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Helix Inversion of Polyaniline by Introducing *o*-Toluidine Units

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ABSTRACT: An optically active copolyaniline, poly(aniline-*co-o*-toluidine), which forms a different helix structure from that of the corresponding homopolymers was obtained by chemically oxidative polymerization with (1*S*)-(+)-10-camphorsulfonic acid as the chiral inductor in organic media. Formation of the genuine copolymer rather than a mixture of the corresponding homopolymers was confirmed by cyclic voltammogram, UV/vis, and circular dichroism spectra. The circular dichroism spectra of polyaniline and poly(aniline-*co-o*-toluidine) at suitable copolymer composition when dissolved in the same organic solvents revealed that their helical windings induced by the same chiral acid are reversed to each other. It is very interesting that the helical conformation of polyaniline can be inverted by inserting *o*-toluidine units into the polymer main chain. Since the chirality of poly(aniline-*co-o*-toluidine) depends on the *o*-toluidine content, this stereo-controlled polymerization of aniline derivatives affords a method to tailor-make electrically conductive materials with specific electrochemical and chiroptical properties. As a proof of concept, extension of this approach to other optically active polymers will be also expected.

Introduction

Helical structures are often observed in biopolymers and appear to play a dominant role in living systems, as exemplified by protein and DNA which adopt a right-handed α-helix and a double-helix, respectively. In polymer chemistry and supermolecular chemistry, controlled helix formation is an attractive goal because of possible applications in material science, chemical sensing, and enantioselective catalysis.[1] Attention has also been recently focused on optically active conjugated organic polymers because of their differential absorption and emission of circularly polarized light.[2] Polyaniline (PANI), an inherently conducting polymer, is optically inactive in nature. However, it can show an induced circular dichroism spectrum when it is protonated with an optically active acid owing to the formation of a prevailing one-handed helical conformation,[3] and the resultant chiral PANI has potential applications in molecular recognition, enantiomeric separation, and electrochemical asymmetric synthesis.[4]

After the discovery of helix inversion phenomenon in synthetic DNA and poly(L-aspartic acid esters), several artificial polymers have been found to undergo helix inversion, which is promoted by external stimuli such as the changes of temperature and solvent composition, chiral additives, the photoinduced isomerization of side chains, etc.[5] Most recently, Kaner et al. demonstrated that the chirality of PANI is critically dependent upon the water content of the polymer before exposure to the CSA dopant, and the water can cause a reversal in chirality.[6]

Copolymerization greatly increases the ability of the polymer scientists to tailor-make a material with specifically desired properties. In addition, copolymerization of enantiopure chiral monomers with achiral monomers or with an enantiomeric excess (ee) of one enantiomer over the other was reported as an effective route to obtain polymers with a preferential screw-sense main chain.[7] It is the presence of the enantiopure chiral "seeds" which results in the adoption of a preferential helical screw sense in even non-enantiopure-substituted backbone regions by the preferential stereorelationship between enantiopure chiral side chains and their nearest neighbors. To attain PANI derivatives combining good solubility with high conductivity, there have been several reports on the copolymerization of aniline with alkyl or alkoxyl ring-substituted anilines.[8] We have found that the steric and electronic properties of aniline ring substituents (H, Me, MeO, etc.) significantly affect the chiroptical properties of PANIs.[9] Different chiroptical properties were also expected for the copolyanilines besides better solution processability because of the presence of various ring substituents on the same polyaniline backbone. We report here the first example of optically active copolyaniline, poly(aniline-*co-o*-toluidine) (PANMA), which was synthesized with 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) as the oxidizer and with (1*S*)-(+)-10-camphorsulfonic acid (CSA) as the chiral inductor involving organic solvents instead of classical aqueous media. The helical conformation of polyaniline can be switched by introducing *o*-toluidine units into the polymer main chain. To our knowledge, maybe this is the first example of helix inversion induced by copolymerization of achiral monomers. Moreover, different electrical and electrochemical properties were also expected compared to either PANI or poly(*o*-toluidine) (PMA).

Experimental Section

Materials. Aniline and *o*-toluidine (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. Tetrahydrofuran (THF) (Kanto Chemical Co.) used as the reaction solvent was

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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 Copolyaniline Emeraldine Salts. Similar to homopolymerization of various aniline derivatives,[9] copolymerization of aniline and *o*-toluidine in cosolvent of chloroform−THF (volume ratio, 3:1) in the presence of (+)-CSA was carried out by addition of DDQ solution in anhydrous THF. Typically, 5 mmol of (+)-CSA, 1.25 mmol of aniline, and 1.25 mmol of *o*-toluidine were well dissolved in 20 mL of chloroform at room temperature. A solution containing 2.5 mmol of DDQ dissolved in 6.7 mL of anhydrous THF was then added dropwise with constant stirring at room temperature in a period of ca. 1 h. The reaction mixture changed to green and then deep-green solution without any precipitate. Thin films of synthesized polymer were dip-coated onto the precleaned glass slides from the homogeneous reaction mixture, followed by drying with an air gun. UV/vis spectra of the dried films were then immediately recorded. After addition of DDQ, the reaction mixture was stirred for another 8 h, and then an excess amount of acetone was added into the reaction mixture to precipitate the as-synthesized copolymer. The copolymer was collected with a glass filter and washed with an excess amount of acetone to remove excess (+)-CSA, unreacted and/ or reduced DDQ, and even unreacted monomers and their oligomers. The purified copolymer was dried under vacuum at 60 °C for 24 h and stored in a desiccator for use. Anal. Found: C, 65.03; H, 6.54; N, 6.38; S, 7.60. Fourier transform infrared (FTIR) (KBr pellet, cm^{-1}): 1725 ($\nu_{C=O}$), 1584 (quinoid), 1481 (benzenoid), 1293 (ν_{C-N}), 1105 and 1030 ($\nu_{O=S=O}$).

To convert the resultant PANMA/(+)-CSA into its base form, 0.15 g of a fine powder of PANMA/(+)-CSA was suspended in 20 mL of 0.5 M NH$_4$OH solution with stirring for 12 h. The mixture was then filtered, and the blue precipitate was washed with 0.5 M NH$_4$OH solution, distilled water, and acetone, followed by drying under dynamic vacuum for ca. 48 h to obtain the base form of the copolymer. Proton NMR spectroscopic study was performed on the base form of the copolymer. ^{1}H NMR (DMSO-d_6, 25 °C, ppm): δ 6.40−7.40 (aromatic), δ 1.95−2.34 (−CH$_3$).

Spectroscopic Studies. The purified optically active copolyanilines were dissolved in various organic solvents and then filtered, and their UV/vis/near-IR and CD spectra were recorded by using a JASCO V-570 spectrophotometer and a JASCO J-720WI spectropolarimeter, respectively. Infrared spectra in KBr pellets of the copolyaniline powders were recorded on a FTIR spectrophotometer (Horiba FT-210). Proton NMR spectra were recorded on a JEOL EX spectrometer operated at 270 MHz. DMSO-d_6 was used as solvent and tetramethylsilane (TMS) as an internal standard.

Cyclic Voltammetry. The electrochemical characterization of PANMA/(+)-CSA film coated onto a platinum electrode was performed in a three-electrode cell at room temperature by using 20 mL of 1.0 M (+)-CSA as the supporting electrolyte. The potential was cycled between −0.2 and +1.2 V (vs SCE) at a scan rate of 30 mV/s.

Conductivity Measurement. The purified copolyaniline powders were well dissolved in *m*-cresol, and then thin films were cast onto precleaned glass slides. The thin films were thoroughly dried under vacuum, and their conductivity was measured by standard four-probe method with a Loresta HP (MCP T410) (Mitsubishi Chemical Co.).

Results and Discussion

The copolymerization process of aniline and *o*-toluidine was investigated by UV/vis spectrophotometry. After addition of DDQ to the polymerization solution, an intense absorption band at 345 nm caused by the reduced DDQ appeared with concomitant disappearance
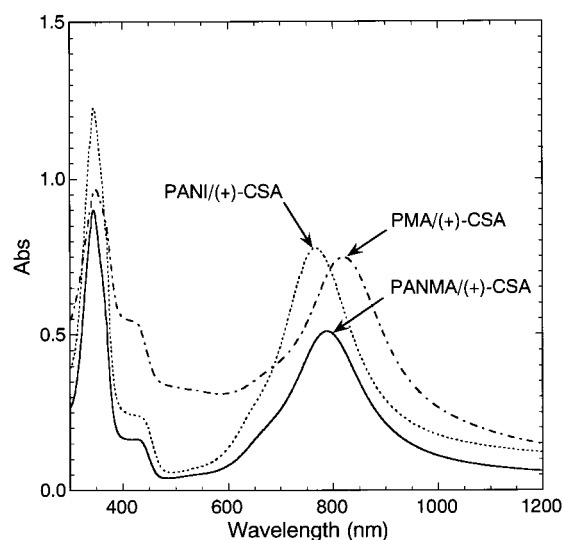

Figure 1. Comparison of UV/vis spectra of PANI/(+)-CSA, PMA/(+)-CSA, and PANMA/(+)-CSA (feed molar ratio, aniline/ *o*-toluidine = 1:1) films dip-coated from the reaction mixtures.

of the absorption band due to DDQ at 388 nm. As the reaction proceeded, a shorter wavelength polaron band at about 430 nm and a well-defined bipolaron band at 789 nm appeared (Figure 1), and their intensity also increased with prolonged reaction time and/or with higher DDQ content. The absorption band assigned to the benzenoid $\pi-\pi^*$ transition[10] was not observed because of overlap with the absorption band at 345 nm caused by the reduced DDQ. For the similarly prepared PANI and PMA, their bipolaron bands were found at 767 and 820 nm, respectively. As previously reported, the reactivity of alkyl-substituted aniline is different from that of aniline.[11] There should be some shift of the bipolaron band for the aniline/*o*-toluidine comonomer system if their reactivities were too different to form a copolymer. Because the shift of the bipolaron band was not observed during the reaction process, the formation of the copolymer rather than a mixture of the corresponding homopolymers was confirmed.

Although different reactivities of aniline and *o*-toluidine in aqueous media have been investigated via electrochemical process, to gain further insights into the reactivities of aniline and *o*-toluidine in the above-mentioned organic media, the course of oxidation of aniline, *o*-toluidine, and aniline/*o*-toluidine comonomer was followed by monitoring the absorbance at 800 nm because the amount of polymer formed is proportional to the absorbance due to the bipolaron band (Figure 2). It can be seen that the initial rate of polymerization of aniline is much faster than that of *o*-toluidine, and this can be interpreted in terms of steric hindrance provided by the methyl group in the formation of the dimeric species.[8b] As suggested by Wei et al.,[12] the initial formation of the aniline dimers is slow in comparison with the succeeding growth of the polymer chains via an electrophilic substitution reaction, and both *p*-aminodiphenylamine type and benzidine type of dimers will contribute to the growth of the polymer chains. Soon after formation, the two dimers will be oxidized to their diimine forms that could be deprotonated to afford nitrenium ions.[13] Apparently, the formation of 2,2′-ditolylhydrazine (**2a**) from *o*-toluidine monomers is less favorable than that of diphenylhydrazine (**1a**) from aniline monomers because of the steric hindrance of the methyl substituent groups. This would result in fewer
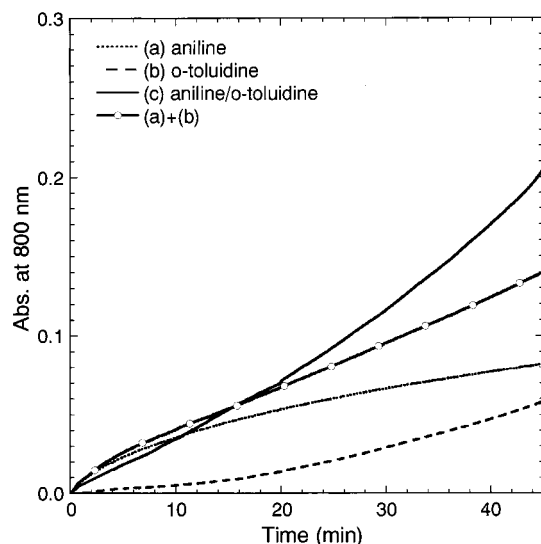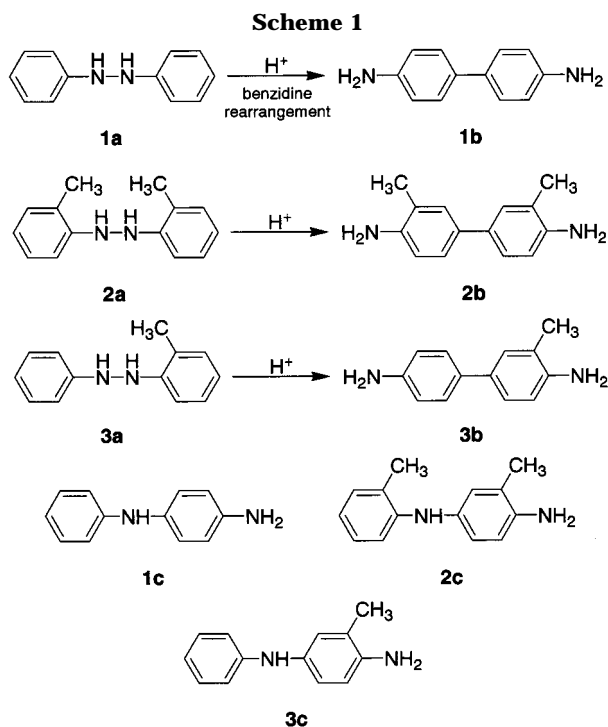
Figure 2. Changes in absorbance at 800 nm after mixing aniline and *o*-toluidine solutions with DDQ solution in cosolvent of chloroform−THF (3:1) (2 mL). (a) aniline/(+)-CSA, 0.05 M/0.1 M, 0.4 mL; DDQ, 2.0×10^{-3} M, 0.4 mL. (b) *o*-toluidine/(+)-CSA, 0.05 M/0.1 M, 0.4 mL; DDQ, 2.0×10^{-3} M, 0.4 mL. (c) aniline/(+)-CSA, 0.05 M/0.1 M, 0.4 mL; *o*-toluidine/(+)-CSA, 0.05 M/0.1 M, 0.4 mL; DDQ, 2.0×10^{-3} M, 0.4 mL.

Scheme 1

3,3′-dimethylbenzidine molecules (**2b**) generated from the benzidine rearrangement, as shown in Scheme 1. Since the polymer chain could grow on both the *p*-aminodiphenylamine type (**c**) and the benzidine type (**b**) of dimers, a lower rate of formation the benzidine-type dimers should lead to a lower initial rate of polymerization. Therefore, the initial rate of polymerization of *o*-toluidine is lower than that of aniline.

After the initial stage, the rate of polymer formation in the *o*-toluidine/(+)-CSA/DDQ system increased significantly in contrast to that in the aniline/(+)-CSA/DDQ system in which the rate of polymer formation slowed gradually. This is consistent with that *o*-toluidine should be more reactive than aniline due to the

electron-donating methyl group as indicated by its Hammett constant ($\sigma_1 = 0.04$). The rate of copolymerization of aniline with *o*-toluidine was found to be between those of homopolymerizations at the initial stage. The absorbance is even weaker than that in the aniline/(+)-CSA/DDQ system at the initial stage, again indicating that copolymerization occurred in the former system rather than homopolymerization of aniline. This is consistent with that the rate of formation 3-methylbenzidine (**3b**) should be between those of formation benzidine (**1b**) and 3,3′-dimethylbenzidine (**2b**) molecules. In addition, the absorbance observed in the aniline/*o*-toluidine/(+)-CSA/DDQ system increased almost linearly in the initial 40 min, in contrast to both the aniline and *o*-toluidine system.

Similar to the procedure demonstrated previously,[9] the as-synthesized polymer was also purified with fresh acetone to remove unreacted DDQ and monomers, reduced DDQ, oligomers of aniline and/or *o*-toluidine, and most of excess (+)-CSA. No band based on unreacted or reduced DDQ was found in its FTIR spectrum, indicating that the product was thoroughly purified with acetone. It was also supported by its UV/vis/near-IR spectrum. After purified with acetone, 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. In addition, no difference in its polaron band and bipolaron band was observed, indicating maintenance of its emeraldine salt state. The elemental analysis of the dried polymer powder showed that the molar ratio of the tetramer unit of emeraldine base and (+)-CSA is approximately 1:2. All these results confirm the formation of the polymer powder in the fully doped emeraldine salt state.

To establish that the resultant material is a genuine copolymer of aniline with *o*-toluidine rather than a mixture of homopolymers of aniline and *o*-toluidine, the product was further characterized by cyclic voltammetry (CV). The cyclic voltammograms of PANI and PMA prepared in the same organic media differ from each other in the redox potentials represented by values of $E_{1/2}$. These results are similar to the previous report on the PANIs chemically or electrochemically prepared in aqueous media.[11] The cyclic voltammogram of the copolymer consists of two redox processes at the $E_{1/2}$ of 0.34 and 0.96 V vs SCE, respectively (Figure 3). They are quite different from those of PANI at 0.22 and 0.83 V and of PMA at 0.32 and 0.67 V. Furthermore, only a single pair of peaks was observed for each redox process, instead of two pairs of peaks which would be expected for a mixture of the two homopolymers. This strongly suggests that oxidation of aniline/*o*-toluidine comonomer by DDQ in organic media generates the expected copolymer rather than the mixture of the corresponding homopolymers.

The copolymer is soluble in several polar solvents, such as *m*-cresol, DMSO, *N*-methyl-2-pyrrolidinone (NMP), and *N,N*-dimethylformamide (DMF), retaining its "compact-coil" conformation except for some shifts in the position of the bipolaron band according to the nature of the organic solvents (Figure 4a). A similar phenomenon was also observed for poly(*o*-anisidine)[14] and poly(*o*-ethoxyaniline).[9b] Different from analogously synthesized PANI/(+)-CSA, which exhibits a free-carrier tail character in the vis/near-IR region of electronic spectrum when dissolved in *m*-cresol, indicating a
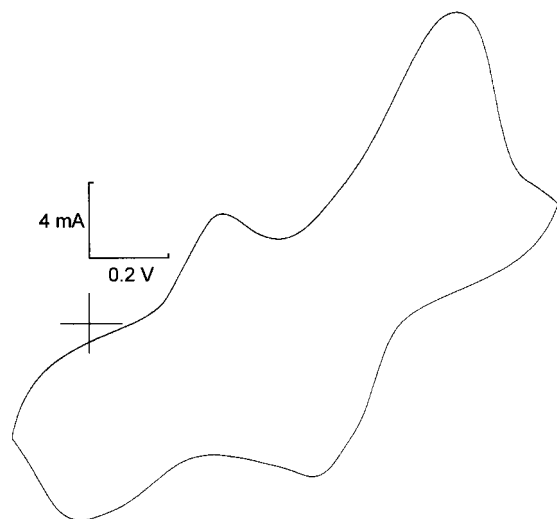
Figure 3. Cyclic voltammogram of a PANMA/(+)-CSA film (feed molar ratio, aniline/*o*-toluidine = 1:1). Conditions: 1.0 M (+)-CSA, Pt electrode, −0.2 to +1.2 V vs SCE, scan rate 30 mV/s, second cycle.

rearrangement from a "compact-coil" to an "extended-coil" conformation,[15] PANMA/(+)-CSA retains its "compact-coil" conformation although its bipolaron band is red-shifted compared with that of the solid film according to slightly expanded polymer chains in *m*-cresol solution. Owing to the presence of some methyl groups on the polymer backbones, their steric hindrance inhibits the interaction between amine of PANMA and hydroxyl of *m*-cresol to enable the PANMA/(+)-CSA backbones to keep the "compact-coil" conformation, which is similar to that of analogously synthesized PMA/(+)-CSA when dissolved in *m*-cresol.

Its CD spectra with two main peaks observed at 400 and 450 nm are exclusively attributed to chiral polymer chain because the incorporated chiral (+)-CSA⁻ anion does not show any Cotton effect at wavelengths longer than 300 nm. Therefore, these two characteristic CD bands have been used to confirm the chirality of the PANIs.[5f,6] It should be noticed that the chiroptical property of the resultant copolymer when dissolved in this series of organic solvents is quite different from that of the homopolymers when dissolved in these solvents. The CD spectra of analogously synthesized chiral PANI doped with (+)-CSA have a negative peak at 400 nm and a positive peak at 450 nm when dissolved in this series of organic solvents. However, the copolymer dissolved in DMF, NMP, DMSO, and *m*-cresol gave almost symmetric CD spectra compared with those of PANI/(+)-CSA, which are almost identical to those of PANI/(−)-CSA (Figure 4b, inset) except for the region around 300 nm in which the (+)- and (−)-CSA⁻ anions incorporated into the polymer show the Cotton effect, indicating that the (+)-CSA-doped PANMA and PANI have symmetric helical structures to each other (Figure 4b). These results are much interesting because the helical structure of PANI can be inverted by inserting *o*-toluidine units into the polymer main chain (Scheme 2). Moreover, PMA/(+)-CSA synthesized in a similar manner showed no detectable CD band in DMF and NMP because of their basic nature to dedope the polymer. It is undoubtedly that rapid rearrangement to an achiral conformation occurs in these solutions if emeraldine salt is absolutely deprotonated to give emeraldine base.[16] Its CD spectrum obtained in DMSO
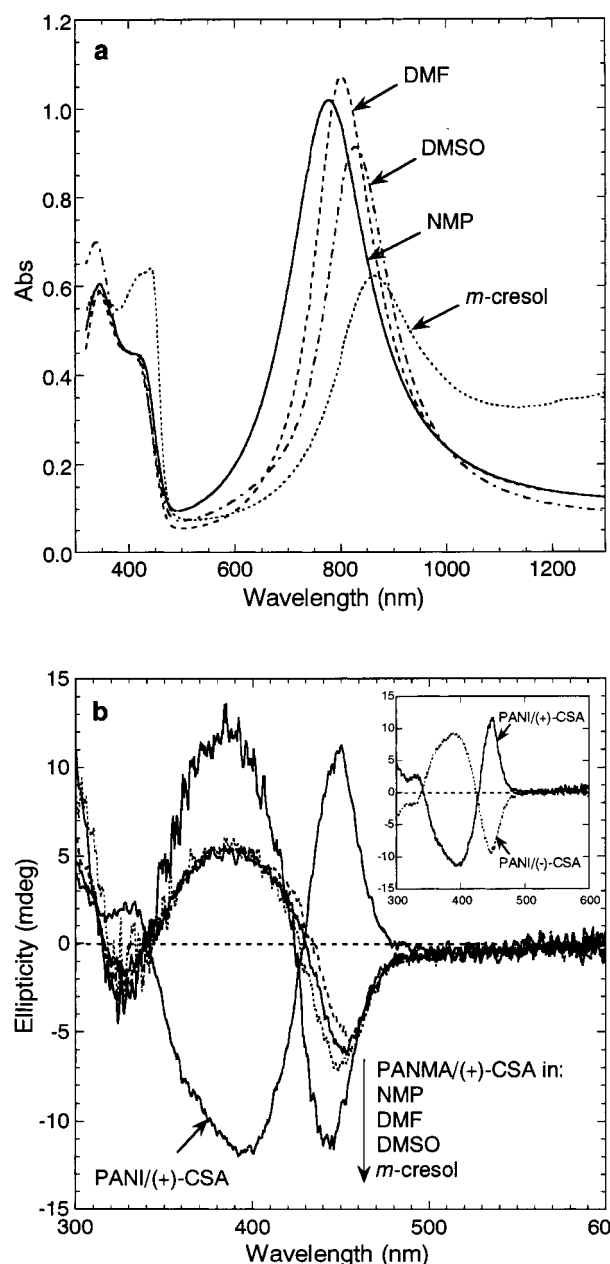

Figure 4. (a) UV/vis and (b) CD spectra of PANMA/(+)-CSA (feed molar ratio, aniline/*o*-toluidine = 1:1) dissolved in *m*-cresol, DMSO, DMF, and NMP combined with CD spectrum of PANI/(+)-CSA dissolved in *m*-cresol (or DMSO, or DMF, or NMP). Inset: mirror-imaged CD spectra of PANI/(+)- and (−)-CSA dissolved in *m*-cresol.

was also symmetrical to that of PANMA. These results resemble the observations described above, again confirming copolymerization of aniline with *o*-toluidine rather than homopolymerization.

A series of PANMAs were synthesized in a similar manner by changing feed comonomer composition, as summarized in Table 1. The composition of copolymers can be determined from the ratio of the peak area of the aromatic to the methyl protons. For all the copolymers, the *o*-toluidine unit content in the copolymer is higher than that in feed because of higher reactivity of *o*-toluidine than that of aniline after the initial stage (Figure 2). Their conductivities were controlled in a wide range by changing the feed comonomer composition. The more *o*-toluidine units in the copolymer, the more decrease in conductivities. This is consistent with that

Table 1. Copolymerization of Aniline (M$_1$) and *o*-Toluidine (M$_2$) in Organic Solvents^a

run	$[M_2]/([M_1] + [M_2])$ in feed (mol %)	yield (wt %)	$[M_2]/([M_1] + [M_2])^b$ in polymer (mol %)	conductivity (S/cm)	CD direction^c 400 nm	450 nm
1	20	48	30	58	−	+
2	41	59	54	2.7	−	+
3	50	62	62	1.7×10^{-1}	+	−
4	59	58	72	1.1×10^{-2}	+	−
5	67	59	81	1.0×10^{-2}	+	−
6	80	49	90	5.9×10^{-3}	+	−

^{a} Conditions: aniline and *o*-toluidine, 2.5 mmol; cosolvent, chloroform−THF (volume ratio, 3:1), 26.7 mL; DDQ, 2.5 mmol; (+)-CSA, 5.0 mmol; rt, 8 h. ^{b} Estimated by ^{1}H NMR in DMSO-d_6. ^{c} Recorded in *m*-cresol.

Scheme 2
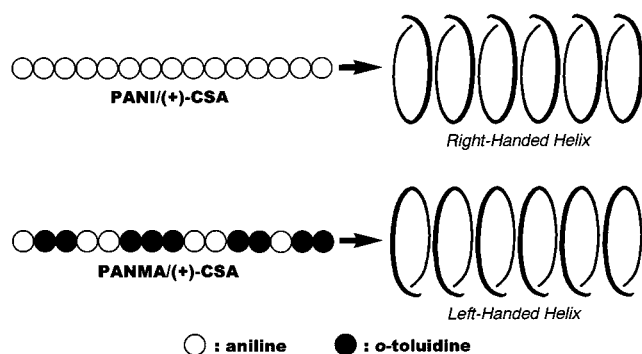
the steric hindrance of the methyl group could result in an increase of the torsional angle between adjacent phenyl rings and, therefore, in a decrease in the π-conjuation along the polymer backbone.[17]

Wallace and co-workers have shown that the presence of a methyl substituent ortho to the N centers obstructs the induction of optical activity in the PMA backbone via postprotonation with (+)-CSA in an organic solvent.[18] This obstruction was well diminished by synchronous induction of optical activity by (+)-CSA during polymerization of various aniline derivatives. The methyl groups have different steric hindrance and electronic property from those of H and subsequently affect electrostatic bonding of the (+)-CSA$^-$ sulfonate anions to the polyaniline −HN$^{•+}$− centers and hydrogen bonding of the (+)-CSA$^-$ carbonyl groups to the −NH− sites for maintaining a preferred one-sense helical screw. Therefore, it is supposed that the above-mentioned inversion of the helicity of the copolymer is presumably attributed to these methyl substituents. In the copolymer, there are two possible neighbors (H and Me) adjacent to the chiral (+)-CSA$^-$ anion instead of either H or Me in the homopolymers, and subsequent synergetic stereorelationships among them enable the formerly mentioned reversal in the chiral conformation in contrast to the corresponding homopolymers. Moreover, chirality of resultant copolymer is also dependent upon the *o*-toluidine unit content in the copolymer. At *o*-toluidine unit content higher than 62 mol % (runs 3−6), all the copolymers gave similar CD spectra that are inverted to those of analogously synthesized PANI/(+)-CSA. At *o*-toluidine unit content lower than 54 mol % (runs 1 and 2), they gave almost symmetric CD results to those of the others except for the region around 300 nm in which the combined (+)-CSA$^-$ anion shows the Cotton effect. Owing to the difficulty of completely dissolving copolyanilines in organic solvents, the concentrations, and therefore the CD intensities, vary from sample to sample, and we failed to normalize the ellipticity and subsequently to obtain the switch point of chirality. For further exploration in fundamental

understanding and in better control of the physical properties of PANI and its derivatives, copolymers of aniline with a variety of substituted anilines are under active investigation in our laboratory.

Conclusions

An optically active copolyaniline, poly(aniline-*co*-*o*-toluidine) (PANMA), was prepared in organic media for the first time with (1*S*)-(+)-10-camphorsulfonic acid as the chiral inductor. A helix inversion of PANMA polymer backbone in contrast to polyaniline was induced by inserting *o*-toluidine units, a well-known achiral monomer, into the polymer main chain. Different electrical conductivity and chirality were obtained for the copolyanilines by changing the feed comonomer composition that induced the different copolymer composition. These results are very interesting because they enable us to tailor-synthesize a material with specially desired electrical, electrochemical, and chiroptical properties and also with better solution processability. This also affords a proof of concept for extension of this approach to other optically active polymers.

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