

Optically Active Polyaniline Derivatives Prepared by Electron Acceptor in Organic System: Chiroptical Properties

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ABSTRACT: A novel synthetic process was developed to yield optically active polyaniline derivatives (PANIs) prepared by electron acceptor, 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ), using either (+)- or (–)-camphorsulfonic acid (CSA) as the chiral inductor in organic media. Either thin films of PANIs/(+)-CSA and PANIs/(–)-CSA or their solutions exhibit mirror-imaged circular dichroism (CD) spectra in the visible region, indicating diastereoselection in the electron-transfer polymerization in the presence of chiral inductor. The films were confirmed to remain their chiral configuration during reversible dedoping/redoping cycles in solid state. Unique chiroptical properties of PANIs/(+)- or (–)-CSA dissolved in *m*-cresol indicate that there exists a solvent effect on the PANIs' chain conformations and subsequent chiroptical properties, and the solvent effect is strongly dependent upon the structure of parent monomer and nature of various organic solvents. The PANIs' chain conformation in *m*-cresol solution forms during the dissolution, and it can be hardly changed by postintroduction of a little amount of another solvent due to the stable interactions among polymer backbone, CSA, and *m*-cresol for maintaining optical activity. However, PMOA doped with the same one-hand CSA can appear in the inverse CD spectrum when dissolved in cosolvent of *m*-cresol and DMSO at various volume ratios.

Introduction

Polyaniline (PANI), an inherently conducting polymer, has attracted considerable attention in the past two decades due to its ease of preparation, environmental stability, and potential use in a wide range of applications including electrochromic devices, light-emitting diodes, electrostatic discharge protection, secondary batteries, and corrosion protecting paint.¹ Because of its low solubility in most common solvents, the industrial application of PANI is limited. Recent research into conducting PANI has targeted improving the solubility and hence processability. Several investigators have developed methods to improve the processability of PANI by a postprocessing step, such as reprotonation of emeraldine base with a second protonic acid² and functionalization of PANI emeraldine base (PANI-EB).³ Previous efforts have also focused on the use of surfactant to aid in processing of PANI derivatives⁴ or polymerization of ring-substituted aniline monomers, containing alkyl, alkoxy, sulfonate, and carboxylate substituents, to enhance organic solubility and even water solubility.⁵

Because of their potential use in diverse areas, such as electrochemical asymmetric synthesis, chiral chromatography, and membrane separation technology, preparation of optically active PANIs has recently been reported using two alternative procedures, involving enantioselective electropolymerization of anilines in the presence of (+)- or (–)-10-camphorsulfonic acid (CSA)⁶ and postprotonation of PANI-EBs with (+)- or (–)-CSA in a variety of organic solvents.⁷ An alternative facile route to optically active polyaniline emeraldine salt has been described by Kane-Maguire et al.⁸ using a modification of an in-situ chemical polymerization procedure for the preparation of thin films of the PANI/HCl salt by replacing the HCl with (+)- or (–)-CSA.

Most recently, Kaner et al. demonstrated that the chirality of polyaniline induced by postprotonation of PANI-EB with either enantiomer of CSA is critically dependent upon the water content of the emeraldine base prior to doping.⁹ It is of interest to synthesize PANI involving organic media to avoid water. This also permits a detailed examination of their "real" chiroptical properties and solvent dependence of chiroptical properties. Reviewing the previous literature demonstrating chemically or electrochemically prepared optically active polyaniline, an aqueous solution was utilized for either the electrochemical polymerization of aniline or chemical preparation of PANI-EB although postprotonation was performed in organic media.^{6,7} It is likely that the water used contributes to the chiral configuration of the polyaniline.⁹ In addition, synthesis of PANIs in organic media is another challenge for the possibility to improve the processability of resultant PANIs in various organic solvents. 2,3-Dichloro-5,6-dicyanobenzoquinone (DDQ), a well-known electron acceptor, is usually used as oxidizing agent, especially in steroid synthesis. Since Mulliken presented the well-known theory of the charge-transfer (CT) interaction between electron donor and acceptor,¹⁰ an interesting subject is the possible role of CT complexes in chemical reactions. In this respect, DDQ is a prospective ideal oxidant for synthesis of polyaniline or polyanisidine in organic solvent.¹¹ In another respect, polymerization proceeds via possible CT complex formed between DDQ and aniline, which can improve the regularity of PANI at the same time that is especially important to optically active PANI emeraldine salt.

We report here a novel strategy that allows the synthesis of soluble optically active PANIs/(+)- and (–)-CSA in organic media by using either enantiomer of CSA as the chiral inductor. Thin films of PANIs/(+)- or (–)-CSA were easily cast from the homogeneous reaction mixture and then purified with fresh acetone. Retention

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of chiral configuration in reversible dedoping/redoping sequences of these films was observed, indicating that they may have potential as new electroactive stationary phases, chiral membranes for the separation of enantiomeric molecules, or novel chiral electrodes in electrochemical asymmetric synthesis. All the PANIs/(+)- and (-)-CSA were found to be soluble in various organic solvents, permitting a detailed examination of their chiroptical properties. Solvent dependence of chiroptical properties of resultant PANIs was to be established according to various aniline ring substituents and the nature of organic solvents, and this is very important for the solution processable PANIs and their potential applications in organic media.

Experimental Section

Materials. Aniline, *o*-anisidine, and *o*-toluidine (Kanto Chemical Co.) were distilled under vacuum and stored below -10°C prior to use. CSA was purchased from Aldrich and was dried under vacuum at 60°C for 24 h prior to use. DDQ was also purchased from Aldrich and used as supplied. THF (Kanto Chemical Co.) used as the reaction solvent was predried using sodium and was distilled prior to use. Unless otherwise stated, other reagents and solvents were of analytical grade from Kanto Chemical Co. and were used without further purification. Microscope glass slides (Matsunami Glass Ind., Ltd.) were precleaned by a piranha solution for 1 h. They were then thoroughly washed with distilled water and dried under vacuum at 60°C for 24 h.

Preparation of PANIs/CSA Salts. Polymerization of aniline, *o*-anisidine, and *o*-toluidine was carried out in cosolvent of chloroform-THF using either (+)- or (-)-CSA as the chiral dopant. Typically, 1.162 g of (+)-CSA and 0.228 mL of aniline were well dissolved in 20 mL of chloroform at room temperature. A solution containing 0.568 g of DDQ dissolved in 6.7 mL of fresh distilled THF was then added dropwise with constant stirring at room temperature in 1 h. A $10\ \mu\text{L}$ reaction mixture was diluted in 5 min intervals in the first 1 h with 5 mL of chloroform. The UV/vis spectrum of the diluted mixture was then immediately recorded. The reaction mixture changed to green and subsequent deep green solution without any precipitate. After 2 h, very thin films were cast onto the precleaned glass slides from the homogeneous reaction mixture, followed by rinsing with acetone to remove excess CSA, unreacted and/or reduced DDQ, and even unreacted aniline and its oligomers. These films were then dried under vacuum at room temperature. The reaction mixture was stirred for a further 6 h at room temperature. After the reaction was completed, the as-synthesized PANI/(+)-CSA was precipitated by adding an excess amount of acetone to the reaction mixture, then filtered, and washed with acetone. The purified PANI/(+)-CSA was dried under vacuum at 60°C for 24 h and stored in a desiccator for use. Anal. Found: C, 62.81; H, 6.20; N, 6.84; S, 7.90. FTIR (KBr pellet, cm^{-1}): 1728, h; 1581, m; 1489, m; 1295, m; 1111, m; 1034, m; 600, s.

Chemical Dedoping/Redoping of the PANIs/CSA Films. Chemical dedoping and redoping of PANIs/CSA films were carried out following the procedure described in the previous literature.^{8,12} Generally, the PANIs/(+)-CSA and PANIs/(-)-CSA films were dedoped to give emeraldine base films by suspending them in 30 mL of aqueous 1.0 M NH_4OH for 30 min and dried using an air gun at room temperature. The EB films were then redoped with HCl to give the corresponding PANIs/HCl films by suspending them in 30 mL of 1.0 M HCl for 30 min and also dried using an air gun at room temperature.

Spectroscopic Studies. The UV/vis/near-IR and circular dichroism (CD) spectra of the optically active PANIs/(+)- or (-)-CSA films (and of related PANIs-EB and PANIs/HCl films) were recorded using a JASCO V-570 spectrophotometer and a JASCO J-720WI spectropolarimeter, respectively. The purified PANIs/(+)- or (-)-CSA were dissolved in various organic solvents and then filtered, and their UV/vis/near-IR and CD

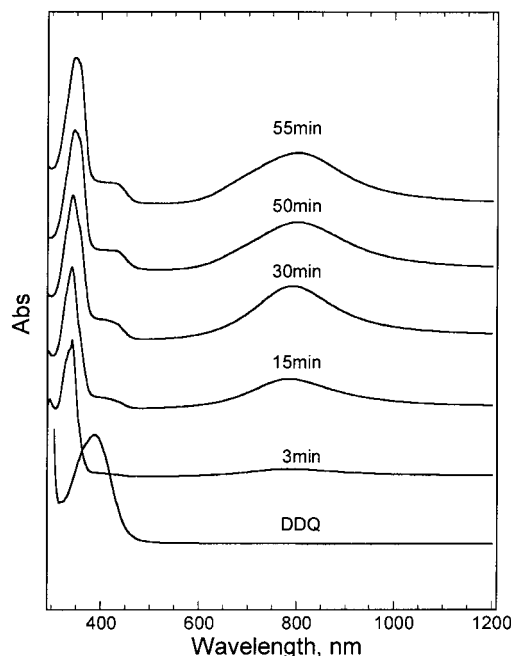


Figure 1. UV/vis/near-IR spectra of DDQ dissolved in chloroform and *o*-toluidine/(+)-CSA/DDQ/chloroform/THF reaction mixture diluted with chloroform vs reaction time.

spectra were also recorded. Infrared spectra in KBr pellets of the PANIs/CSA powders were recorded on a FTIR spectrophotometer (Horiba FT-210).

Cyclic Voltammetry. The electrochemical characterization of PANIs/(+)-CSA films coated onto a platinum electrode was performed in a three-electrode cell at room temperature using 20 mL of 1.0 M (+)-CSA as supporting electrolyte. The potential was cycled between -0.2 and $+0.8$ V (vs Ag/AgCl) at a scan rate of 30 mV/s.

Conductivity Measurement. A powder sample of PANIs/(+)- or (-)-CSA was pressed into a pellet, and the conductivity was measured by standard *four-probe* method with a Loresta HP (MCP T410) (Mitsubishi Chemical Co.). The conductivity of the films cast from the reaction mixtures or the solutions of purified PANIs/(+)- or (-)-CSA in various organic solvents was also measured by the same method.

Results and Discussion

Preparation of PANIs/CSA Salts. The reaction process was investigated by UV/vis/near-IR spectrophotometry. For all the reaction mixtures, an absorption band at 388 nm assigned to DDQ quickly disappeared after it was introduced into the reaction system, and an absorption band at 345 nm assigned to the reduced DDQ appeared at the same time (Figure 1). It is supposed that oxidative polymerization of aniline proceeds due to electron transference from aniline to DDQ via the outer charge-transfer complex intermediate formed between them. We could not detect the intermediate by the absorption spectrum measurement, and this might be due to its unstability at room temperature. Via the intermediate, the electron of aniline can be easily transferred to the electron acceptor, DDQ, to form a radical cation. Then, combination of the radical cations forms an oligomer of aniline and even PANI. Alongside the reaction process, for all the three aniline derivatives, a well-defined bipolaron band at around 800 nm as well as a lower wavelength absorption band at about 430 nm assigned as the second polaron band appears, and their intensity also increases with longer reaction time and/or higher content of DDQ introduced.

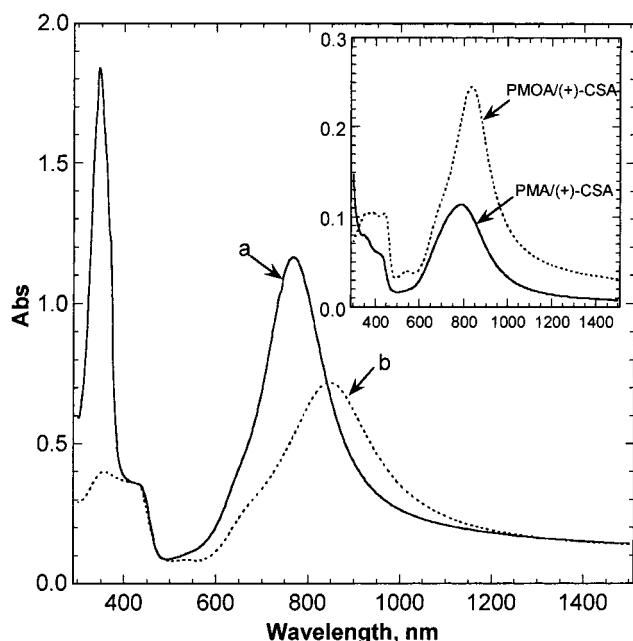


Figure 2. UV/vis/near-IR spectrum of PANI/(+)-CSA film (a) before and (b) after purified with acetone. Inset: UV/vis/near-IR spectra of PMA/(+)-CSA and PMOA/(+)-CSA films after purified with acetone.

The UV/vis/near-IR spectrum of PANI/(+)-CSA film cast from the homogeneous reaction mixture exhibits an intense, well-defined bipolaron band at 767 nm, as well as a lower wavelength polaron band at 435 nm (Figure 2a). The absorption band assigned to the benzenoid $\pi-\pi^*$ transition¹³ was not found due to overlap with the absorption band at 345 nm assigned to the reduced DDQ. After purified with fresh acetone to remove unreacted DDQ and aniline, reduced DDQ, oligomer of aniline, and most of free (+)-CSA, the intense absorption band assigned to the reduced DDQ completely disappeared, and the absorption band assigned to the benzenoid $\pi-\pi^*$ transition was found at 355 nm (Figure 2b). The bipolaron band of PANI/(+)-CSA was red-shifted to 847 nm at the same time, and this absorption spectrum is identical to that of PANI/HCl or PANI/CSA film prepared by chemical or electrochemical method and is consistent with a "compact coil" conformation for the polymer chains. No band based on unreacted or reduced DDQ was found in the FTIR spectrum, indicating that PANI/CSA was absolutely purified with fresh acetone and still maintained its emeraldine salt state. Before purification, there are still some unreacted and/or reduced DDQ, and they may still combine with the PANI backbones to affect their electronic environment significantly. Therefore, fresh cast PANI/(+)-CSA film shows the bipolaron band at lower wavelength than the purified one. Most of free CSA was also washed away simultaneously. The elemental analysis of the dried PANI/CSA showed that the molar ratio of the tetramer unit of emeraldine base and CSA is approximately 1:2. The purified PANI/(+)-CSA powder and film were confirmed to be fully doped emeraldine salt from their elemental analysis, FTIR, and UV/vis spectra.

Besides PANI/(+)- or (-)-CSA, poly(*o*-toluidine) (PMA)/(+)- or (-)-CSA and poly(*o*-anisidine) (PMOA)/(+)- or (-)-CSA were also synthesized at relatively high yield via the analogous process (Table 1). For comparison with that of PANI/(+)-CSA film, UV/vis/near-IR spectra of

Table 1. Preparation of PANIs/(+)- or (-)-CSA in Organic Solvents^a

anilines	yield, wt %	conductivity, S/cm
<i>o</i> -toluidine	72.0	4.8×10^{-1}
<i>o</i> -anisidine	48.6	3.5×10^{-4}
aniline	46.2	33

^a Conditions: anilines, 2.5 mmol; DDQ, 2.5 mmol; (+)- or (-)-CSA, 5.0 mmol; cosolvent, chloroform-THF (3:1), 26.7 mL; rt; 8 h.

purified PMA/(+)-CSA and PMOA/(+)-CSA films were shown as the inset of Figure 2. Their absorption band assigned to the benzenoid $\pi-\pi^*$ transition was found at 355 nm, which is at the same wavelength as that of PANI/(+)-CSA film. However, the bipolaron band of PMA/(+)-CSA and PMOA/(+)-CSA is shifted to the shorter wavelength at 793 and 837 nm, respectively, and their second polaron band was found at 430 and 443 nm, respectively. It is supposed that presence of a methyl or methoxy substituent induces a different electronic environment in their backbones from the parent PANI salt, but they are still consistent with the "compact coil" conformation for the polymer chains, which is nearly identical to that of electrochemically deposited PANIs films. PANI/(+)- or (-)-CSA, PMA/(+)- or (-)-CSA, and PMOA/(+)- or (-)-CSA showed the conductivity as the order of 10 , 10^{-1} , and 10^{-4} S/cm, respectively, which is the same order as that of PANIs prepared from the other processes.

The cyclic voltammograms of PANI/(+)-CSA, PMOA/(+)-CSA, and PMA/(+)-CSA films cast onto platinum electrode display two reversible redox responses respectively similar to those of reported electrochemically or chemically generated PANIs/CSA,^{12,14} confirming that they are electroactive. For PANI/(+)-CSA, the redox couples at 0.22 V may be assigned to the conversion of leucoemeraldine to emeraldine salt, while the peak at 0.53 V corresponds to the subsequent oxidation to the pernigraniline state. The redox couples of PMOA/(+)-CSA and PMA/(+)-CSA are at 0.18, 0.60 V and 0.32, 0.67 V, respectively. All the results confirmed that the absolutely purified PANIs fully doped with CSA were obtained from electron-transfer polymerization of various aniline derivatives in organic media.

Chiroptical Properties of PANIs/(+)- and (-)-CSA Films. The PANIs/(+)-CSA films possessed characteristic CD bands at wavelengths longer than 300 nm, which are attributed to optical activity in the polymer backbones since CSA does not show any CD bands in this region, to be confirmed optically active (Figure 3). Wallace and co-workers have shown that the presence of a methyl or methoxy substituent ortho to the N centers obstructs the induction of optical activity in the polymer backbone via postprotonation with (+)-CSA in organic media.^{14a} This obstruction was well diminished by synchronous induction of optical activity by (+)-CSA during polymerization of various aniline derivatives in organic media.

PANI/(+)-CSA film (600 Å) and PMA/(+)-CSA film (100 Å) exhibited similar CD bands at 370, 432, and 650 nm. The CD band at 370 nm is probable one of bisignate exciton-coupled CD bands associated with the benzenoid $\pi-\pi^*$ transition absorption band shown at 355 nm, and another CD band at 432 nm may be one of another pair of bisignate exciton-coupled CD bands corresponding to the polaron absorption band at 430 nm. Only one of bisignate exciton-coupled CD bands was observed for them maybe partly due to overlap of these two pairs of

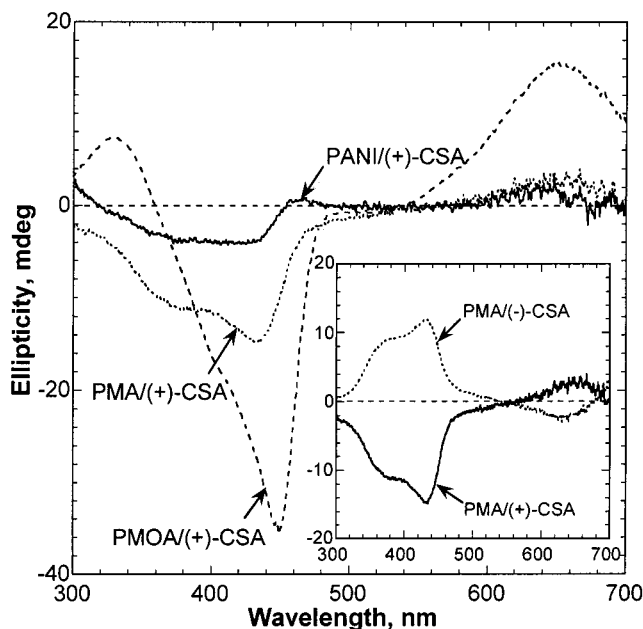


Figure 3. CD spectra of PANI/(+)-CSA, PMA/(+)-CSA, and PMOA/(+)-CSA films from Figure 2. Inset: the mirror-imaged CD spectra of PMA/(+)-CSA and PMA/(-)-CSA films.

bisignate. The CD band observed at 650 nm is probably the lower wavelength component of the expected pair of bisignate exciton-coupled CD bands associated with the bipolaron absorption band. We failed to record the CD bands at the wavelengths longer than 700 nm due to the strong absorption of PANIs/CSA salts in this region. The CD spectrum of PMOA/(+)-CSA film (200 Å) is slightly different from that of PANI/(+)-CSA or PMA/(+)-CSA. The CD bands at 330 and 400 nm associated with the benzenoid $\pi-\pi^*$ transition absorption band were clearly observed. Partly overlapping with them is probably another pair of bisignate exciton-coupled bands corresponding to the polaron absorption band of which only one band at 460 nm was observed. It is slightly red-shifted due to the polaron absorption band at the longer wavelength compared with that of PANI/(+)-CSA or PMA/(+)-CSA. The CD band associated with the bipolaron band was also observed at 650 nm.

Similar to observations previously reported by Wallace and co-workers for electrochemically or chemically generated PANIs/(+)- and (-)-CSA films,^{6a,8,12} mirror-imaged CD spectra were also observed for these PANIs/(+)- and (-)-CSA films, indicating that the electron-transfer polymerization of former aniline derivatives in organic media is enantioselective by using either enantiomer of CSA as the chiral inductor. However, the similarity of CD spectra of PANIs/(+)-CSA demonstrated here contrasts with the difference between CD spectra of electrochemically generated PANI/(+)-CSA^{6a,15} and PMOA/(+)-CSA¹² on ITO-coated glass. No attempts succeeded to grow films of PMA/(+)-CSA on ITO-coated glass via analogous electropolymerization of *o*-toluidine in the presence of (+)-CSA,¹⁶ at least indicating similar stereoregularity of former generated PANIs/(+)-CSA. According to the different CD spectra for electrochemically deposited PMOA/(+)-CSA and PANI/(+)-CSA films, the authors conclude that the PMOA/(+)-CSA has a different conformation from the analogous prepared parent PANI/(+)-CSA.¹² However, since the electrochemically prepared chiral PANIs were

electropolymerized in an aqueous solution, it is likely that the water used in the electrochemical process contributes to the chiral configuration of the PANIs, which may be in accordance with the various aniline ring substituents. The similar chiroptical property of PANIs/(+)-CSA films despite different ring substituents indicates that polymerization of these aniline derivatives oxidized by DDQ in organic system in the presence of (+)- or (-)-CSA results PANIs whose optical activity is only slightly affected by various aniline ring substituents in the solid state. At the same time, a relatively high intensity of CD bands corresponding to PMA/(+)-CSA and PMOA/(+)-CSA backbones was also obtained despite ultrathin films of PMA/(+)-CSA and PMOA/(+)-CSA. The CD signal at about 300 nm assigned to the (+)-CSA⁻ dopant anion incorporated into the polymer backbone is markedly weaker than that of PANI/(+)-CSA or PMOA/(+)-CSA prepared by electrochemical polymerization^{6a,12} and is even overlapped with CD bands associated with PANIs/(+)-CSA backbones. All these results indicate that optically active PANIs with high regularity and strong optical activity were obtained from the procedure demonstrated here. The similarity of CD spectra of these PANIs/(+)-CSA films also contrasts with the difference among CD spectra of previously reported optically active PANIs/(+)-CSA induced by postprotonation in various organic solvents^{9,14a,17} since there would be a solvent effect on the chirality of PANIs/(+)-CSA, which is in accordance with various aniline ring substituents and nature of organic solvents, as will be discussed below.

Wallace and co-workers have previously demonstrated that electrochemically deposited PANI/(+)-CSA^{14b} and PMOA/(+)-CSA¹² and chemically deposited PANI/(+)-CSA films⁸ from aqueous media can be dedoped to emeraldine base and subsequently redoped with HCl with retention of chiral configuration. The authors conclude that chiral holes may be formed in the polymer matrix during both redox and chemical dedoping/redoping cycles with PANI/(+)-CSA salt films.^{14b} Similar behavior was also found here for all the former PANIs/(+)-CSA salt films. As the first sample of optically active PMA/(+)-CSA film successfully generated by in-situ chemical polymerization of *o*-toluidine using (+)-CSA as the chiral inductor, retention of absolute chiral configuration during reversible dedoping/redoping cycles in the solid state was presented here (Figure 4). Treatment of PMA/(+)-CSA emeraldine salt film with 1.0 M NH₄OH resulted in rapid deprotonation to produce a blue emeraldine base film, which exhibits two absorption bands at 330 and 600 nm, characteristic of emeraldine base (Figure 4a). The CD spectrum of this PMA-EB film shows that it is still optically active, with strong bands at 355, 500, and ~700 nm (Figure 4b) associated with the former EB absorption bands, indicating retention of optical configuration despite removal of the (+)-CSA⁻ anion. The retention of optical activity in the PMA-EB film again demonstrates that the observed optical activity for the film arises from the macroasymmetry of the polymer backbone and not the (+)-CSA⁻ dopant anion. The blue EB films obtained from PMA/(+)- and (-)-CSA films exhibit mirror-imaged CD spectra confirming enantiomeric nature of the two PMA-EB films (inset of Figure 4b).

Redoping of the above optically active PMA-EB film with aqueous 1.0 M HCl regenerated an UV/vis spectrum identical to that of the initial PMA/(+)-CSA film.

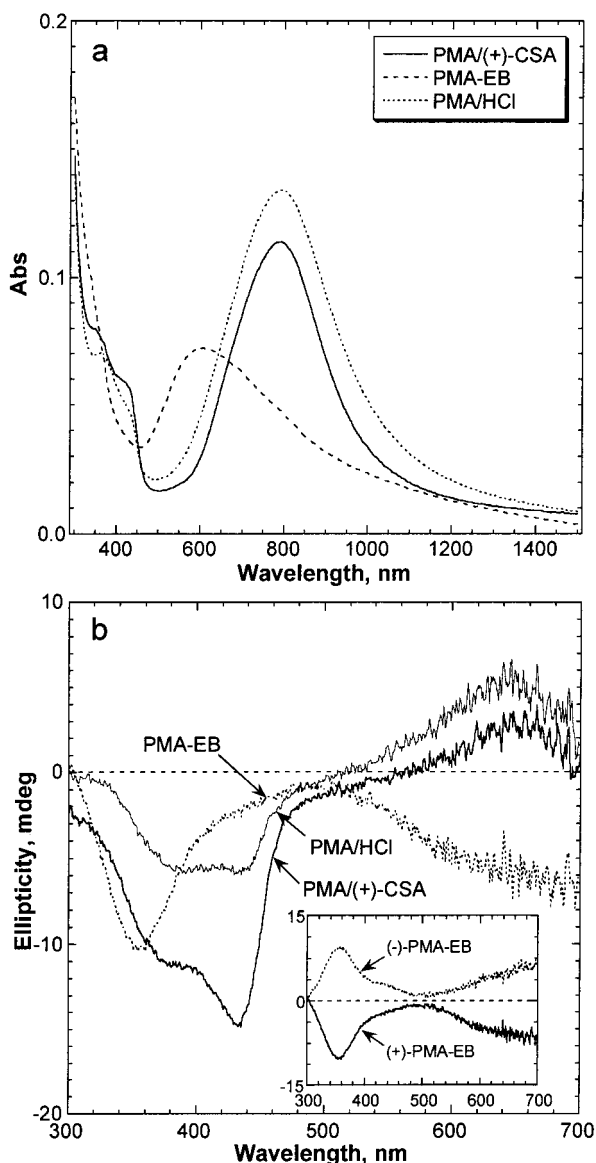


Figure 4. UV/vis/near-IR (a) and CD (b) spectra of PMA/(+)-CSA film after dedoping with aqueous 1.0 M NH_4OH and redoping with 1.0 M HCl. Inset: the mirror-imaged CD spectra of optically active PMA emeraldine bases.

The CD spectrum of the regenerated PMA/HCl film was also identical to the initial CD spectrum of the PMA/(+)-CSA film showing CD bands at 370, 430, and 650 nm. Retention of the polymer backbone configuration during the dedoping/redoping sequence presumably arises from steric constraints in the solid state in contrast to the easy rearrangement that readily occurs in solution.⁸

Chiroptical Properties of PANIs/(+)- and (-)-CSA Solutions. The purified PANIs/(+)- and (-)-CSA were still found to be soluble in various organic solvents although they were precipitated from the reaction mixture, and the unreacted and/or reduced DDQ complexed with the polymer backbone was removed by washing with acetone. However, the CD spectra for solutions are significantly different from the solid films, indicating that dissolution results in some change to the polymer chain conformation, but these solutions still remain their enantiomeric nature.

PANI/(+)-CSA indicates a free-carrier tail characterization in the vis/near-IR region of electronic spectrum

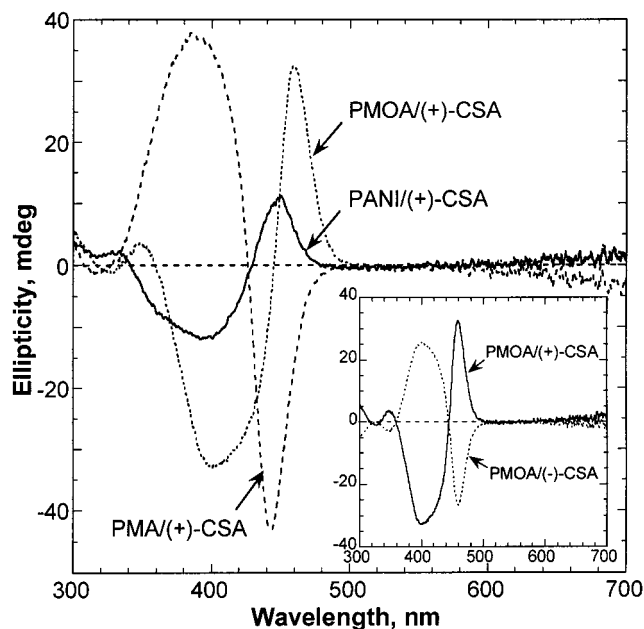


Figure 5. CD spectra of PANIs/(+)-CSA solutions in *m*-cresol. Inset: the mirror-imaged CD spectra of PMOA/(+)- and (-)-CSA solutions in *m*-cresol.

when dissolved in *m*-cresol, indicating rearrangement from a "compact coil" to an "extended coil" conformation.¹⁸ PMOA/(+)-CSA and PMA/(+)-CSA are also soluble in *m*-cresol, but remaining their "compact coil" conformations despite the red-shifted bipolaron absorption band according to slightly expanded polymer chains in solution. It is interesting that all the PANIs/(+)-CSA are still optically active when dissolved in *m*-cresol (Figure 5), and this is quite different from the previous demonstrations by Havinga et al.^{7a} and Wallace et al.¹⁶ They have shown that solutions of PANI/(+)-CSA obtained by analogous doping of achiral EB with (+)-CSA in *m*-cresol do not exhibit any visible CD bands. In addition, there is no other report update which demonstrates any optically active polyaniline derivatives keeping their optical activity when dissolved in *m*-cresol. Maintenance of optical activity in *m*-cresol solutions of PANIs/(+)-CSA generated via the procedure demonstrated here at least proves that they have relatively higher regularity than the optically active PANI/(+)-CSA generated from postprotonation of achiral EB in organic solvents. Also, the H- and electrostatic bands^{6,7} between CSA and polymer backbone maintaining chiral configuration are strong enough to restrain the polaric *m*-cresol. It is necessary to note the maintenance of optical activity of PANI/(+)-CSA although the rearrangement from a "compact coil" to an "extended coil" conformation as one of the reasons proposed by Wallace et al.¹⁶ for the loss of optical activity in *m*-cresol. All the PANIs/(+)-CSA solutions in *m*-cresol are very stable, and there is no decrease in the intensity of their CD bands although they were stored for over 1 year. Thus, there would be a stable interaction among polymer backbone, (+)-CSA, and *m*-cresol.

As suggested by Ikkala et al.,¹⁹⁻²¹ the carbonyl group in CSA can form a hydrogen bond to the hydroxy group of *m*-cresol, whereby the phenyl ring becomes coplanar with one of the PANI rings, thus enabling enhanced van der Waals interaction when CSA was used as the dopant. Besides well-known electrostatic band between (+)-CSA⁻ anion and HN^{+} sites and H-bonding between carbonyl group of (+)-CSA⁻ anion and HN centers albeit

partly destroyed by H-bonding between the hydroxy group of *m*-cresol and carbonyl group of (+)-CSA[−] anion, the enhanced van der Waals interaction between phenyl rings of *m*-cresol and PANI may also act as an indispensable interaction to maintain a preferred helical configuration. They both promote solubility of PANI in *m*-cresol and maintain chiral configuration of PANI. Also, they present the stability of formed chiral configuration in *m*-cresol. Since the enhanced van der Waals forces form on the basis of H-bonding between carbonyl group in (+)-CSA and hydroxy group of *m*-cresol, they are presumably assigned as two synergetic forms of molecular recognition, including that between polyaniline backbone and *m*-cresol and that between polyaniline backbone and (+)-CSA. This can also interpret the achiral configuration of PANI/(+)-CSA generated from postprotonation of achiral EB in *m*-cresol. That is, H-bonding between the carbonyl group of CSA and HN centers cannot form due to the strong H-bonding between the hydroxy group of *m*-cresol and carbonyl group of CSA formed prior to it. This is also a novel example that induced chirality of conducting polymer is present in solution of a good solvent, as *m*-cresol to polyaniline, in contrast to the previous demonstration that induced chirality is only present if the polymers are either in the solid state or in an agglomerated or associated phase in a poor solvent.^{22,23}

For the PANIs with different ring substituents doped with the same one-hand CSA when dissolved in *m*-cresol, they exhibit quite different chiroptical properties. On omission of red-shifted CD bands of PMOA/(+)-CSA at 400 and 460 nm compared with those of PANI/(+)-CSA or PMA/(+)-CSA due to the polaron absorption band at the longer wavelength, PANI/(+)-CSA and PMOA/(+)-CSA have the same chiral configuration based on CD, which is inverted to that of PMA/(+)-CSA. On this discovery, the CD spectra of (+)-CSA and (−)-CSA doped polyanilines when dissolved in *m*-cresol can appear identical depending upon various aniline ring substituents.

The different electronic and CD spectra for PANIs/(+)-CSA solutions in *m*-cresol confirm that they have different chain conformations after dissolution of stiff PANIs/(+)-CSA backbones, and the difference in conformation is presumably due to the different steric hindrance and/or electronic properties of various ring-substituents (H, Me, and MeO). Because of presence of methyl or methoxy group, the steric hindrance of them inhibits the interaction between amine of PANIs and hydroxy of *m*-cresol to enable the PMA/(+)-CSA and PMOA/(+)-CSA backbones to keep the "compact coil" conformation. The presence of a methyl or methoxy group may also inhibit electrostatic bonding of the (+)-CSA[−] sulfonate ion to the polyaniline HN⁺ centers, H-bonding of the (+)-CSA[−] carbonyl group to NH sites, and even former mentioned van der Waals interaction to change repeating units apart along the polymer chain which maintain the preferred one-sense helical screw. For PMOA/(+)-CSA, there may also be a strong H-bonding interaction of *m*-cresol hydroxy group to methoxy group, and it is competition with that of carbonyl group of (+)-CSA[−] anion to *m*-cresol hydroxy group inducing different chiroptical property from that of PMA/(+)-CSA.

PANIs/(+)-CSA also exhibit different chiroptical properties when dissolved in DMSO. They are similar to those of electrochemically and chemically generated

optically active PANIs/(+)-CSA when dissolved in DMSO.^{8,12,14a} Unlike *m*-cresol, an example of a hydrogen bonding donor, DMSO is an example of hydrogen bonding acceptor. Its sulfoxide group is strongly polar. A DMSO solution of PANI/CSA completely different from the *m*-cresol solution was suggested by Ikkala et al., leading to strongly perturbed protonation.¹⁹ It is undoubtedly that rapid rearrangement to an achiral configuration occurs in solution if emeraldine salt is absolutely deprotonated to give EB at low concentration.⁸ Albeit at least partial deprotonation can be induced when DMSO is used as the solvent, the H- and electrostatic bonds are still strong enough to keep the helical configuration of polymer backbones at high concentration. Interestingly, PMOA/(+)-CSA dissolved in *m*-cresol and DMSO exhibit almost mirror-imaged CD spectra except for the CD band (~290 nm) due to (+)-CSA[−] anion incorporated in the polymer. A similar phenomenon was also found for PMA/(+)-CSA. Unlike PANIs/(+)-CSA dissolved in *m*-cresol whose helical configuration is maintained by former mentioned three types of interaction, the helical configuration of PANIs/(+)-CSA when dissolved in DMSO is maintained with well-known H- and electrostatic bonds although they are partially perturbed by some bound DMSO molecules. On this point, the difference in CD spectra of PANIs/(+)-CSA when dissolved in *m*-cresol and DMSO can be easily interpreted. It confirms that there exists a solvent effect on the PANIs' chain conformations and subsequent chiroptical properties, and the solvent effect is strongly dependent upon the structure of parent monomer and nature of various organic solvents.

To give insight into real role of solvent effect on chain conformations as well as chiroptical properties of PANIs/(+)-CSA, CD spectra of PMOA/(+)-CSA dissolved in cosolvent of *m*-cresol and DMSO at various volume ratios were also recorded (Figure 6a). To prepare the solution, *m*-cresol and DMSO at various volume ratios were well mixed first (total volume is 10 mL), and then a specific weight of PMOA/(+)-CSA was added under stirring. The mixture was magnetically stirred until formation of homogeneous solution. It can be seen that recorded CD spectrum of PMOA/(+)-CSA dissolved in *m*-cresol/DMSO (99:1) was significantly different from that of PMOA/(+)-CSA dissolved in *m*-cresol. The bisignate exciton-coupled CD bands at 325 and 350 nm assigned to PMOA/(+)-CSA solution in *m*-cresol completely disappeared to show only those of PMOA/(+)-CSA solution in DMSO at 325 and 375 nm, and the intensity of those at 425 and 460 nm assigned to PMOA/(+)-CSA solution in *m*-cresol markedly decreased. When 3 vol % DMSO was introduced for preparation of cosolvent, the bisignate exciton-coupled CD bands at 430 and 460 nm assigned to PMOA/(+)-CSA solution in *m*-cresol nearly disappeared.

Wallace et al.¹⁶ have demonstrated the complete loss of optical activity over the visible region when *m*-cresol was added into the initially generated PANI/(+)-CSA solution in chloroform. The authors conclude both the H- and electrostatic bands would be expected to be diminished as chloroform solvent is replaced by the more polar and strongly H-bonding *m*-cresol. For comparison, PMOA/(+)-CSA was initially dissolved in *m*-cresol, and then various contents of DMSO were postadded. However, no difference in UV/vis and CD spectra of solution was recorded although over 5 vol % of DMSO was postintroduced. This again supports the stability of helical

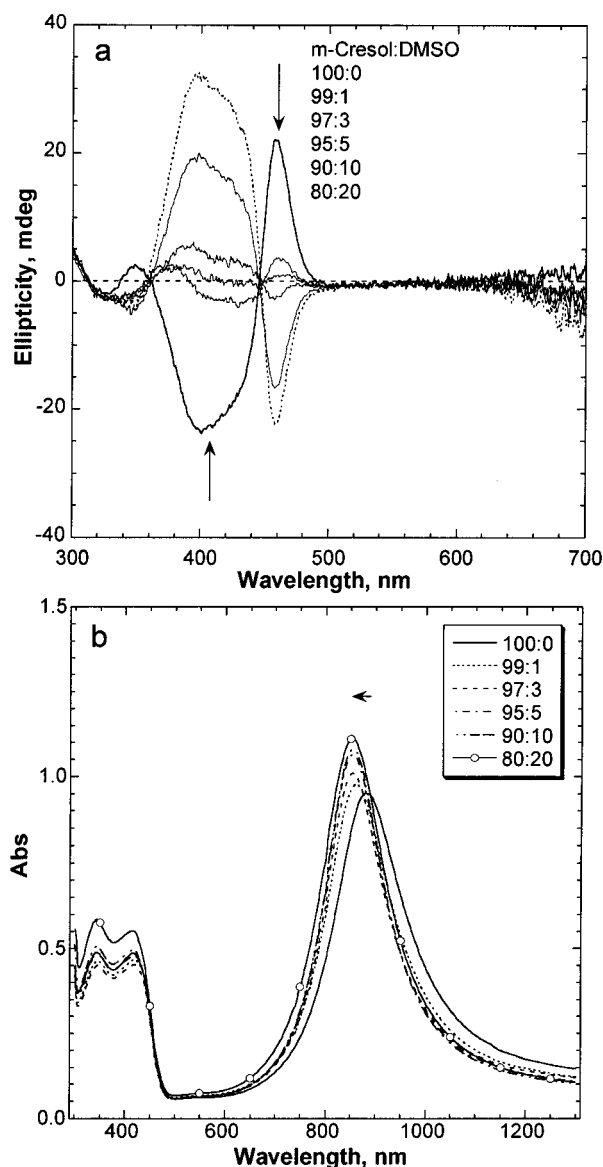


Figure 6. CD (a) and UV/vis/near-IR (b) spectra of PMOA/(+)-CSA dissolved in cosolvent of *m*-cresol and DMSO at various volume ratios.

configuration of PMOA/(+)-CSA after dissolution in *m*-cresol, and *m*-cresol combined with (+)-CSA and then polymer backbone for maintaining helical configuration cannot be replaced by DMSO. It is supposed that PMOA/(+)-CSA backbone combines with DMSO prior to *m*-cresol during the dissolution when cosolvent of *m*-cresol and DMSO was used to dissolubilize PMOA/(+)-CSA. Therefore, neither hydrogen bonding of *m*-cresol to carbonyl of CSA nor subsequent van der Waals interaction can form due to the presence of a little amount of DMSO, a strong H-bonding acceptor, around polymer backbone, and thus form the reverse helical configuration based on CD to that of PMOA/(+)-CSA solution in *m*-cresol; then the appearance intensity of CD bands decreases significantly. In the presence of a little larger amount of DMSO (5 vol %), the bisignate exciton-coupled CD bands assigned to PMOA/(+)-CSA solution in *m*-cresol completely disappeared and produced only those of PMOA/(+)-CSA solution in DMSO, which are at the same wavelength but inverted to those of PMOA/(+)-CSA solution in *m*-cresol.

The positions of bipolaron band in the UV/vis spectra of these solutions also support this interpretation (Figure 6b). The PMOA/(+)-CSA solution in *m*-cresol exhibits a well-defined bipolaron band at 880 nm. However, the bipolaron band of PMOA/(+)-CSA when dissolved in cosolvent of *m*-cresol and DMSO (99:1) is violet-shifted to 861 nm despite presence of only a little amount of DMSO. When 3 vol % of DMSO was introduced to prepare the cosolvent, the bipolaron band of PMOA/(+)-CSA solution is violet-shifted again to 854 nm and then saturates at a higher content of DMSO. The shift in bipolaron band is just parallel to what was found for change in CD spectra.

Conclusions

A novel process was developed to synthesize optically active PANIs in organic media by using 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) as the oxidizer and either enantiomer of camphorsulfonic acid (CSA) as the chiral inductor. It readily dispels the potential influence of water involved in the classical aqueous media on their chirality. Thin films of PANIs/(+)-CSA and PANIs/(−)-CSA cast from the reaction mixture exhibit mirror-imaged circular dichroism (CD) spectra in the visible region, indicating diastereoselection in the former electron-transfer polymerization. PANIs/(+)-CSA films exhibit a similar chiroptical property and strong intensity independent of various ring substituents, indicating that high regularity of PANIs is obtained from the coupling of aniline radical cations formed by electron transference from electron donor (anilines) to acceptor (DDQ) in organic media. They may also be dedoped in aqueous ammonia to give optically active PANI emeraldine bases, and redoping of the emeraldine base films regenerates the CD and UV/vis/near-IR spectra identical to those of the original films, confirming retention of configuration during reversible dedoping/redoping cycles in the solid state.

Unique chiroptical properties of PANIs/(+)- or (−)-CSA dissolved in *m*-cresol indicate that there exists a solvent effect on their chain conformations and subsequent chiroptical properties, and the solvent effect is strongly dependent upon the structure of parent monomer and nature of various organic solvents. A novel additional specific interaction between PANI/(+)-CSA and *m*-cresol is suggested here. That is, the phenyl rings in *m*-cresol and PANI interact through enhanced van der Waals forces. It may also act as one interaction combined with the well-known H- and electrostatic bonds to maintain the chiral configuration of PANIs/(+)-CSA in *m*-cresol solution. The chain conformation of PMOA/(+)-CSA in solution forms during the dissolution step, and postintroduction of another solvent does not induce any detectable change in the UV/vis spectrum as well as appearance of optical activity due to the stability of the former mentioned three types of interaction. However, PMOA doped with the same one-hand CSA can appear in the inverse CD spectrum when dissolved in cosolvent of *m*-cresol and DMSO at various volume ratios. These optically active PANIs may have such potential applications as electrochemical asymmetric synthesis, chiral electrocatalyst, and chiral chromatography. The solvent dependence of their chiroptical properties is an important preliminary step toward these applications in organic media.

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