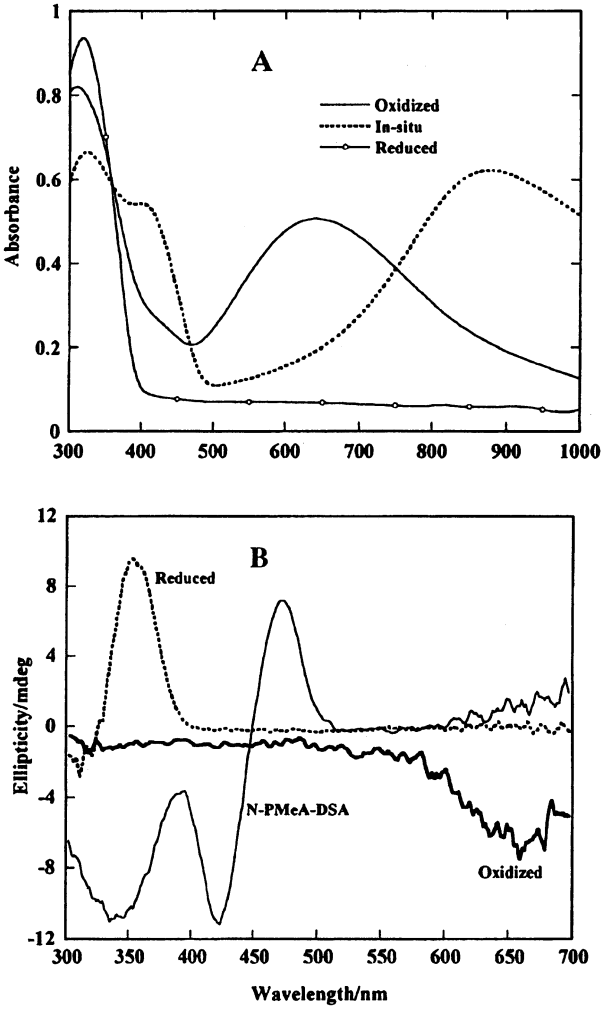


Figure 5. UV−vis spectra of *N*-PMeA−DSA aqueous solutions in in-situ synthesized form, reduced form, and oxided form (A) and corresponding CD spectra in these redox forms (B).

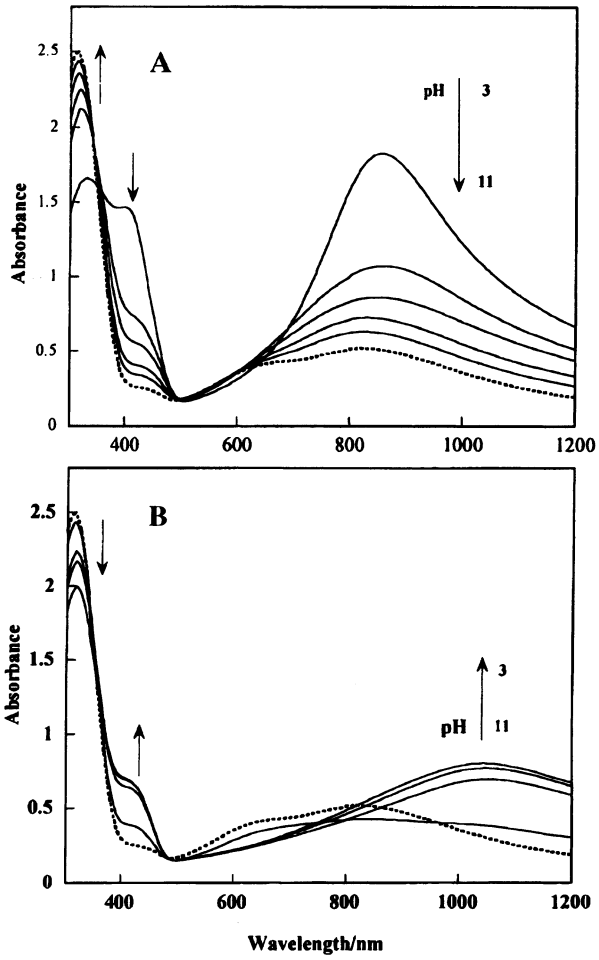


Figure 6. Change in UV−vis spectra of *N*-PMeA−DSA during titration by 1 M NaOH from pH 3 to 11 (A) and then by 1 M HCl from 11 to 3 in aqueous solution (B).

in a previous report.[14] After dialysis out NaCl, no defined CD band was observed for *N*-PMeA prepared in the presence of 0.3 M NaCl. We believed that the presence of Na^+ competitively hindered the electrostatic bonding of protonated monomer to DSA^- prior to polymerization, and thus the resultant *N*-PMeA was free from the complexation of DSA. As the result, the *N*-PMeA main chain lost its macromolecular asymmetry and solubility in absence of in situ doping and intertwining with DSA. In another control experiment, NaCl was postly added into the dialyzed *N*-PMeA−DSA aqueous solution after it was synthesized in the absence of NaCl in order to completely investigate the effect of ionic strength on the chiroptical properties of final polymers. To minimize the effect of other kinds of salt, the as-synthesized *N*-PAAs−DSA solution was repeatedly dialyzed against deionized water for several times. While NaCl was added to the solution up to 0.3 M, we just observed a little shift in CD bands rather than the loss of its optical activity. After dialysis NaCl out the solution, the CD spectrum was almost resumed. Such a change in CD spectra in the cycle of adding and dialyzing NaCl may be considered as an equilibrium property of the *N*-PMeA−DSA complex at different salt concentrations in aqueous solution. Of course, the complex was deposited from solution at very high concentrations of salt. From this point, it is understood that the conformation of *N*-PMeA in the resultant complex is rather stable against the effect of salts.

Chiroptical Properties of *N*-PMeA at Various pH Values. The optical properties of PANI are pH-sensitive.[22] The absorption and CD spectra of the *N*-PMeA−DSA complex were studied with varying pH in aqueous solution. The as-synthesized *N*-PMeA is in its poloran form. After dialyzing and diluting with deionized water, the initial pH value for spectrum measurement is ca. 3−4. Figure 6A shows the change in absorption spectra of complex with increasing pH from 3 to 11 by titrating its aqueous solution with 1 M NaOH. As the pH of the solution increased, the intensity of polaron bands at 420 and 860 nm gradually decreases. At the same time, the band at 320 nm due to the $\pi-\pi^*$ transition increased with a pH increase. At pH 11, the complex shows an intensive band at 320 nm and two weak bands at 860 nm (benzenoid form) and 650 nm (quinoid form). The reverse titration from pH 11 to 3 was carried out using 1 M HCl. While the pH of the solution decreases, the polaron band at 420 nm is partly resumed, and the localized polaron band shifts to 1050 nm (Figure 6B), which suggests that the conjugated length in *N*-PMeA has changed after such a cycle of titration.[23] Obviously, these changes in *N*-PMeA during titration are different from that of parent and ring-substituted PANIs, which reversibly show color change and bands shift during reverse titration due to deprotonation and protonation in PANI.[17,20,22] Such a difference in *N*-PMeA from PANI

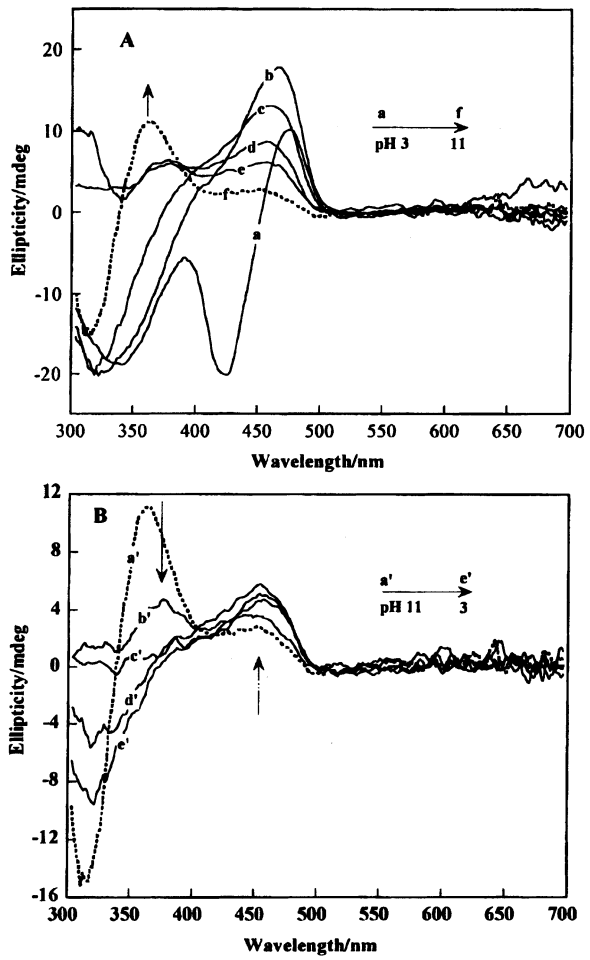


Figure 7. Change in CD spectra of *N*-PMeA−DSA during titration corresponding to Figure 6.

could be understood from its structure[11] because the doping of *N*-PMeA is not protonation-dependent. In reverse, this result proves our hypothesis that it may be impossible, at least very difficult, to induce a helical structure on *N*-PMeA by protonating it with low molecular weight chiral acid, such as camphorsulfonic acid.

Figure 7 shows the change in CD spectra of *N*-PMeA with varying pH in solution. While pH increases to 11, *N*-PMeA shows intensive CD bands at 310 and 360 nm, which are tentatively assigned as bisignate bands associated with the absorption band at 320 nm. Because of the overlap of this and another possible bisignate CD bands at 420 and 470 nm, the change in CD bands of *N*-PMeA is complex with varying pH. Unlike that of parent and ring-substituted PANIs,[14] neither the bands nor its intensity can be resumed to the original form after pH increases to 3. Such a result suggests that a conformational change in the chain of *N*-PMeA may occur after a cycle of dedoping and redoping, since CD spectra are highly sensitive to the change of molecular conformation.[24]

Conclusions

Several optically active and water-processable *N*-PPAs−DSA complexes, such as *N*-PMeA, *N*-PEtA, and *N*-PPrA, were synthesized by chemical polymerization of the corresponding monomer in the presence of DSA. The induction of chirality on *N*-PAAs was confirmed by CD spectra, and this is the first example to synthesize optically active N-substituted polyanilines. The conductivity of them was significantly improved possibly due to the guidance of structure-ordered DSA. The detailed investigation of the ionic strength effect on the optical activity in *N*-PMeA supported that excess one-handed helical structure was induced into *N*-PPAs by doping and intertwining them with DSA in the polymerization. *N*-PPAs showed different optical and chiroptical behaviors to that of parent and ring-substituted PANIs with varying pH in aqueous solution. The study on the conductivity of *N*-PMeA and chiroptical properties of it in different redox states provides proof for it to be used as chiral electrode. The different redox potential in *N*-PAAs exhibited the potential for them to be used as potential-selectable chiral electrode material. Furthermore, structure-ordered DSA was incorporated into *N*-PPAs, extending the possibility for them to be used as electroactively enantioselective separation material.

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