A Novel Strategy for Synthesis of Optically Active Polyanilines in Organic System

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Optically active polyanilines that were readily soluble in various organic solvents were prepared by oxidation of aniline with an electron acceptor, 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) in the presence of (+)- or (–)-camphorsulfonic acid (CSA). Their chiroptical properties in solutions are strongly dependent on the nature of organic solvents and structure of monomers.

Because of their potential use in diverse areas, such as electrochemical asymmetric synthesis, chiral chromatography and membrane separation technology, preparation of optically active polyaniline (PANI) derivatives has recently been reported using two alternative procedures, involving the enantioselective electropolymerization of anilines in the presence of (+)- or (–)-CSA,[1] or post-protonation of PANI emeraldine bases (EB) with (+)- or (–)-CSA in a variety of organic solvents.[2] To our knowledge, there is no example for the chemical polymerization of anilines in organic media due to insolubility of inorganic oxidant, such as ammonium persulfate (APS), in organic solvents, except for the example using emulsion polymerization method.[3] In addition, it is well known that resultant PANI is codoped with the acid introduced and the anion of sulfate, the reductant of APS, inducing a detrimental effect on the structure and regularity of PANI while APS is used as the oxidant in aqueous media. Finally, synthesis of PANI in organic solvents is another challenge for the possibility to improve the processability of resultant PANI in various organic solvents. 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,[4] 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.[5] In another respect, polymerization proceeds via possible CT complex formed between DDQ and aniline, which can improve the stereoregularity of PANI, and it is especially important to optically active PANI emeraldine salt. We report here a novel strategy that allows the synthesis of optically active PANIs/(+)- and (–)-CSA in organic media. All the PANIs/(+)- and (–)-CSA are found to be soluble in various organic solvents, permitting a detailed examination of their chiroptical properties.

Polymerization of aniline, *o*-anisidine and *o*-toluidine in co-solvent of chloroform–THF (3:1) in the presence of (+)- or (–)-CSA was carried out by addition of DDQ solution in THF. Dark-green-colored homogeneous reaction mixtures were obtained without any precipitate. Thin films of PANIs/(+)- or (–)-CSA were cast from the homogeneous reaction mixtures, followed by rinsing with acetone to remove excess amount of CSA, unreacted DDQ and its reductant, and even unreacted anilines and their oligomers. No band due to unreacted DDQ or its reductant was found in the FTIR spectra of purified PANIs/CSA. The elemental analysis of the dried PANIs/CSA showed that the molar ratio of the tetramer unit of emeraldine base and CSA is approximately 1:2, which suggests that the PANIs are fully doped with CSA and most of free CSA can be washed away simultaneously. The electronic spectra of purified films are identical to those of PANIs/HCl[6] and PANIs/CSA[7] films prepared by chemical or electrochemical method and are consistent with a ‘compact coil’ conformation for the polymer chains. The films in emeraldine salt state were obtained directly compared with those deposited from the aqueous media in the most highly oxidized (pernigraniline) state by using APS as the oxidant.[8] It is supposed that polymerization of aniline proceeds due to electron transfer between aniline and DDQ via the charge transfer complex intermediate formed between them. We could not detect the intermediate by the absorption spectrum measurement, and this may be due to its unstability at room temperature. Via the intermediate, the electron of aniline can be easily transferred to electron acceptor, DDQ, complexed with it to form radical cation. Then, combination of the radical cations forms oligomer of aniline and even PANI.

The PANIs/(+)-CSA films possessed characteristic circular dichroism (CD) bands at longer wavelength than 300 nm, which are attributed to a chiral architecture of the polymer backbone since CSA does not show any CD band in this region (Figure 1). The CD spectrum of poly(*o*-anisidine) (PMOA)/(+)-CSA is slightly different from that of PANI/(+)-

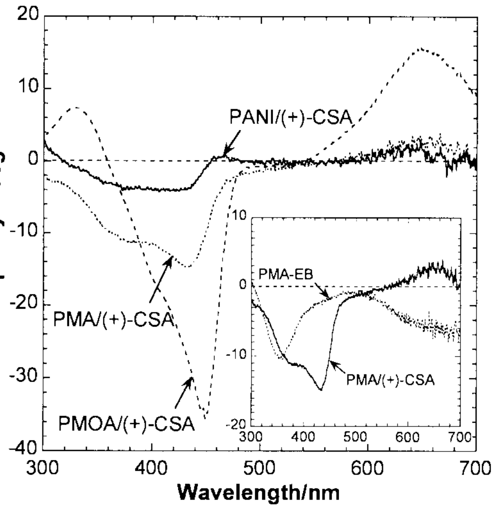

Figure 1. CD spectra of PANI/(+)-CSA, PMA/(+)-CSA, and PMOA/(+)-CSA films. Inset: CD spectrum of PMA-EB film and that of initial PMA/(+)-CSA salt film.

CSA or poly(*o*-toluidine) (PMA)/(+)-CSA. The CD bands at 330 nm and 400 nm that may be tentatively assigned as the bisignate exciton-coupled bands associated with the benzenoid π–π* transition absorption band were clearly observed.[7,9] These bands overlapped with the band at 460nm, one of another pair of bisignate which is red-shifted due to the polaron absorption band of PMOA/(+)-CSA at longer wavelength than that of PANI/(+)-CSA or PMA/(+)-CSA. The CD signal at about 300 nm due to the (+)-CSA$^-$ dopant anion incorporated into the polymer backbones is markedly weaker than that of electropolymerized PANIs/(+)-CSA and is even overlapped with the strong CD bands according to PANIs/(+)-CSA polymer backbones. The mirror-imaged CD spectra were also observed for PANIs/(+)- and (–)-CSA films. Treatment of PMA/(+)-CSA film with 1.0 M NH_4OH resulted in rapid deprotonation to produce EB film. The CD spectrum of resultant PMA-EB film shows that it is still optically active despite the removal of the (+)-CSA$^-$ anion (inset of Figure 1), indicating that the observed optical activity for the solid film arises from the macroasymmetry of the polymer backbone and not the (+)-CSA dopant. Similar phenomenon was also observed for PANI/(+)- or (–)-CSA and PMOA/(+)- or (–)-CSA films. Retention of optical configuration in EB state is important if the EB forms are to be used as chiral exchange materials for enatiomeric separations.[9]

The purified PANIs/(+)- and (–)-CSA were still found to be soluble in various kinds of organic solvents. However, the CD spectra for solutions (Figure 2) are significantly different from the solid films, indicating that the dissolution results in some change to the polymer chain conformations but remaining their optical activity and mirror-imaged CD spectra. Interestingly, for the PANIs doped with the same one-hand CSA dissolved in *m*-cresol, they show different chiroptical properties. PMOA/(+)- CSA and PANI/(+)-CSA dissolved in *m*-cresol show the similar chiroptical property except a red-shifted bisignate of PMOA/(+)- CSA compared with that of PANI/(+)-CSA due to localized polaron band at longer wavelength. However, PMA/(+)-CSA shows almost the mirror-imaged CD spectrum to that of PANI/(+)-CSA at the longer wavelength than 340 nm. The different electronic and CD spectra for PANIs/(+)-CSA solutions confirm that they have different conformations, and this change in conformation of the polymer backbone is presumably due to the dissolution of stiff PANIs' backbones which is relevant to their structures and strong interaction between polymer backbone and organic solvent. Another interest is that PMOA/(+)-CSA dissolved in m-cresol and DMSO show almost the mirror-imaged CD spectra at the longer wavelength than 340 nm. Similar phenomenon was also found for PMA/(+)- or (–)-CSA. It is supposed that there is a solvent effect on the PANIs' chain conformations that subsequently affects their chiroptical properties and the solvent effect is strongly dependent on the structure of monomers, nature of various organic solvents, and the balance of interactions among polymer backbone (amine and ring-substituents), CSA, and organic solvents. Further work is in progress to confirm this interpretation.

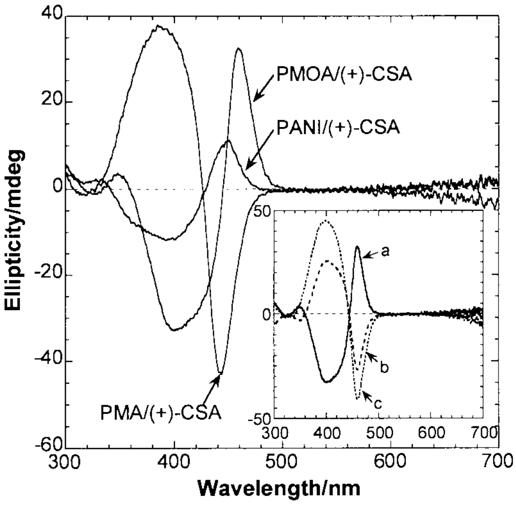

Figure 2. CD spectra of PANI/(+)-CSA, PMA/(+)-CSA, and PMOA/(+)-CSA dissolved in *m*-cresol. Inset: CD spectra of (a) PMOA/(+)- and (b) (–)-CSA dissolved in *m*-cresol and CD spectrum of (c) PMOA/(+)-CSA dissolved in DMSO.

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