Water-Processable Chiral Polyaniline Derivatives Doped and Intertwined with Dextran Sulfate: Synthesis and Chiroptical Properties

Guo-Li Yuan and Noriyuki Kuramoto*

Graduate Program of Human Sensing and Functional Sensor Engineering, Graduate School of Science and Engineering, Yamagata University, 4-3-16 Jonan, Yonezawa, Yamagata 992-8510, Japan

Received June 11, 2002; Revised Manuscript Received September 25, 2002

ABSTRACT: Water-processable molecular complexes between dextran sulfate (DSA) and polyaniline derivatives (PANIs) have been synthesized by chemical polymerization of corresponding achiral monomer in the presence of DSA. The formation of the macromolecular complex was proved by the FTIR and UV−vis spectra. Interestingly, chiral macromolecular architecture was induced into PANIs due to the induction of DSA as macromolecular dopant in the formation of intermacromolecular complex, which was confirmed by the CD spectra. Furthermore, it was found that the substituents in aniline ring have a great effect on the chirality of final PANIs. Through the studies on ionic strength effect, dedoping and redoping, and thermochromism, it was established that the electrostatic interaction not only drove the interpolymer complexation but also played an important role in holding the chiral architecture of PANIs in the resultant macromolecular complexes. The study has also been performed toward the electrochemical activity, chirality in various redox states, and conductivity of PANI−DSA. The design and synthesis of such macromolecular complexes provides another example that the chiral macromolecular architecture of a synthetic macromolecule could be controlled at the molecular level by intermacromolecular complex formation, which often occurs in biopolymers.

Introduction

The important functions of biological macromolecules appear to be controlled by not only their first-order structures but also those of higher-order structure, e.g., a double helix of DNA.[1] In polymer chemistry[2] and supramolecular chemistry,[3] the research field on control of chiral architecture of synthetic macromolecules has received considerable attention because of possible application in numerous scientific fields. In recent years, a lot of interest has been focused on synthesis of chiral conjugated polymers in view of their potential applications to circularly polarized electroluminesence and chiral electrode for asymmetric synthesis.[4] Furthermore, since most important biological events and interaction of biomacromolecules occur in aqueous solution, it is a significant goal to control the helical conformation of synthetic macromolecules in aqueous solution, a cost-effective, safe, environment-friendly solvent.[5]

Polyaniline (PANI) and its derivatives have emerged as one group of most promising organic conducting polymers due to their high environmental stability, facile redox and pH switching behavior, and low cost. The potential for the use of PANI in a wide range of applications has already been demonstrated.[6−8] Helical PANI and some ring-substituted polyanilines have recently been enantioselectively synthesized by using low molecular camphorsulfonic acid (CSA^-H^+) as chiral dopant, in which the macromolecular asymmetry presumably arose from electrostatic bonding of CSA^- sulfate ion to PANI $HN^{\bullet+}$ centers and H-bonding of the CSA^- carbonyl group to HN sites.[9]

However, the inherent intractability of PANI limited its potential application. A major goal of recent studies has been to achieve water-soluble or water-dispersible PANI due to its environmental feasibility. The molecular complex between PANI and polyelectrolyte has been developed to prepare a water-soluble (or dispersible) polyaniline (PANI) by polymerization of aniline in the presence of anionic polyelectrolyte (polymeric acid), where the polyelectrolyte imparts the water solubility of such an interpolymer complex.[10] In these cases, an anionic polyelectrolyte was used to align the protonated monomer molecules along its chain through electrostatic interaction prior to polymerization, and the synthesized PANI was doped and intertwined by the chain of anionic polyelectrolyte to form an intimate PANI−polyelectrolyte molecular complex. Furthermore, the effect of stoichiometry has been intensively investigated to tune the intermacromolecular complexation, the water solubility, and conductivity of the final PANI−polyelectrolyte complex.[10e,f]

Yang et al. suggest that such interpolymer complexation forms a side-by-side intertwined molecular complex where polyaniline and the polyelectrolyte are bounded mainly by electrostatic interaction.[11] However, there have been few reports that the chiral macromolecular architecture was directly induced into PANI in such an intertwined PANI−polyelectrolyte macromolecular complex, although anionic polyelectrolyes have been used as codopant to improve the water processability[12] or stabilize the helical conformation against the racemization[11b] of chiral CSAH-doped PANI.

Most recently, Tripathy et al.[13] have found that it was possible for PANI to adopt a preferred one-sense helical screw in the complex of polyaniline−DNA by enzymatic polymerization of aniline in the presence of DNA as anionic polyelectrolyte template, where the chiral macromolecular architecture in PANI stems from its intertwining with DNA strand in the formation of intermacromolecular complex. Similarly, helical conformation has been induced into the main chain of polythiophene derivates due to the ionic complexation between DNA

* To whom correspondence should be addressed: e-mail Kuramoto@dip.yz.yamagata-u.ac.jp; Tel and Fax +81-238-26-3051.

10.1021/ma0209139 CCC: $22.00
Published on Web 11/12/2002

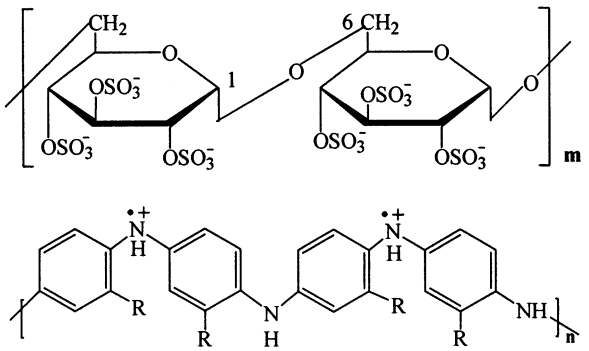

Figure 1. Structure of dextran sulfate and polyanilines (R− = −H, $-CH_3$, $-C_2H_5$, $-OCH_3$, $-OC_2H_5$).

and cationic polythiophenes.[14] So, it is significant to investigate the chirality of PANI in such macromolecular complex while other kinds of polyelectrolyte were selected as dopant for PANI, a synthetic chiral polyelectrolyte rather than DNA. Dextran sulfate (DSA), a semisynthetic polysaccharide, is a linear sulfated polysaccharide containing α-1,6-linked D-glucopyranose unites with three sulfate groups per one D-glucose unit (Figure 1) and has been employed as chiral selectors in capillary electrophoresis for enantiomer separation owing to its highly ordered structure and chirality.[15] It is expected that, besides behaving as other anionic polyelectrolyte dopants to impart the water solubility of the final PANIs−DSA molecular complex, chiral DSA would serve to induce a preferred one-handed helical structure into PANI while it bounds and intertwines with the PANI chain through the intermacromolecular complex formation.[16]

In this paper we report in detail the synthesis of PANI and some ring-substituted polyanilines (PANIs) (Figure 1) by chemical polymerization of corresponding achiral monomer in the presence of dextran sulfate. In addition to the water processability, all of PANIs adopted a helical structure while they were doped by DSA to form an intertwined macromolecular complex, which is different from that induced by chiral CSAH as referred above. Further investigations on the chirality of PANIs were carried out to explore the role of macromolecular interaction in the formation and maintenance of chiral structure of PANIs in the complex. The helical conformation in PANIs was investigated by circular dichroism (CD) spectropolarimetry, which is a well-known method for it.[17]

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^+ forms (DSA^-H^+) by ion exchange, and DSAH was concentrated in 50 mL of aqueous solution by distilling under reduced pressure. The molar acid concentration in the solution was determined by titration with standard NaOH solution (ca. 1.1 mmol in 50 mL of solution). All of the other chemicals were of reagent grade or better and used as received. The monomers of 2-ethylaniline and 2-ethoxyaniline were purchased from Tokyo Chemical Industry Co., Ltd. (Japan). The monomers of aniline, 2-methylaniline, 2-methoxyaniline, and other reagents were purchased from Kanto Chemical Company (Japan).

Preparation of PANIs−DSA Complex. Polyaniline (PANI), poly(2-methylaniline) (PMA), poly(2-ethylaniline) (PEA), poly(2-methoxyaniline) (PMOA), and poly(2-ethoxyaniline) (PEOA) were synthesized respectively by chemical polymerization of corresponding monomer in the presence of dextran sulfate. Typically, aniline monomer (1 mmol) was added to DSAH aqueous solution (1.1 mmol in 50 mL) with vigorous stirring for 30 min. Chemical polymerization was initiated by adding dropwise ammonium persulfate 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 the dialysis membrane with the molecular weight cutoff at ca. 8 000 Da, a homogeneous dark green PANI−DSA aqueous solution was obtained. The PANI−DSA complex could be precipitated from the solution after being dipped into excess acetone, and the excess DSA was removed from the complex by this procedure. After filtering, washing with 1:1 acetone/deionized water solution, and drying sequentially, a green powder of PANI−DSA (0.24 g) was obtained, and it could be redispersed in water. For all of other PANIs, green powdery complexes were also obtained by the procedure described above: PMA−DSA, 0.23 g; PEA−DSA, 0.21 g; PMOA−DSA, 0.22 g; and PEOA−DSA, 0.20 g. FTIR of PANI−DSA complex (KBr pellet, cm^{-1}): 1 561 (quinoid); 1 461 (benzenoid); 1 300 (ν_{C-N}); 1 122 and 1 055 ($\nu_{O=S=O}$).

Preparation of Aqueous Solution and the Film of the PANIs−DSA Complex. All of the solutions and films of PANIs−DSA was prepared in a similar procedure. Typically, 2 mg of dried PANI−DSA complex was completely dispersed in 32 mL of water to form a homogeneous solution for further study, and no particle (0.1−600 μm) was found by light scattering analysis. After evaporation of water in concentrated PANI−DSA aqueous solution on a glass substrate at room temperature, a continuous and smooth PANI−DSA film was obtained for thermochromism study or measurement of conductivity and spectrum.

Spectroscopic Studies and Light Scattering Analysis. UV−vis and CD spectra of PANIs were recorded by a JASCO V-570 UV−vis−NIR spectrophotometer and a JASCOV-720WI spectropolarimeter, respectively. The spectra measurement was done in 10 mm quartz cell for aqueous solutions or on glass substrate for coated films. FT-IR spectra of dried sample were recorded using a Fourier transform infrared spectrometer (HORIBA F-210) with KBr pellet. The light scattering measurement of PANIs−DSA aqueous solutions was performed on a HORIBA laser scattering particle size distribution analyzer LA-300 (0.1−600 μm).

Cyclic Voltammetry. The electrochemical characterization of PANIs−DSA films cast on Pt electrode was performed using cyclic voltammetry. The cyclic voltammograms were obtained with a potentiostat/galvanostat (Hokuto Denko model HA-301) and an 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.

Thermochromism and the Conductivity Studies. The PANI−DSA film for thermochromism study was exposed for 10 min periods to successively higher temperatures from 80 to 240 °C in an oven under atmospheric conditions. After each 10 min treatment, the film was cooled to room temperature before measuring its CD, UV−vis spectra, and conductivity. The conductivity of PANI−DSA film was measured using the standard four-probe method with a Loresta HP (MCP 410) (Mitsubishi Chemical Co.).

Results and Discussion

Chiroptical Properties of PANIs−DSA Complexes. For each PANIs−DSA, a homogeneous dark green solution was obtained by dispersing the powdery complex in water, which indicates that a water-processable PANIs−DSA complex is synthesized. The result of light-scattering analysis also confirms the yielded PANIs−DSA complexes are well dispersed (or dissolved) in aqueous solutions. The product of PANIs−DSA salt is proved by UV−vis spectra of these solutions shown in Figure 2a. Each PANIs possess the characteristic

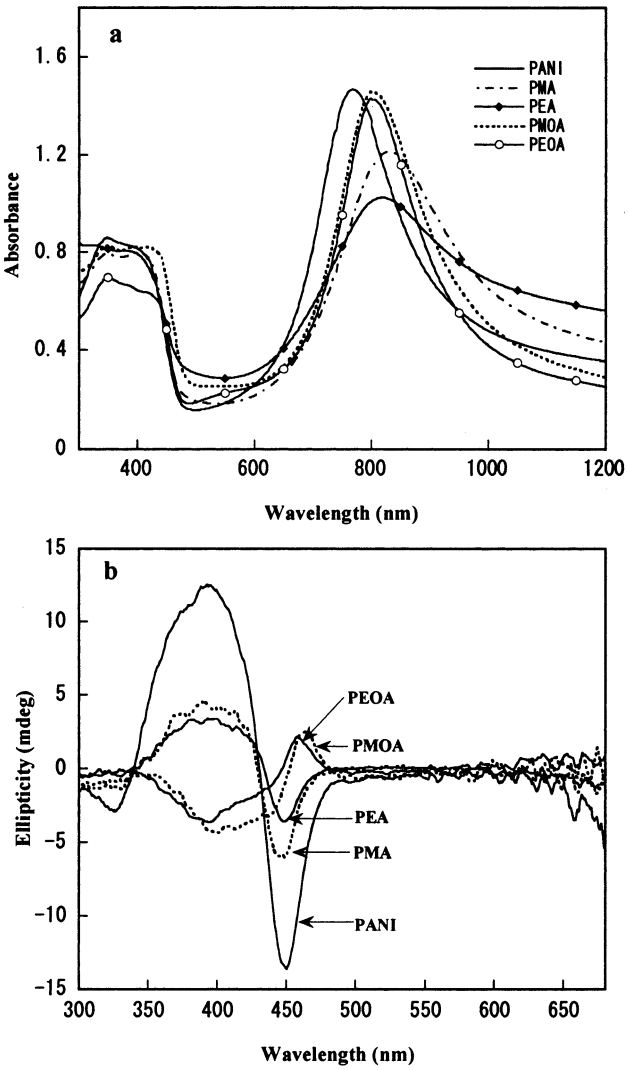

Figure 2. UV−vis spectra of PANI−DSA, PMA−DSA, PEA−DSA, PMOA−DSA, and PEOA−DSA in aqueous solution (a) and the corresponding CD spectra (b).

electronic spectrum for emeraldine salt with absorption bands at 340 ± 5, 420 ± 10, and 800 ± 30 nm. For instance, PMOA−DSA exhibits an intense, well-defined localized polaron band at 800 nm, as well as two lower wavelength absorption band at 430 and 340 nm, assigned as the second polaron band and benzenoid $\pi-\pi^*$ transition, respectively. This absorption spectrum is nearly identical to that of PMOA−CSA salt in organic solvents with a "compact coil" conformation for polymer chains.[9f] In the case of PANI−DSA, the polaron bands observed at 420 and 770 nm confirm that PANI was doped by DSA in the form of emeraldine salt, which is consistent with that of PANI doped and complexed by other kinds of anionic polyelectrolyte.[10c,f] Combining with the FTIR data, it is evidently believed that an interpolymer complex between PANI and DSA was synthesized where PANI was doped and complexed by DSA.

The circular dichroism (CD) spectra observed in Figure 2b show that all of these PANIs−DSA complexes were optically active. For PANI, the bisignate CD bands are centered at ca. 450 and 400 nm between 300 and 650 nm, which is consistent with that of chiral PANI doped with camphorsulfonic acid and has been used to confirm the helical structure in PANI by Wallace et al.[9] These observed CD bands are exclusively attributed to the chiral architecture of the polyaniline backbones in PANI−DSA because DSA does not show any CD band in this region. In such an intermacromolecular complex, it is reasonable to presume that the chirality in PANI arose from the chiral superstructure where PANI predominantly adopted one-handed helical structure while it was doped and intertwined by the DSA to form a macromolecular complex. The almost similar CD spectra of PMA−DSA and PEA−DSA to that PANI−DSA suggest that of PMA and PEA also predominantly adopted a one-handed helical structure in each complex and shared a helicity identical with that of PANI.

However, PMOA and PEOA exhibit quite different chiroptical properties from that observed in polyaniline. Based on the CD spectra, PMOA and PEOA share an opposite chirality to that of PANI on omission of the negligible difference and red shift of the CD bands due to the red shift of absorption bands compared with that of PANI. In other words, PMOA and PEOA predominantly adopted an opposite-handed helical structure to that of PANI while they were doped and intertwined by the DSA to form a macromolecular complex. Such a difference in helicity of PMOA and PEOA undoubtedly stems from the presence of methoxy and ethoxy substituents in the aniline ring. As suggested by Liu et al.,[18] in the formation of the PANI−polyelectrolyte complex, the charged aniline monomers were first aligned along the anionic polyelectrolyte chain by electrostatic interaction by which the complexation of resultant PANI and polyelectrolyte was driven. In this case, it is believed that the formation of macromolecular complexes was also mainly driven by electrostatic interaction. Nevertheless, for PMOA or PEOA, the strong interaction between hydrophilic substituents (methoxy or ethoxy) ring and the water made the monomer more loosely aligned on the DSA in a different order compared with that of aniline. Upon combination of the steric hindrance of substituent (methoxy or ethoxy), the resultant PMOA (or PEOA) was more loosely complexed with DSA than that of PANI. In such a loose complex, PMOA and PEOA predominantly adopted an opposite-handed helical screw while intertwining with DSA compared with that of PANI.

Although the helicity of the PMOA in final complex was greatly affected by the presence of methoxy substituent, the helical structure of PMOA was well held in either solid or aqueous solution after the formation of the interpolymer complex. As shown in Figure 3, the final dialyzed as-synthesized solution shows almost identical CD spectra to that of solution by redispersing powdery PMOA in water. At the same time, the PMOA−DSA film (3 μm) also exhibits an identical CD spectrum to those in aqueous solution. Similar results have also been observed for all of other PANIs−DSA.

Effect of NaCl. We investigated the effect of salt content (ionic strength) on the formation and the chirality of the PANI−DSA complex. After adding various amounts of NaCl to the solution before polymerization, it is observed a decrease in CD peak intensity at 400 and 450 nm (Figure 4) with increasing concentration of NaCl. The CD spectra were measured by diluting 0.1 mL of the reaction solution to 4.0 mL with deionized water after ultrasonication. We believed that the presence of NaCl competitively hindered the electrostatic bounding of protonated aniline to DSA, since it is kinetically favorable for NaCl to compete with DSA to complex with the protonated aniline. Subsequently,

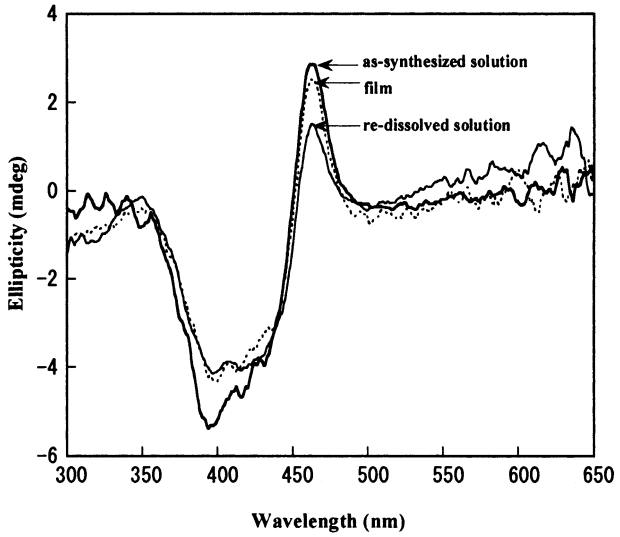

Figure 3. CD spectra of PMOA−DSA in as-synthesized solution after dialysis (0.1 mL diluted to 4 mL with deinoic water), film (3 μm), and redispersed aqueous solution.

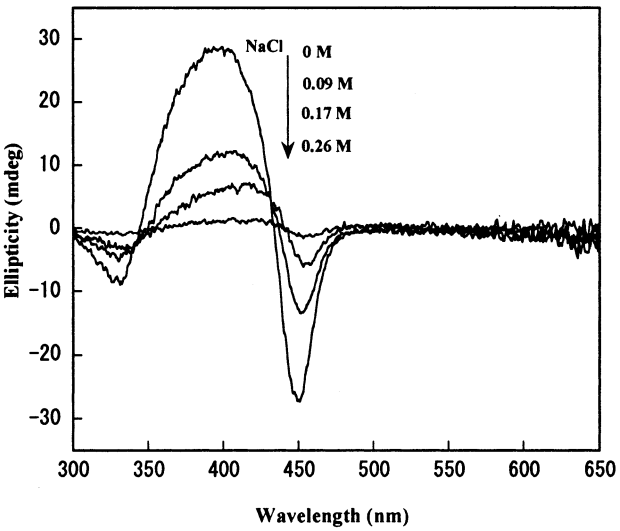

Figure 4. CD spectra of PANI complex obtained by polymerization of aniline−DSAH at various concentration of NaCl (0.1 mmol of aniline, 0.11 mmol of DSAH in 50 mL of aqueous solution).

the formation of intimately intertwined PANI−DSA complex was interrupted due to the competitive action of NaCl. Therefore, the chirality of the synthesized polyaniline decreased as increasing NaCl concentration in reaction dispersion. When the polymerization was carried out in the presence of 0.35 M NaCl, the synthesized PANI almost lost its water solubility (or dispersibility). The CD spectrum of its aqueous dispersion, dispersed by ultrasonication, shows that the resultant PANI is optically inactive. It is presumed that the electrostatic interaction to form the PANI−DSA complex was minimized due to the competitive shielding of NaCl. As a result, the PANI main chain lost its macromolecular asymmetry and solubility in absence of doping and intertwining with DSA. This behavior is strong evidence that the electrostatic interaction has driven the formation of macromolecular complex as proposed above, and the chiral architecture was induced into PANIs by such interpolymer complex formation.

Dedoping and Redoping. To determine the stability of the helical conformation in such interpolymer

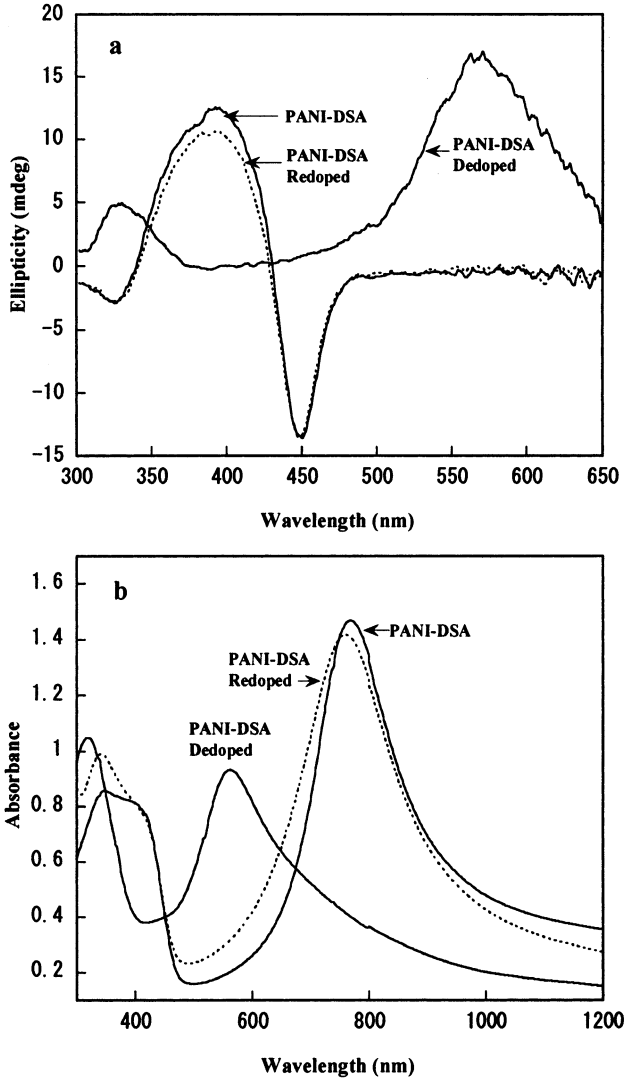

Figure 5. CD spectra of PANI−DSA aqueous solution after dedoping and redoping cycle (a) and the corresponding UV−vis spectra (b).

complexes, PANI−DSA and PMOA−DSA were dedoped and redoped by addition of NaOH and HCl in aqueous solution, respectively.

After titration of PANI−DSA aqueous solution with 0.5 M NaOH to pH 11, PANI is completely deprotonated in the form of emeraldine base (EB), which was confirmed by the disappearance of the polaron bands at 770 and 420 nm and the appearance of the characteristic absorption bands for EB at 320 and 565 nm (Figure 5b). The CD bands (Figure 5a) observed at 570 and 330 nm are tentatively associated with the absorption band at 565 and 320 nm, respectively, which is similar to that reported in chiral EB film.[9c] The PANI was redoped by titration of the solution with 0.5 M HCl to pH 3, which was confirmed by the recovered UV−vis spectrum. After such a dedoping and redoping cycle, the CD spectrum for PANI is essentially identical with that of original one. Although the results are not shown here, it was observed that there was no obvious change in CD spectrum even after three cycles of dedoping and redoping. These results suggest that its chirality remains; that is, the helical conformation of PANI in the PANI−DSA complex is stable to undergo the dedoping and redoping cycles.

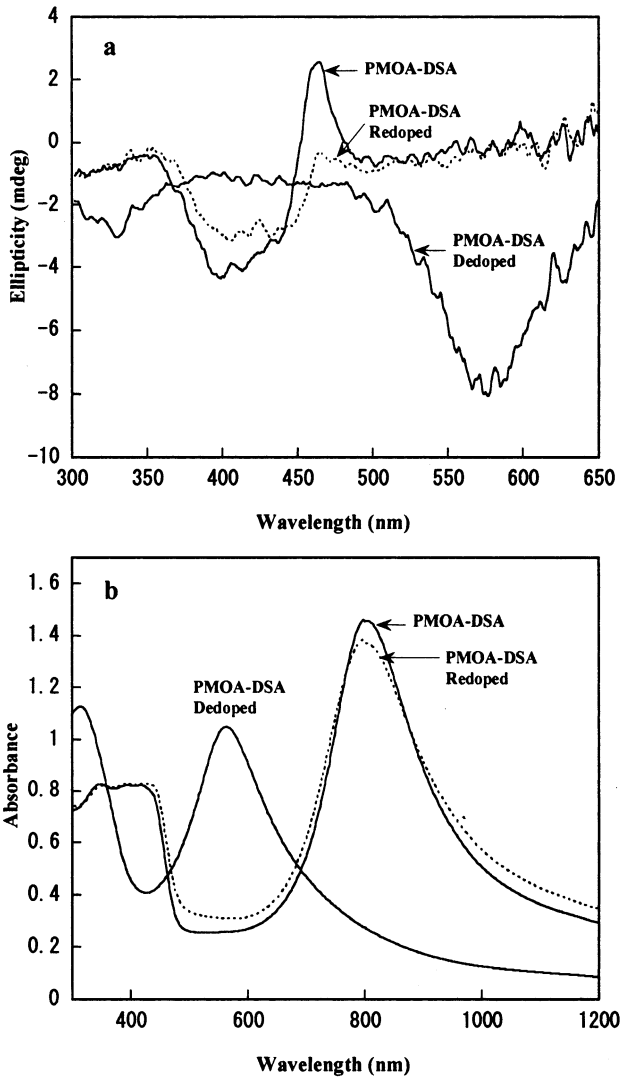

Figure 6. CD spectra of PMOA−DSA aqueous solution after dedoping and redoping cycle (a) and the corresponding UV−vis spectra (b).

On the contrary, a great decrease in CD bands intensity (Figure 6a) is observed for PMOA after first cycle of dedoping and redoping, although the almost quantitatively recovered UV−vis spectra (Figure 6b) confirm the redoping of PMOA to form the interpolymer complex. Such a decrease in CD bands intensity indicates the partial loss of chirality in PMOA. Compared with that of PANI−DSA, the loss of chirality presumably attributes to the effect of hydrophilic methoxy substituent on the conformation change in PMOA. In the dedoped state, the complete deprotonation in PMOA minimized the electrostatic force between PMOA and DSA. Although H-bonding and van der Waals forces between PMOA and DSA maintained the interpolymer complex, the strong interaction between methoxy and water made the POMA more loosely complexed with DSA. As a result, PMOA chains easily underwent the inversion required for racemization in absence of the restriction of the electrostatic force between two polymers. The irreversible racemization in PMOA main chain causes the partial loss of the chirality in PMOA despite that the electrostatic interaction between two polymers was resumed after redoping. From this point, it conversely proves that the electrostatic interaction between two polymers played an important role in

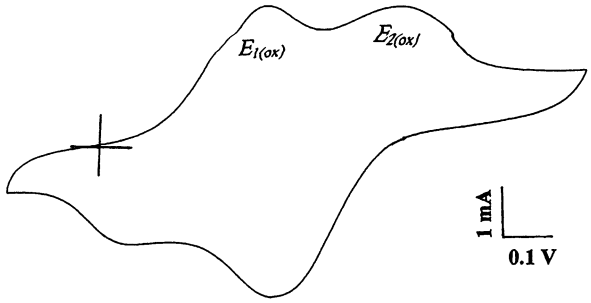

Figure 7. Cyclic voltammogram for PMOA−DSA in 1.0 mol dm^{-3} HCl, −0.2 to 1.0 V vs Ag/AgCl, Pt electrode, scan rate 50 mV/s.

Table 1. Anodic Peaks Observed for PANIs−DSA in 1 M HCl at a Scan Rate of 50 V/s

	anodic peaks (V vs Ag/AgCl)	
PANIs	$E_{1(ox)}$	$E_{2(ox)}$
PANI−DSA	0.17	0.73
PMA−DSA	0.29	0.57
PEA−DSA	0.32	0.45
PMOA−DSA	0.30	0.56
PEOA−DSA	0.39	0.44

maintaining the chiral conformation of PANIs in the complex as proposed above, and the hydrophilic substituents have a great effect on the chirality of final PANIs in the complexes.

Cyclic Voltammetry. The electrochemical nature of PANIs in the complexes was measured by cyclic voltammetry, and all of them were electroactive. For PMOA−DSA (Figure 7), two anodic peaks and two cathodic peaks were observed. Compared with previous reports, the anodic peaks $E_{1(ox)}$ and $E_{2(ox)}$ may be assigned to the oxidations of leucoemeraldine to emeraldine salt and of emeraldine salt to pernigraniline, respectively. Table 1 shows the anodic peaks of all other PANIs−DSA. It is observed that, with the introduction of substituents, a positive shift is observed for the first anodic peak of the substituted PANIs−DSA compared with PANI−DSA. On the contrary, the second anodic peak is shifted to a lower potential. Analogous results have also been reported for PANIs−HCl by Leclerc et al.[19] It is postulated that the positive shift in the first peak arises from the substituents inducing some nonplanar conformations that decrease the conjugation along the polymer backbone, thus giving higher oxidation potentials. On the other hand, the contribution of the electrodonating effect of the substituents leads to the negative shift of the second anodic peak.

Oxidation and Reduction of PANI−DSA. Addition of one drop of aqueous solution of ammonium persulfate to the PANI−DSA solution caused a rapid change in color from green to blue/violet. Oxidation to pernigraniline form was confirmed by characteristic absorption band at 510 nm (Figure 8b). The CD band (Figure 8a) observed at ca. 520 nm associated with this absorption band confirms the retention of chiral structure in fully oxidized PANI. Following the color change, violet pernigraniline precipitated at the bottom of tube. It is presumed that the additional protonated imine units in the pernigraniline complexed with those free sulfate groups in DSA chain again, which had served to impart the solubility of the complex.

Reduction of emeraldine salt was carried out by addition of aqueous solution of phenylhydrazine to PANI−DSA solution. The formation of leucoemeraldine

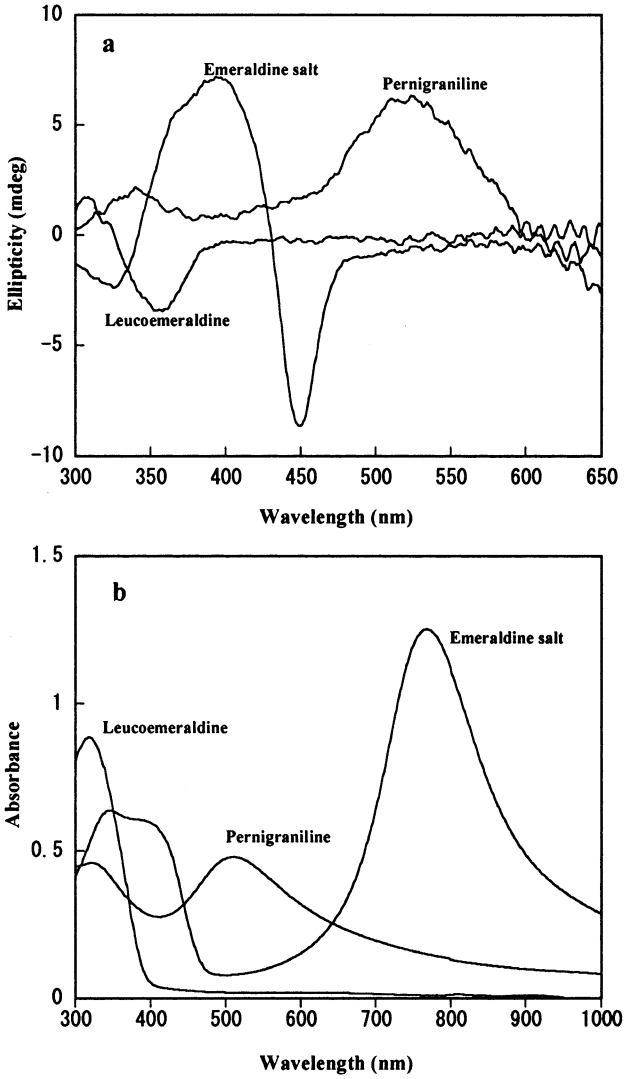

Figure 8. CD spectra of PANI-DSA in the forms of emeraldine salt, pernigraniline and leucoemeraldine (a) and the corresponding UV−vis spectra (b) in aqueous solution.

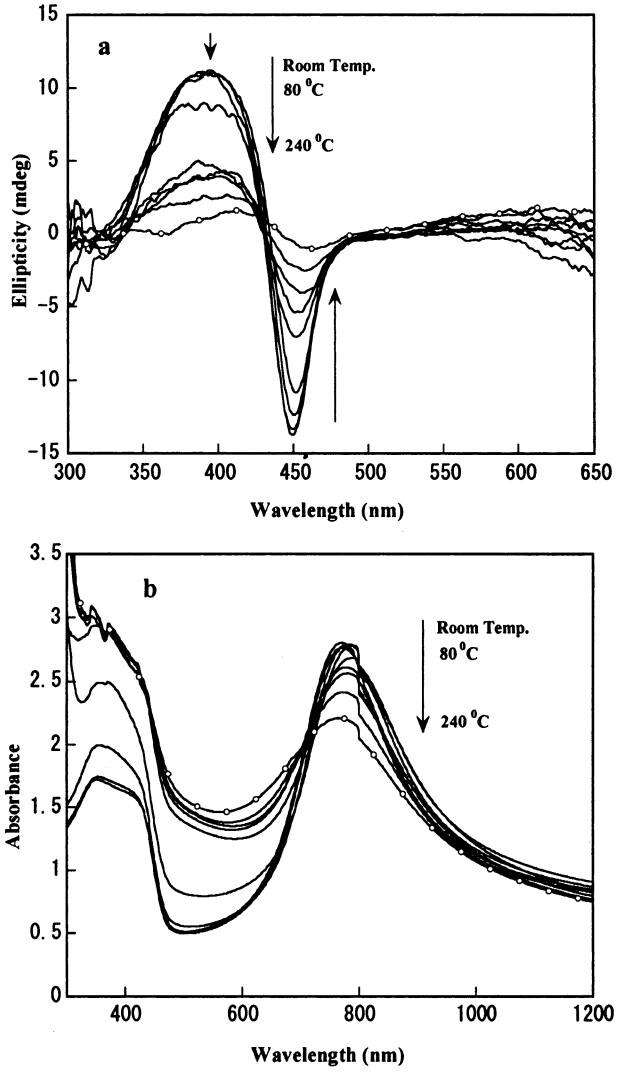

Figure 9. CD spectra of PANI−DSA film (4 μm) after thermal treatment at various temperature (a) and the corresponding UV−vis spectra (b).

base was confirmed by the disappearance of the initial visible region absorption bands and the characteristic UV bands at 320 nm due to the $\pi-\pi^*$ transition (Figure 8b). The CD bands (Figure 8a) observed at 350 and 305 nm for the solution are tentatively assigned as the bisignate exciton-coupled bands associated with this absorption band. It indicates that the helical conformation in PANI could be retained at room temperature at fully reduced state (leucoemeraldine) in the intertwined macromolecular complex. The retention of the chiral structure in PANI in different redox states is very important for it to be applied as chiral electrodes in electrochemically asymmetric synthesis and electroactively chiral membranes.[20]

Thermochromism in PANI−DSA Complex. The temperature dependence of the circular dichroism (CD) and UV−vis spectra of the PANI−DSA film is shown in Figure 9. There is no obvious change in UV−vis and CD spectra of the PANI−DSA film while heated to 120 °C. Although there is a progressive dedoping while heating greater than that, PANI is still partially doped by DSA and shows a characteristic bipolaron band at 770 nm for emeraldine salt even after heating the film to 240 °C for 10 min. Such a high stability against the thermal dedoping is presumably attributed to the strong interaction in the interpolymer complex and the stability of polymeric dopant. It is well-known that PANI has high stability against the thermal decomposition. Also, thermogravimetric analysis, not shown here, shows that no more than 5% weight loss is observed for DSANa until heated to 250 °C. Nevertheless, the strong CD band for PANI diminishes gradually with increasing temperature higher than 120 °C, until it is almost optically inactive after 10 min at 240 °C. As suggested by Kane-Maguire et al.[21] that CD spectroscopy is highly sensitive to the change of molecular conformation, the loss of CD bands indicates that PANI chains almost lost a preferred one-handed helical conformation. Such a loss in optical activity may arise from the partial dedoping

Table 2. Conductivity (S/cm) of PANI−DSA Film after Thermal Treatment

		after thermal treatment (°C, 10 min)							
conditions	after desiccation	80	120	140	160	180	200	220	240
conductivity	4.5×10^{-2}	4.1×10^{-2}	4.2×10^{-2}	1.9×10^{-2}	1.9×10^{-3}	6.7×10^{-4}	4.5×10^{-4}	3.8×10^{-4}	3.2×10^{-4}

in PANI, namely, the partial deprotonation of doped PANI. The thermal dedoping weakened restriction of the electrostatic action between PANI and DSA, and thus PANI chain has sufficient mobility to undergo inversion required for racemization.

Conductivity measurement was carried out for the film after each 10 min thermal treatment, and the result is consistent with that observed in spectra. There is no obvious change in conductivity (Table 2) of the PANI−DSA film while heating to 120 °C because of no thermal dedoping and chain conformation change occurred as proved by the UV−vis and CD spectra. The conductivity of the film is comparable to that of PANI doped by poly(styrenesufonic acid).[10b] While heating higher than 120 °C, the decreasing in the conductivity arose from the progressive thermal dedoping of PANI. Nevertheless, the film still keeps its conductivity after heated at 240 °C for 10 min, which again proves the thermal stability of the PANI−DSA complex against dedoping observed in UV−vis spectra.

Conclusions

Interpolymer complexes of DSA and some ring-substituted polyaniline derivatives (PANIs) were synthesized by chemical polymerization of the corresponding achiral monomer in the presence of DSA, such as PANI−DSA, PMA−DSA, PEA−DSA, PMOA−DSA, and PEOA−DSA. The water dispersibility of these complexes realized the goal to synthesize water-processable PANIs. Under the induction of the DSA, the chiral architecture was induced into the chain of PANIs where PANIs were doped and intertwined by DSA to form macromolecular complexes. Interestingly, it was found that the chirality of the PANIs was affected by the substituents in aniline ring, and PMOA and PEOA shared an opposite chirality to that of PANI. It was also established that the electrostatic interaction not only drove the formation of intermacromolecular complexes but also played an important role in holding the chiral conformation of PANIs in the resultant complexes, which was supported by the studies on ionic strength effect, dedoping and redoping, and thermochromism. The studies toward the conductivity, electrochemical activity, and the chirality in various redox states of PANIs−DSA provide proof for them to be applied as chiral electrodes in electrochemically asymmetric synthesis and electroactively chiral membranes. The design and synthesis of such macromolecular complexes offers another example that the chiral architecture of a synthetic macromolecule could be controlled at the molecular level by macromolecular complex formation, which often occurs in biopolymers.

Acknowledgment. G.-L. Yuan is grateful to Professor M. Takeishi for his helpful discussions as well as to the Ministry of Education, Culture, Sports, Science and Technology, Japan, for a scholarship.

References and Notes

(1) Stryer, L. In *Biochemistry*; W. H. Freeman & Company: New York, 1995.

(2) (a) Green, M. M.; Peterson, N. C.; Sato, T.; Teramoto, A.; Cook, R.; Lifson, S. *Science* **1995**, *268*, 1860−1866. (b) Nakano, T.; Okamoto, Y.; *Chem. Rev.* **2001**, *101*, 4013−4038. (c) Cornelissen, J. J. L. M.; Rowan, A. E.; Nolte, R. J. M.; Sommerdijk, N. A. J. M. *Chem. Rev.* **2001**, *101*, 4039−4070. (d) Yashima, E.; Maeda, Y.; Okamoto, Y. *J. Am. Chem. Soc.* **1998**, *120*, 8895−8896.

(3) (a) Lehn, J. M. In *Supramolecular Chemistry*; VCH: Weinheim, 1995. (b) Ky Hischberg, J. H. K.; Brusveld, L.; Ramzi, A.; Jef, A. J. M.; Meijer, E. W. *Nature (London)* **2000**, *407*, 167−170.

(4) (a) Peeters, E.; Christiaans, M. P. T.; Janssen, R. A. J.; Schoo, H. F. M.; Dekkers, H. P. J. M.; Meijer, E. W. *J. Am. Chem. Soc.* **1997**, *119*, 9909−9910. (b) Pu, L. *Macromol. Rapid Commun.* **2000**, *21*, 795. (c) Yashima, E.; Goto, H.; Okamoto, Y. *Macromolecules* **1999**, *32*, 7942−7945.

(5) Saito, M. A.; Maeda, K.; Onouchi, H.; Yashima, E. *Macromolecules* **2000**, *33*, 4616−4618.

(6) Gustafasson, G.; Cao, Y.; Treacy, G. M.; Klavetter, F.; Colaneri, N.; Heeger, A. J. *Nature (London)* **1992**, *357*, 477−479.

(7) Jelle, B. P.; Hagen, G. J. *J. Electrochem. Soc.* **1993**, *140*, 3560.

(8) Deberry, D. W. *J. Electrochem. Soc., Electrchem. Sci. Technol.* **1985**, *132*, 1022.

(9) (a) Majidi, M. R.; Kane-Maguire, L. A. P.; Wallace, G. G. *Polymer* **1994**, *35*, 3113−3115. (b) Havinga, E. E.; Bouman, M. M.; Meijer, E. W.; Pomp, A.; Simenon, M. M. J. *Synth. Met.* **1994**, *66*, 93−97. (c) Kane-Maguire, L. A. P.; MacDiarmid, A. G.; Norris, I. D.; Wallace, G. G.; Zheng, W. *Synth. Met.* **1999**, *106*, 171−176. (d) Su, S.-J.; Kuramoto, N. *Macromolecules* **2001**, *34*, 7249−7256. (e) Egan, V.; Bernstein, R.; Hohmann, L.; Tran, T.; Kaner, R. B. *Chem. Commun.* **2001**, 801−802. (f) Norris, I. D.; Kane-Maguire, L. A. P.; Wallace, G. G. *Macromolecules* **2000**, *33*, 3237−3243.

(10) (a) Angelopoulos, M.; Patel, M.; Shaw, J. M. N.; Labianca, C.; Rishton, S. A. *J. Vac. Sci. Technol. B* **1993**, *11*, 2794. (b) Shannon, K.; Fernandez, J. E. *J. Chem. Soc., Chem. Commun.* **1994**, 643−644. (c) Liu, W.; Kumar, J.; Tripathy, S.; Senecal, K. J.; Samuelson, L. *J. Am. Chem. Soc.* **1999**, *121*, 71−78. (d) Chandrasekhar, P. In *Conducting Polymer, Fundamentals and Applications*; Kluwer Academic Publishers: Boston, 1997; p 211. (e) Nagarajan, R.; Tripathy, S.; Kumar, J.; Bruno, F. F.; Samuelson, L. *Macromolecules* **2000**, *33*, 9542−9547. (f) Yuan, G.-L.; Kuramoto, N.; Su, S. *Synth. Met.* **2002**, *129*, 173−178.

(11) (a) Sun, L.; Liu, H.; Clark, R.; Yang, S. C. *Synth. Met.* **1997**, *84*, 67−68. (b) McCarthy, P. A.; Huang, J.; Yang, S. C.; Wang, H. L. *Langmuir* **2002**, *18*, 259−263.

(12) Innis, P. C.; Norris, I. D.; Kane-Maguire, L. A. P.; Wallace, G. G. *Macromolecules* **1998**, *31*, 6521−6528.

(13) Nagarajan, R.; Liu, W.; Kumar, J.; Tripathy, S. K. *Macromolecules* **2001**, *34*, 3921−3927.

(14) Ho, H.-A.; Boissinot, M.; Bergeron, M. G.; Corbeil, G.; Doré, K.; Boudreau, D.; Leclerc, M. *Angew. Chem., Int. Ed.* **2002**, *41*, 1548.

(15) (a) In *The Merck Index*, 13th ed.; Merck & Co., Inc.: Whitehouse Station, NJ, 2001; p 520. (b) Nishi, H.; Nakamura, K.; Nakai, H.; Sato, T.; Terabe, S. *Eletrophoresis* **1994**, *15*, 1335−1340.

(16) Yuan, G. L.; Kuramoto, N. *Chem. Lett.* **2002**, 544−545.

(17) Ciszkowska, M.; Kotlyar, I. *Anal. Chem.* **1999**, *71*, 5013−5017.

(18) Liu, W.; Cholli, A. K.; Nagarajan, R.; Kumar, J.; Tripathy, F. F. B.; Samuelson, L. *J. Am. Chem. Soc.* **1999**, *121*, 11345−11355.

(19) Leclerc, M.; Guay, J.; Dao, L. H. *Macromolecules* **1989**, *22*, 649−653.

(20) Maguire-Kane, L. A. P.; Norris, I. D.; Wallace, G. G. *Synth. Met.* **1999**, *101*, 817−818.

(21) Norris, I. D.; Maguire-Kane, L. A. P.; Wallace, G. G. *Macromolecules* **1998**, *31*, 6529−6533.

MA0209139