

# In Situ Synthesis of Optically Active Poly(*o*-ethoxyaniline) in Organic Media and Its Chiroptical Properties

Shi-Jian Su 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 July 3, 2001. Revised Manuscript Received September 21, 2001

Optically active poly(*o*-ethoxyaniline) (PEOA) was prepared in situ in organic solvents with (+)- or (–)-camphorsulfonic acid (CSA) as the chiral dopant. This presented an effective facile route to prepare optically active polyaniline derivatives with large ring substituents and to dispel the potential influence of water involved in the classical aqueous media on their chirality. Thin films of PEOA/(+)- and (–)-CSA or their solutions exhibit mirror-imaged circular dichroism spectra in the UV/visible region, indicating diastereoselection in the former in situ polymerization system. The optical activity can be ‘memorized’ in the solid state during dedoping/redoping cycles indicating that the observed optical activity arises from the macroasymmetry of the polymer backbone and not the (+)-CSA dopant. A strong solvent effect exists on the PEOA’s chain conformation and subsequent chiroptical property. Changing the nature of the solvent has a significant influence on the positions of the bipolaron band in the UV/visible spectrum and the bisignate exciton-coupled bands in the circular dichroism spectrum. Moreover, PEOA/(+)-CSA lost its optical activity completely when dissolved in dimethyl sulfoxide despite maintenance of the emeraldine salt character, confirming that a preferred one-screw is maintained by both the electrostatic bonding of the enantiomeric (+)-CSA<sup>–</sup> anions to HN<sup>+</sup> centers and the hydrogen bonding of (+)-CSA<sup>–</sup> carbonyl groups to NH sites.

## Introduction

Chiral recognition is of particular importance in living systems. In polymer chemistry and supermolecular chemistry, control of helicity is an attractive goal because of possible applications in material science, chemical sensing, and enantioselective catalysis.<sup>1–5</sup> Recently, there has been considerable interest in induced macromolecular helicity of polymers, such as stereoregular poly(phenylacetylene)s bearing various functional groups, upon complexation with optically active compounds, such as amines, sugars, and acids, respectively.<sup>6–10</sup> The helix exhibited a characteristic induced circular dichroism in the UV/visible (vis) region, enabling it as a novel probe for the assignments of the

absolute configuration of the chiral compounds. Polyaniline (PANI), a low-cost inherently conducting polymer, is also an optically inactive polymer in nature. However, it can show an induced circular dichroism if it is protonated with a type of optically active acid, such as (+)-10-camphorsulfonic acid (CSA)<sup>11–14</sup> and (+)-10-tartaric acid,<sup>15</sup> because of formation of a preferred one-sense helical screw in the polymer backbone. Besides promising applications including electrostatic dissipation, anticorrosion coatings, electrochromic devices, secondary batteries, and light-emitting diodes, as reported previously for the achiral PANI,<sup>16–19</sup> such chiral PANI also has potential applications in molecular recognition and electrochemical asymmetric synthesis.<sup>13,20</sup>

\* To whom all correspondence should be addressed. E-mail: kuramoto@dip.yz.yamagata-u.ac.jp.

- (1) Amabilino, D. B.; Stoddart, J. F. *Chem. Rev.* **1995**, *95*, 2725.
- (2) Okamoto, Y.; Nakano, T. *Chem. Rev.* **1994**, *94*, 349.
- (3) Green, M. M.; Peterson, N. C.; Sato, T.; Teramoto, A.; Cook, R.; Lifson, S. *Science* **1995**, *268*, 1860.
- (4) Pu, L. *Acta Polym.* **1997**, *48*, 116.
- (5) Okamoto, Y.; Yashima, E. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 1020.
- (6) Yashima, E.; Matsushima, T.; Okamoto, Y. *J. Am. Chem. Soc.* **1995**, *117*, 11596.
- (7) Yashima, E.; Nimura, T.; Matsushima, T.; Okamoto, Y. *J. Am. Chem. Soc.* **1996**, *118*, 9800.
- (8) Yashima, E.; Matsushima, T.; Okamoto, Y. *J. Am. Chem. Soc.* **1997**, *119*, 6345.
- (9) Yashima, E.; Maeda, Y.; Okamoto, Y. *Chem. Lett.* **1996**, 955.
- (10) Saito, M. A.; Maeda, K.; Onouchi, H.; Yashima, E. *Macromolecules* **2000**, *33*, 4616.

- (11) Majidi, M. R.; Kane-Maguire, L. A. P.; Wallace, G. G. *Polymer* **1994**, *35*, 3113.
- (12) Havinga, E. E.; Bouman, M. M.; Meijer, E. W.; Pomp, A.; Simenon, M. M. J. *Synth. Met.* **1994**, *66*, 93.
- (13) Majidi, M. R.; Kane-Maguire, L. A. P.; Wallace, G. G. *Polymer* **1995**, *36*, 3597.
- (14) Norris, I. D.; Kane-Maguire, L. A. P.; Wallace, G. G. *Macromolecules* **1998**, *31*, 6529.
- (15) Ashraf, S. A.; Kane-Maguire, L. A. P.; Majidi, M. R.; Pyne, S. G.; Wallace, G. G. *Polymer* **1997**, *38*, 2627.
- (16) Kobayashi, T.; Yoneyama, H.; Tamura, H. *J. Electroanal. Chem.* **1984**, *161*, 419.
- (17) Paul, E. W.; Ricco, A. J.; Wrighton, M. S. *J. Phys. Chem.* **1985**, *89*, 1441.
- (18) Ohtani, A.; Abe, M.; Higuchi, H.; Shimidzu, T. *J. Chem. Soc., Chem. Commun.* **1988**, 1545.
- (19) Gustafsson, G.; Cao, Y.; Treacy, G. M.; Colaneri, N.; Heeger, A. J. *Nature* **1992**, *357*, 477.

Because of its low solubility in most common solvents, the industrial application of PANI is limited. Much recent research has focused on improving its solubility and even processability. Polymerization of ring-substituted aniline monomers containing alkyl, alkoxy, sulfonate, and carboxylate substituents resulted in PANI derivatives soluble in organic solvents and even in water because of the incorporation of flexible groups onto the polymer chains.<sup>21–24</sup> Among these PANI derivatives, poly(alkoxyaniline)s have been considered because of their good solubility in a range of organic solvents.<sup>25–28</sup> Similar to optically active PANI induced by chiral dopants, optically active poly(*o*-methoxyaniline) (PMOA) has most recently been reported with the use of two alternative procedures, involving either the enantioselective electrochemical polymerization of *o*-methoxyaniline in the presence of (+)- or (–)-CSA,<sup>29</sup> or post-protonation of PMOA emeraldine base (EB) with (+)- or (–)-CSA in organic solvent.<sup>30</sup> The acid doping of the emeraldine base form of PMOA with (+)-CSA in dimethyl sulfoxide (DMSO) solvent causes chiral induction into PMOA chains. However, it is much slower than for the analogous acid doping of the parent PANI-EB because of steric hindrance to polymer rearrangement by the methoxy ring substituent.<sup>30</sup> On this point, it is much more difficult to induce chirality into poly(*o*-ethoxyaniline) (PEOA) chains because of the larger bulkiness of the ethoxy group than that of the methoxy group. Moreover, as reported by Egan et al.,<sup>31</sup> it is likely that the water used in the classical procedure for either chemical or electrochemical preparation of CSA-doped PANIs contributes to their chiral configurations.

In our laboratory, a novel process has been developed for the preparation of PANI in organic media with 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ), a well-known electron acceptor, as the oxidant.<sup>32</sup> Synthesis of optically active PANI involving organic solvent to avoid water deduces the potential influence of water on the chirality of CSA-doped PANI to a great extent and enables detailed examination of solvent dependence of its chirality.

We report here optically active PEOA, in situ synthesized in a cosolvent of chloroform-tetrahydrofuran (THF) with either enantiomer of CSA as the chiral inductor. To our knowledge, this is the first time for the

successful preparation of optically active PEOA. The presence of a flexible ethoxy group decreases the rigidity of the polymer backbone inducing organic solubility and then permitting a detailed examination of its chiroptical property. At the same time, the detrimental effect of steric hindrance from a large ethoxy substituent was effectively diminished by synchronous induction of optical activity by (+)- or (–)-CSA during in situ polymerization of *o*-ethoxyaniline. This presents a novel route to prepare PANIs with large ring substituents doped with organic acid with large bulkiness. It was particularly interesting to establish the influence of the alkoxy substituents on the chirality of the corresponding polymers and to compare the chain conformations of PMOA and PEOA with different steric hindrances, as revealed by circular dichroism (CD) and UV/vis/near-IR spectra. Thin films of PEOA/(+)- or (–)-CSA were easily cast from the homogeneous reaction mixture. The dedoping of the PEOA/(+)-CSA salt film with aqueous ammonia was also explored to ascertain whether the chirality of the PEOA chains is altered by the removal of the dopant (+)-CSA<sup>–</sup> anion; this is very important if it is to be used as chiral ion exchange material for enantiomeric separations.

## Experimental Section

**Materials.** *o*-Methoxyaniline and *o*-ethoxyaniline (Kanto Chemical Co.) were distilled under vacuum and stored at less than –10 °C before use. CSA was purchased from Aldrich and was dried under vacuum at 60 °C for 24 h before use. DDQ was also purchased from Aldrich and used as supplied. THF (Kanto Chemical Co.) used as the reaction solvent was predried by using sodium and was distilled before 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 washed thoroughly with distilled water and dried under vacuum at 60 °C for 24 h.

**Preparation of Poly(*o*-alkoxyaniline)s/CSA Salts.** Polymerization of *o*-methoxyaniline or *o*-ethoxyaniline was performed in cosolvent of chloroform-THF with either (+)- or (–)-CSA as the chiral dopant (Scheme 1). Typically, 5 mmol of (+)-CSA and 2.5 mmol of *o*-ethoxyaniline 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. The reaction mixture changed to green and then deep-green solution without any precipitate. After the addition of DDQ, the reaction mixture was stirred for a further 7 h at room temperature. Then, 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 *o*-ethoxyaniline and its oligomers. These films were then dried under vacuum at room temperature. The as-synthesized PEOA doped with (+)-CSA was precipitated by adding an excess amount of acetone to the reaction mixture, then filtered, and washed with acetone. The purified PEOA/(+)-CSA was dried under vacuum at 60 °C for 24 h and stored in a desiccator for use.

Spectroscopic data of PEOA/(+)-CSA: Fourier transform infrared (FTIR) (KBr pellet, cm<sup>–1</sup>): 1735 ( $\nu_{C=O}$ ), 1575 (quinoid), 1490 (bezenoid), 1293 ( $\nu_{C-N}$ ), 1124 and 1030 ( $\nu_{O-S=O}$ ). <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 25 °C, ppm):  $\delta$  6.94, 7.12, 7.31 (aromatic);  $\delta$  ~4 (–OCH<sub>2</sub>–);  $\delta$  1.29 (–CH<sub>3</sub>). Anal. Found: C, 62.71; H, 6.80; N, 5.31; S, 6.43.

**Chemical Dedoping/Redoping of the PEOA/CSA Films.** Chemical dedoping and redoping of PEOA/CSA films were

(20) Guo, H. L.; Knobler, C. M.; Kaner, R. B. *Synth. Met.* **1999**, *101*, 44.

(21) Wei, Y.; Focke, W. W.; Wnek, G. E.; Ray, A.; MacDiarmid, A. G. *J. Phys. Chem.* **1989**, *93*, 495.

(22) Chan, H. S. O.; Ng, S. C.; Sim, W. S.; Tan, K. L.; Tan, B. T. G. *Macromolecules* **1992**, *25*, 6029.

(23) Wei, X. L.; Wang, Y. Z.; Long, S. M.; Bobeczko, C.; Epstein, A. J. *J. Am. Chem. Soc.* **1996**, *118*, 2545.

(24) Ye, S.; Do, N. T.; Dao, L. H.; Vigh, A. K. *Synth. Met.* **1997**, *88*, 65.

(25) MacInnes, D.; Funt, B. L. *Synth. Met.* **1988**, *25*, 235.

(26) Mattoso, L. H. C.; Bulhões, L. O. S. *Synth. Met.* **1992**, *52*, 171.

(27) Mattoso, L. H. C.; Manohar, S. K.; MacDiarmid, A. G.; Epstein, A. J. *J. Polym. Sci. Part A: Polym. Chem.* **1995**, *33*, 1227.

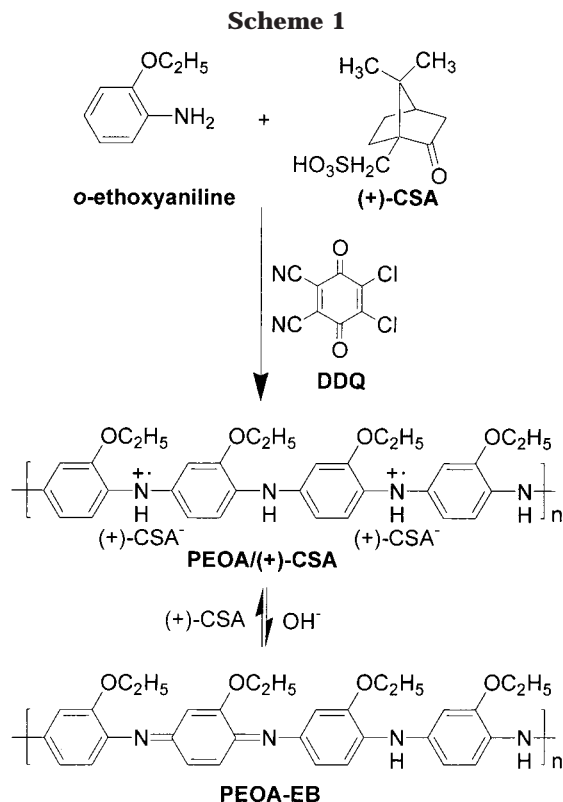
(28) Liao, Y. H.; Angelopoulos, M.; Levon, K. *J. Polym. Sci. Part A: Polym. Chem.* **1995**, *33*, 2725.

(29) Norris, I. D.; Kane-Maguire, L. A. P.; Wallace, G. G. *Macromolecules* **2000**, *33*, 3237.

(30) Norris, I. D.; Kane-Maguire, L. A. P.; Wallace, G. G.; Mattoso, L. H. C. *Aust. J. Chem.* **2000**, *53*, 89.

(31) Egan, V.; Bernstein, R.; Hohmann, L.; Tran, T.; Kaner, R. B. *Chem. Commun.* **2001**, 801.

(32) Su, S.-J.; Kuramoto, N. *Chem. Lett.* **2001**, 504.



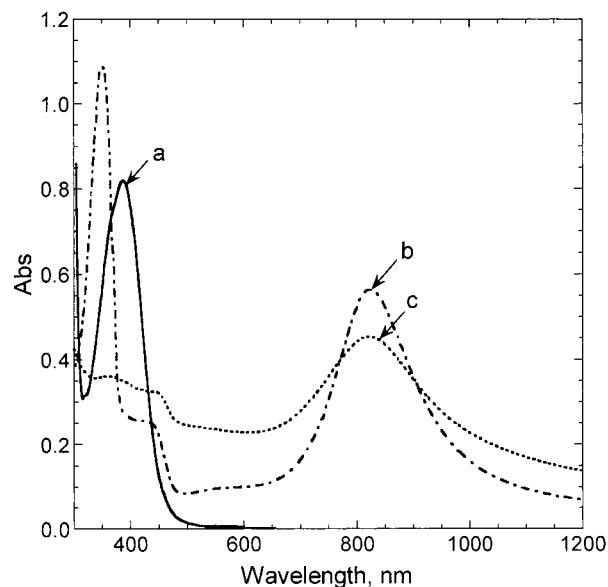
performed using the procedure described previously.<sup>29,33</sup> In general, the PEOA/(+)-CSA and PEOA/(−)-CSA films were dedoped to give EB films by suspending them in 30 mL of aqueous 1.0 M  $\text{NH}_4\text{OH}$  for 30 min and dried by using an air gun at room temperature (Scheme 1). The EB films were then redoped with HCl to give the corresponding PEOA/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 CD spectra of the optically active PEOA/(+)- or (−)-CSA films (and of related PEOA-EB and PEOA/HCl films) were recorded by using a JASCO V-570 spectrophotometer and a JASCO J-720WI spectropolarimeter, respectively. The purified PEOA/(+)- or (−)-CSA were dissolved in various organic solvents and then filtered, and their UV/vis/near-IR and CD spectra were also recorded. Infrared spectrum in KBr pellet of the PEOA/CSA powder was recorded on a FTIR spectrophotometer (Horiba FT-210). The  $^1\text{H}$  NMR spectrum of PEOA/CSA (DMSO- $d_6$  as the solvent) was recorded with a JEOL EX spectrometer operated at 270 MHz.

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

## Results and Discussion

The reaction process was investigated by UV/vis/near-IR spectrophotometry. An absorption band at 388 nm due to DDQ (Figure 1a) quickly disappeared after it was introduced into the reaction system, and an absorption band at 345 nm that is assigned to the reduced DDQ appeared at the same time. It is supposed that an outer charge-transfer complex intermediate is formed between DDQ, a well-known electron acceptor, and *o*-ethoxy-



**Figure 1.** UV/vis spectra of (a) DDQ solution in chloroform, (b) diluted reaction mixture and thin film cast from the reaction mixture, and (c) thin film purified with acetone.

aniline, an electron donor. Via the intermediate, the electron of *o*-ethoxyaniline can be easily transferred to the electron acceptor, DDQ, to form a radical cation, and DDQ is simultaneously reduced. Then, combination of the radical cations forms an oligomer of *o*-ethoxyaniline and even PEOA. We could not detect the intermediate by the aid of the absorption spectrum measurement, possibly because of its instability at room temperature. Alongside the reaction process, a well-defined bipolaron band at about 820 nm and a lower wavelength polaron absorption band at about 440 nm appears, and their intensity increases with longer reaction time and/or higher content of DDQ introduced.

The UV/vis/near-IR spectrum of the homogeneous reaction mixture diluted with chloroform exhibits an intense, well-defined bipolaron band at 824 nm, and a lower wavelength polaron band at 445 nm (Figure 1b). The absorption band caused by the benzenoid  $\pi-\pi^*$  transition<sup>34</sup> was not found because of overlap with the absorption band at 345 nm assigned to the reduced DDQ. Thin film was cast from the homogeneous reaction mixture, and its absorption spectrum was identical with that of diluted reaction mixture. After it was purified with fresh acetone to remove unreacted DDQ and *o*-ethoxyaniline, reduced DDQ, oligomers of *o*-ethoxyaniline, and most of free (+)-CSA, the intense absorption band caused by the reduced DDQ completely disappeared, and a well-defined absorption band assigned to the benzenoid  $\pi-\pi^*$  transition was found at 355 nm. This absorption spectrum is identical with that of PANIs/HCl<sup>35</sup> and PANIs/CSA<sup>14</sup> film prepared by a chemical or electrochemical method and is consistent with a 'compact-coil' conformation for the polymer chains.

The FTIR spectrum of PEOA/CSA exhibits peaks at 1575, 1490, and 1293  $\text{cm}^{-1}$ , which are due to quinoid

(33) Kane-Maguire, L. A. P.; MacDiarmid, A. G.; Norris, I. D.; Wallace, G. G.; Zheng, W. *Synth. Met.* **1999**, *106*, 171.

(34) Roe, M. G.; Ginder, J. M.; Wigen, P. E.; Epstein, A. J.; Angelopoulos, M.; MacDiarmid, A. G. *Phys. Rev. Lett.* **1988**, *60*, 2789.

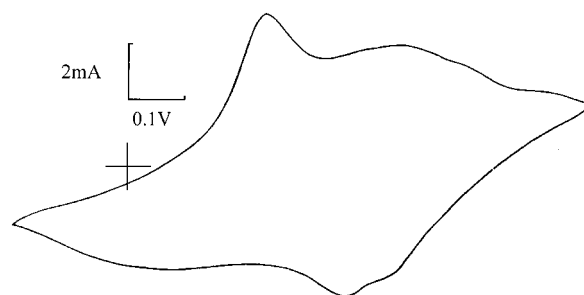
(35) Zheng, W.; Min, Y.; Lee, S.-J.; MacDiarmid, A. G.; Angelopoulos, M.; Liao, Y.-H.; Epstein, A. J. *Synth. Met.* **1997**, *84*, 63.



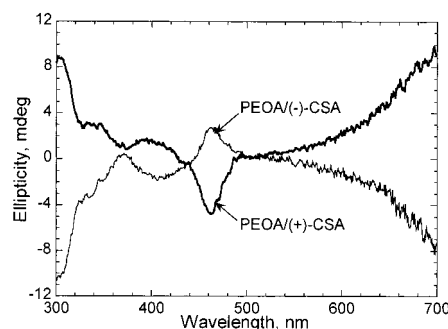
and benzenoid rings, and C–N stretching vibration, respectively.<sup>36–37</sup> The peaks at 1124 and 1030  $\text{cm}^{-1}$  can be assigned to the asymmetric and symmetric O=S=O stretching vibrations indicating the existence of a  $\text{SO}_3^-$  group. The absorption peak at 1735  $\text{cm}^{-1}$  can be assigned to the C=O stretching vibration of CSA. In addition, no band due to unreacted and/or reduced DDQ was found in the FTIR spectrum, indicating that PEOA/CSA can be absolutely purified with fresh acetone and keeps its emeraldine salt state. The elemental analysis of the dried PEOA/CSA showed that the molar ratio of the tetramer unit of emeraldine base and CSA is approximately 1:2, which suggests that the PEOA is still fully doped by CSA although most of free CSA was washed away simultaneously. NMR spectrum of PEOA/(+)-CSA exhibits peaks attributed to the aliphatic protons of the  $-\text{OCH}_2-$  group ( $\sim 4$  ppm) and of the  $-\text{CH}_3$  group (1.29 ppm), and the aromatic protons ( $\sim 7$  ppm), and they are nearly identical with those of PEOA prepared in aqueous media.<sup>28</sup> It also clearly exhibits peaks attributed to (+)-CSA incorporated into the polymer, which are identical with those of (+)-CSA.

Besides PEOA/(+)-CSA, PMOA/(+)-CSA was also synthesized via the same process. UV/vis/near-IR spectrum of PMOA/(+)-CSA film shows an absorption band assigned to the benzenoid  $\pi-\pi^*$  transition at 355 nm and the polaron band at 445 nm, which are at the same wavelengths as those of PEOA/(+)-CSA film. However, its bipolaron absorption band is red-shifted to 837 nm compared with that of PEOA/(+)-CSA seen at 824 nm. It is supposed that presence of methoxy or ethoxy electron-donating substituent induces a different electronic environment in their backbones from the parent PANI salt resulting in increased localized electronic density. At the same time, the presence of a methoxy or ethoxy group also induces a steric effect between the methoxy or ethoxy group and hydrogen on the adjacent nitrogen atom to form more twisted polymer chains, which are consistent with a 'compact-coil' conformation.<sup>38–39</sup> This is nearly identical with that of electrochemically deposited PANIs films or chemically polymerized PANIs.<sup>40</sup>

The cyclic voltammogram of a PEOA/(+)-CSA film cast onto a platinum electrode displays two reversible redox responses similar to those reported PANIs/CSA films prepared by electrochemical polymerization, confirming that the PEOA/(+)-CSA is electroactive (Figure 2). The redox couples at 0.25 V may be ascribed to the two-electron per tetramer oxidation of the neutral leucoemeraldine state of the polymer to the emeraldine form, whereas the second major oxidation peak appears at 0.49 V corresponding to the subsequent two-electron oxidation to the pernigraniline state per tetramer.<sup>41–42</sup> The broadness of the features of the cyclic voltammogram may be the result of the ethoxy groups in the



**Figure 2.** Cyclic voltammogram of a PEOA/(+)-CSA film. Conditions: 1.0 M (+)-CSA, Pt electrode,  $-0.2$  to  $+0.8$  V vs Ag/AgCl, scan rate 30 mV/s, second cycle shown.



**Figure 3.** The mirror-imaged CD spectra of PEOA/(+)- and (-)-CSA films cast from their reaction mixtures.

backbone, leading to a distribution of potentials.<sup>39</sup> The redox couples of PMOA/(+)-CSA are 0.18 and 0.60 V. They also exhibit weak oxidation processes at about 0.40 V, which were attributed to structural defects,<sup>43–44</sup> but the weakness of these features again supports the stereo regularity of the resultant poly(alkoxyaniline)s. All these results confirmed that the poly(alkoxyaniline)s fully doped with CSA were obtained from electron-transfer polymerization of alkoxyanilines in organic media.

The PEOA/(+)- and (-)-CSA films possessed characteristic CD bands at wavelengths longer than 300 nm, which were attributed to optical architecture in the polymer backbones because CSA does not show any CD bands in this region,<sup>11–14</sup> confirming induced macromolecular helicity of PEOA. PEOA/(+)-CSA exhibits the CD bands at 340, 370, 400, and 460 nm (Figure 3). The CD bands at 340 and 370 nm are probably bisignate exciton-coupled CD bands associated with the benzenoid  $\pi-\pi^*$  transition absorption band seen at 355 nm, and another couple of CD bands at 400 and 460 nm may be another pair of bisignate exciton-coupled CD bands corresponding to the polaron absorption band at 445 nm. In contrast to PEOA/(+)-CSA, only two single CD bands according to two pairs of bisignate exciton-coupled CD bands, respectively, were observed for PMOA/(+)-CSA, due, in part, to their overlapping. Also, it exhibits a CD band at 650 nm assigned to the lower wavelength component of the expected pair of bisignate exciton-coupled CD bands associated with the bipolaron band at about 800 nm. PEOA/(+)-CSA does not exhibit any well-defined CD bands, but a long tail character between 500 and 700 nm may be due to the CD band at

(36) Yin, W.; Ruckenstein, E. *Macromolecules* **2000**, *33*, 1129.

(37) Kue, C.-T.; Chen, C.-H. *Synth. Met.* **1999**, *99*, 163.

(38) Baughman, R. H.; Wolf, J. F.; Eckardt, E.; Shacklette, L. W. *Synth. Met.* **1988**, *25*, 121.

(39) Pullen, A. E.; Swager, T. M. *Macromolecules* **2001**, *34*, 812.

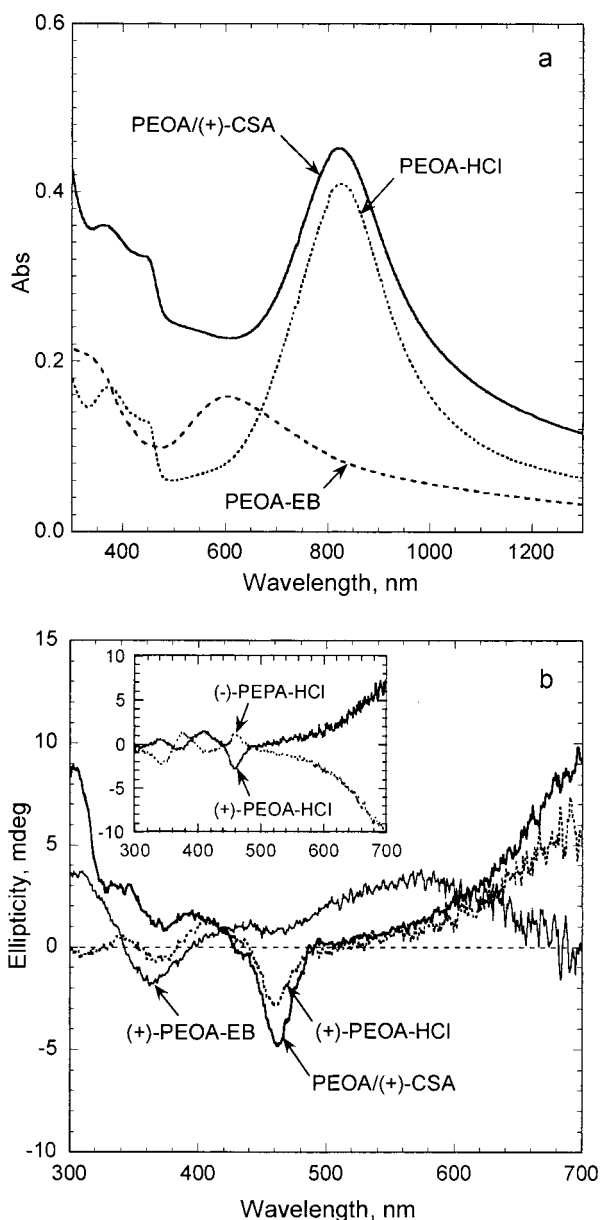
(40) Patil, S.; Mahajan, J. R.; More, M. A.; Patil, P. P. *Mater. Lett.* **1998**, *35*, 108.

(41) MacDiarmid, A. G.; Epstein, A. J. *J. Chem. Soc., Faraday Discuss.* **1989**, *88*, 317.

(42) Huang, W. S.; Humphrey, B. D.; MacDiarmid, A. G. *J. Chem. Soc., Faraday Trans.* **1986**, *82*, 2385.

(43) Geniès, E. M.; Penneau, J. F.; Lapkowski, M. *J. Electroanal. Chem.* **1988**, *249*, 97.

(44) Leclerc, M.; D'Aprano, G.; Zotti, G. *Synth. Met.* **1993**, *55–57*, 1527.



**Figure 4.** UV/vis/near-IR (a) and CD (b) spectra of PEOA/ (+)-CSA after dedoped with 1.0 M  $\text{NH}_4\text{OH}$  and then redoped with 1.0 M HCl. Inset: the mirror-imaged CD spectra of optically active PEOA-HCl films.

wavelengths longer than 700 nm. However, we failed to record the CD bands at the wavelengths longer than 700 nm because of the strong absorption of PEOA in this region. Mirror-imaged CD spectra were observed for PEOA/ (+)- and (-)-CSA films, indicating that the electron-transfer polymerization of *o*-ethoxyaniline in the presence of (+)- or (-)-CSA in organic solvents is diastereoselective.

Treatment of PEOA/ (+)-CSA emeraldine salt film with 1.0 M  $\text{NH}_4\text{OH}$  resulted in rapid deprotonation to give a blue EB film. Typically, UV/vis spectrum of PEOA EB film exhibits two absorption bands at 330 and 600 nm assigned as the benzenoid  $\pi-\pi^*$  transition absorption and the molecular exciton associated with the quinoid group, respectively, characteristic of emeraldine bases (Figure 4a). CD spectrum of this PEOA-EB film shows that it is still optically active, with CD bands at 310, 360, and 580 nm, indicating retention of chiral

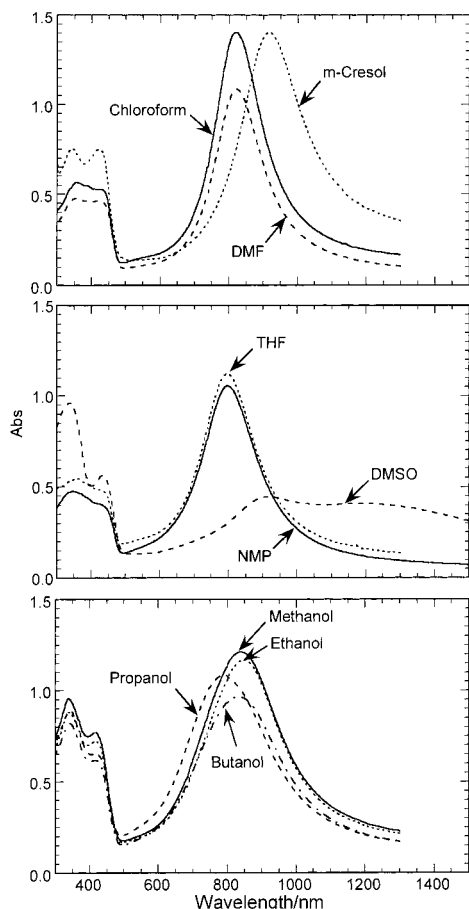
configuration in the polymer backbone (Figure 4b). The CD bands at 310 and 360 nm may be assigned as the bisignate exciton-coupled bands associated with the benzenoid  $\pi-\pi^*$  transition absorption band seen at 330 nm. Only one broad band assigned as one of the bisignate exciton-coupled bands was observed at 580 nm, and another one may be hidden because of the broadness of the band at 580 nm. The blue-shifted CD band at 580 nm of PEOA-EB in contrast to that of PEOA/ (+)-CSA salt is the result of the molecular exciton absorption band of PEOA in the EB state at a lower wavelength than for the bipolaron band of PEOA in the emeraldine salt state. Retention of chiral configuration in the polymer backbone, although in the EB state, provides a facile route to produce optically active films of PEOA in the EB state and enables them to be potential candidates of chiral ion exchange materials for enantiomeric separations. The 'memory' of chiral configuration in the PEOA-EB film, despite removal of the (+)-CSA<sup>-</sup> anion, again demonstrates that the observed optical activity arises from the macroasymmetry of the polymer backbone and not the (+)-CSA dopant. The blue EB films obtained from PEOA/ (+)- and (-)-CSA salt films also exhibit mirror-imaged CD spectra, which indicates their enantiomeric nature.

Redoping of the above-mentioned optically active PEOA-EB film with aqueous 1.0 M HCl regenerated an UV/vis spectrum identical with that of the initial PEOA/ (+)-CSA film (Figure 4a). The CD spectrum of the regenerated PEOA-HCl film was also identical with the initial CD spectrum of the PEOA/ (+)-CSA film exhibiting CD bands at 340, 370, 410, and 460 nm, except that the bands according to the incorporated (+)-CSA (~300 nm) and PEOA-EB (310 and 580 nm) were absent. The obtained (+)- and (-)-PEOA-HCl films also exhibit mirror-imaged CD spectra, again confirming the enantiomeric nature of the two PEOA films and the 'memory' of their absolute configurations during dedoping/redoping cycles in the solid state (Figure 4b, inset). Similar behavior was also found for PMOA/ (+)- and (-)-CSA films. Yashima et al. recently demonstrated that macro-molecular helicity induced on a stereoregular *cis-transoidal* poly[(4-carboxyphenyl)acetylene] by an optically active amine can be 'memorized' when the amine is replaced by various achiral amines in organic solvents.<sup>45</sup> However, it reverts to the original optically inactive (nonhelical) polymer when it is freed by a stronger acid. The 'memory' of helicity in the PEOA-EB, although in the absence of any anions, is presumably caused by the steric constraints in the solid state.

The purified PEOA/ (+)-CSA was more soluble than the corresponding PANI/ (+)-CSA and poly(*o*-toluidine)/ (+)-CSA in a range of organic solvents, such as *N*-methyl-2-pyrrolidinone (NMP), *N,N*-dimethylformamide (DMF), *m*-cresol, DMSO, THF, chloroform, and alcohols (methanol, ethanol, propanol, and butanol). The improved solubility of PEOA/ (+)-CSA is believed to be caused by the flexible and polar ethoxy substituent, which decreases the stiffness of the polyaniline chains and increases the overall polarity of the polymer chains.

The UV/vis/near-IR spectrum of PEOA/ (+)-CSA dissolved in each of these organic solvents indicates

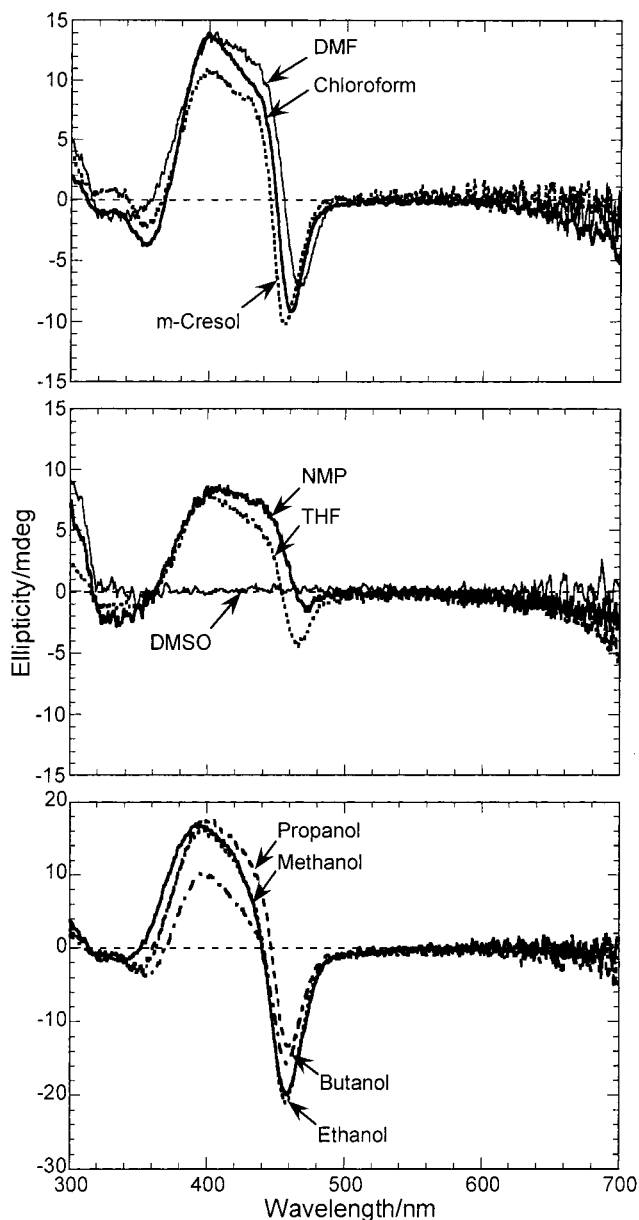
(45) Yashima, E.; Maeda, K.; Okamoto, Y. *Nature* **1999**, *399*, 449.



**Figure 5.** UV/vis/near-IR spectra of PEOA/(+)-CSA dissolved in a variety of organic solvents.

maintenance of 'compact-coil' conformation except for that of DMSO solution, which exhibits a red-shifted bipolaron band combined with a strong free-carrier tail in the near-infrared region (Figure 5). This suggests at least a partial 'expanded-coil' conformation for the PEOA/(+)-CSA dissolved in DMSO. The corresponding CD spectrum of PEOA/(+)-CSA after dissolution in each of these solvents exhibits similar CD bands at 340( $\pm$ 10) and 400 nm, which are assigned as the bisignate exciton-coupled bands associated with the benzenoid  $\pi$ - $\pi^*$  absorption band seen at 350 nm. It also exhibits a broad shoulder at 440 nm and a well-defined peak at 463( $\pm$ 8) nm, which may be assigned as the bisignate exciton-coupled bands associated with the polaron absorption band seen at 440 nm (Figure 6). These spectra are similar to those of PANI/(+)-CSA when in the 'compact-coil' conformation.

PEOA/(+)-CSA lost its optical activity completely when dissolved in DMSO despite maintenance of emeraldine salt state and the CD band at  $\sim$ 300 nm assigned to (+)-CSA<sup>-</sup> dopant anions combined with the polymer backbone. Loss of optical activity was also observed for diluted solutions of PANI/(+)-CSA in DMF, NMP, and DMSO,<sup>13</sup> but this is undoubtedly because of the spontaneous deprotonation of the emeraldine salt to give EB. For the deprotonated PANI, it is supposed that the preferred helical configuration maintains in the solution in the absence of (+)-CSA<sup>-</sup> anion only for a very short time and rapidly rearranges to an achiral configuration. However, for the former solid PEOA/(+)-CSA film, steric constraints in the solid state presumably



**Figure 6.** CD spectra of PEOA/(+)-CSA dissolved in a variety of organic solvents.

prevent such a conversion that can occur readily in solution. For the PEOA/(+)-CSA solution in DMSO, it might not be appropriate to interpret the loss of optical activity as the former because (+)-CSA<sup>-</sup> anions are still linking with HN<sup>+</sup> centers for the maintenance of emeraldine salt character. It was postulated that the observed macroasymmetry arises from the polyaniline chain adopting, at least partially, a preferred one-screw which is maintained by the enantiomeric (+)- or (-)-CSA<sup>-</sup> anions linking HN<sup>+</sup> and NH centers repeating units apart along the polymer chain.<sup>11-15</sup> Therefore, the deprotonated PANI clearly loses its optical activity because of the loss of both of these types of interaction and easy rearrangement in solution. However, for the PEOA/(+)-CSA when dissolved in DMSO, only the H-bonding of the (+)-CSA<sup>-</sup> carbonyl groups to PEOA NH sites was completely destroyed because of the large steric hindrance of ethoxy group and strong interaction between DMSO and NH sites. Loss of optical activity, although electrostatic bonding of the (+)-CSA<sup>-</sup> sulfonate



**Table 1. Solvent Dependence of UV/Vis/near-IR and CD Spectra of PEOA/(+)-CSA**

solvent	bipolaron band in UV/vis/near-IR spectrum (nm)	longer wavelength component of bisignate associated with polaron band in CD spectrum (nm)
NMP	797	472
THF	797	467
DMF	823	467
chloroform	822	460
methanol	839	458
<i>m</i> -cresol	917	455
DMSO	919, free-carrier tail	—

ions to the PEOA HN<sup>+</sup> centers is maintained, again proves that not one of these two types of interaction can be omitted to keep the chiral configuration of PANIs. Again, the observed optical activity arises not from the (+)-CSA<sup>-</sup> anions but from the macroasymmetry of the polymer backbone, because the PEOA/(+)-CSA dissolved in DMSO still maintains the CD band at ~300 nm assigned to the (+)-CSA<sup>-</sup> anions, although it loses all the CD bands that can be assigned to PEOA/(+)-CSA backbones. The enhanced van der Waals interaction<sup>46–47</sup> between phenyl rings and PANIs may also act as an indispensable interaction to maintain a preferred helical configuration in *m*-cresol solutions besides the electrostatic and hydrogen bonds already mentioned. They both promote solubility of PANIs in *m*-cresol and present the stability of formed chiral configuration. Because the enhanced van der Waals forces form on the basis of H-bonding between the carbonyl group in (+)-CSA and the hydroxyl group of *m*-cresol, they are also affected by the adjacent ring substituents and subsequently affect the appearance of the CD feature based on the chiral configuration of polymer backbones. Thus, the difference in PANIs with various ring substituents when dissolved in *m*-cresol can be easily interpreted.

Although similar conformation was maintained in each of these solvents except for DMSO, changing the nature of the solvent significantly influences the positions of the bipolaron band in the UV/vis/near-IR spectrum and the bisignate exciton-coupled bands in the CD spectrum, as summarized in Table 1. In contrast, the effect on the positions of the benzenoid  $\pi$ - $\pi^*$  absorption band and the polaron band is relatively slight.

The wavelength of the bipolaron band is significantly red-shifted along the following series, NMP, THF <

chloroform < DMF < MeOH < *m*-cresol < DMSO, indicating an increase in the conjugation length of the PEOA/(+)-CSA chain along this series of solvents. It may reflect a change from a 'poor' to a 'good' solvent for the PEOA/(+)-CSA along this series. This trend is similar to that of PMOA/(+)-CSA dissolved in this series of solvents because of the similar polarity of methoxy and ethoxy groups. However, 'compact-coil' conformation of PEOA/(+)-CSA changed to a partial 'expanded-coil' conformation when dissolved in DMSO to show a longer conjugation length than that of PMOA/(+)-CSA. As mentioned previously, this may be due to the large steric hindrance of the ethoxy group, which destroys the hydrogen bonding of the (+)-CSA<sup>-</sup> carbonyl groups to PEOA NH centers and then the preferred one-screw. The exceptionally low wavelength of bipolaron band observed in NMP may reflect the high basicity of this solvent, which facilitates the partial deprotonation of emeraldine salt to emeraldine base with a concomitant decrease in the wavelength of the observed bipolaron band. The longer wavelength component at 463(±8) nm of the bisignate exciton-coupled bands associated with the polaron band is also red-shifted, but along an almost reverse series, *m*-cresol < MeOH < chloroform < DMF, THF < NMP, and its relative intensity also decreases along the same series. It can also be interpreted by the difference among the basicities of these solvents.

## Conclusions

An effective facile route was developed to prepare (+)- or (-)-CSA-induced optically active PEOA in organic media, and it readily dispels the potential influence of the water involved in the classical aqueous media on its chirality. The mirror-imaged CD spectra found for thin films of PEOA/(+)- and (-)-CSA or their solutions in the UV/vis region indicate the enantiomeric nature of the resultant PEOA, which arises from the macroasymmetry of the polymer backbone and not the (+)-CSA dopant due to the 'memory' of chiral configuration in the absence of any anions in the solid state. Presence of the flexible ethoxy group induces better organic solubility than its parent PANI/CSA salt to enable the solution processability of PEOA, and a strong solvent effect on the polymer's chain conformation and subsequent chiroptical property exists. Optically active PANIs may have potential applications such as electrochemical asymmetric synthesis, chiral chromatography, and chiral electrocatalysis. Solvent dependence of their chiroptical properties is of particular importance toward their applications in organic media.

CM010663V

(46) Ikkala, O. T.; Pietilä, L. O.; Ahjopalo, L.; Österholm, H.; Passiniemi, P. J. *J. Chem. Phys.* **1995**, *103*, 9855.

(47) Vikki, T.; Pietilä, L. O.; Österholm, H.; Ahjopalo, L.; Takala, A.; Toivo, A.; Levon, K.; Passiniemi, P. J.; Ikkala, O. T. *Macromolecules* **1996**, *29*, 2945.