

## Textile-Surface Interfacial Asymmetric Polymerization

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**ABSTRACT:** This research demonstrated that polymerization of aniline on cellulose produces chiroptically active composites. Polymerization of aniline in the presence of cotton fibers consisting of chiral cellulose are performed to prepare a polyaniline (PANI)/cotton composite. The polymerization is conducted at the cotton interface. The resultant PANI/cotton composite shows chiroptical activity elucidated with diffuse reflectance circular dichroism. In this reaction, textile-surface interfacial asymmetric polymerization is performed with imprinting of chiral structure from the cotton as a natural chiroptically active polymer to the PANI. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 41118.

**KEYWORDS:** chirality; conducting polymers; fibers; optical properties; textiles

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### INTRODUCTION

Asymmetric synthesis is one of the most important issues in chemistry. Amino acids, proteins, RNA, DNA, and sugars have molecular chirality. Consideration of molecular chirality of materials is needed for medical applications because affinity with biomaterials is required for performing desired chemical reaction in biosystems.

Synthesis and characterization of chiral polymers have been studied.<sup>1</sup> Chiral conjugated polymers can form main-chain helicity and chiral aggregation.<sup>2</sup> Synthetic methods for obtaining optically active chiral polymers have been developed, such as application of chiral catalysts in the polymerization process,<sup>3</sup> introduction of optically active substituent onto the polymer side-chains,<sup>4</sup> induction of helicity with terminal chiral residues,<sup>5</sup> static interaction with chiral compounds,<sup>6</sup> and treatment of polymers in chiral liquid crystal medium (reconstruction of chiral structure).<sup>7</sup> In particular, polymerization in chiral liquid crystals produces optically active polymers from achiral monomers. In this case, polymerizations are performed with transcription in helically aggregated chiral liquid crystal media.

Natural textiles consist of chiral biomaterials. Cellulose as a natural biopolymer having asymmetric structure forms aggregation in the formation of paper and cotton. In the present research, polymerizations of aniline at the surface of cotton are performed to conduct a chiral surface reaction on the natural chiral textile.

Polyaniline (PANI) is one of the most promising conducting polymers. Polymerization of aniline on carboxyl-group-modified fibers has been performed.<sup>8</sup> PANI-TiO<sub>2</sub> hybrid-coated cotton,<sup>9</sup> conductive latex/PANI,<sup>10</sup> and Ni nanostructures on PANI<sup>11</sup> were developed. Doping agents such as amphiphilic sulfonic acid dopant<sup>12</sup> and hydrofluoric acid have been applied to obtain new forms of PANI. PANI has been applied as a buffer layer in electrode devices, anticorrosion materials, and sensors.<sup>13</sup>

The application of textile technology to the production of conducting materials is expected to lessen the processing drawbacks.<sup>14,15</sup> Generally, synthesis of PANI is performed in water.<sup>16</sup> Cotton fibers possess good affinity with water, thus polymerization of aniline in the presence of dispersed cotton fiber in water is expected to form composites between cotton and PANI in polymerization.

In this study, we carried out polymerization of aniline in the presence of cotton fiber, and confirmed optical activity of the surface due to transcription of chirality from the cotton. Furthermore, molecular imprinting (MIP) at the molecular level may have occurred in the polymerization on the chiral textile surface. In this case, cellulose plays the role of a template. The PANI layer cannot be mechanically separated from the cellulose surface with the imprinted structure. Therefore, the PANI cannot be used as an imprinted cavity for applications. However, note that the PANI may imprint asymmetric structures from cellulose via the MIP process. This mechanism may add a new opportunity for MIP.

Additional Supporting Information may be found in the online version of this article.

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**Table I.** Polymerization of Aniline in the Presence of Cotton (Cellulose)<sup>a</sup>

Polymer	Aniline (g)	Cotton (g)	Aniline/cotton (feed%)	Y (Quantity) (g)	N/O <sup>b</sup>
PANI-C1	0.02	1	2	0.989	–
PANI-C2	0.05	1	5	0.883	0.03
PANI-C3	0.10	1	10	0.949	0.04
PANI-C4	0.25	1	25	0.954	0.09
PANI-C5	0.50	1	50	1.186	0.15
PANI-C6	1.00	1	100	1.288	0.30

<sup>a</sup>Water 250 mL, H<sub>2</sub>SO<sub>4</sub> 3 mL (H<sub>2</sub>SO<sub>4</sub> = 1.84 g/mL), APS = 1.01 g

<sup>b</sup>Nitrogen/oxygen ratio estimated by XPS.

## MATERIALS AND METHODS

### Materials

Sulfuric acid (Wako, Japan), ammonium persulfate (APS; Kanto Chemical, Japan), and nonfabric cotton (gossypium absorbents, Hakujiji, Japan) were used as received. Aniline (Wako, Japan) and water were purified prior to use.

### Polymerization

Synthetic process for PANI is environmentally friendly because the polymerization is generally performed in the water (nonorganic solvent). In this study, polymerization was performed in the presence of dispersed fiber cotton in water. First, aniline was dissolved in water, then sulfuric acid was added to produce aniline sulfuric salt. This is a necessary procedure before polymerization. The solution was cooled to 0°C, then APS was added for polymerization. Table I shows quantities of aniline as a monomer, sulfuric acid, cotton, and APS. The reaction for 24 h afforded PANI deposited on the cotton surface. We prepared six samples of the PANI composite. As-prepared composite was washed with a large volume of water, and subsequently with a large volume of methanol (ca. 200 mL). Filtration yielded bulk PANI/cotton composite. The composites thus prepared are abbreviated as PANI-C<sub>n</sub> (*n* = 1–6).

This is a suitable method for industrial applications because synthesis and purification processes of the composite can be performed in water. The reaction vessels were relatively clean after the reaction because most of the resultant PANI is deposited onto the textile.

Quantities of the compounds for polymerization in the presence of cotton and yield of the resultant composite are summarized in Table I. The aniline and cotton feed ratio can change the amount of resultant PANI layer. Figure S1 (Supporting Information) shows change in pH during the polymerization after addition of APS (0.2 g) to the solution containing cotton (1 g), aniline (0.1 g), and sulfuric acid (0.2 mL) to illustrate changes in pH during the polymerization. In this experiment, a small amount of sulfuric acid was added to show clearly the change in pH because an addition of 3 mL of sulfuric acid decreases pH value to <0.1. The pH value was decreased with the polymerization time. An inflection point was observed at 325 min. A pH minimum value was observed at 809 min, and the pH then gradually increased. This may be due to the polymerization of aniline in the presence of cotton being complete by 809 min,

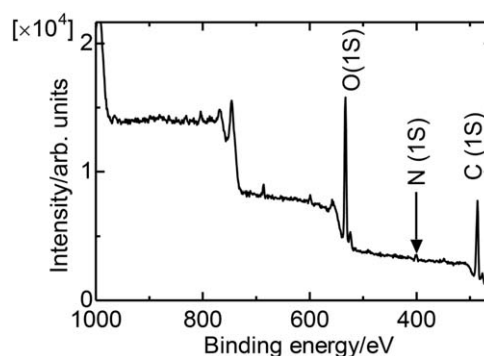
and the resultant PANI fractions on the cotton were gradually doped with residual acid.

### Instruments

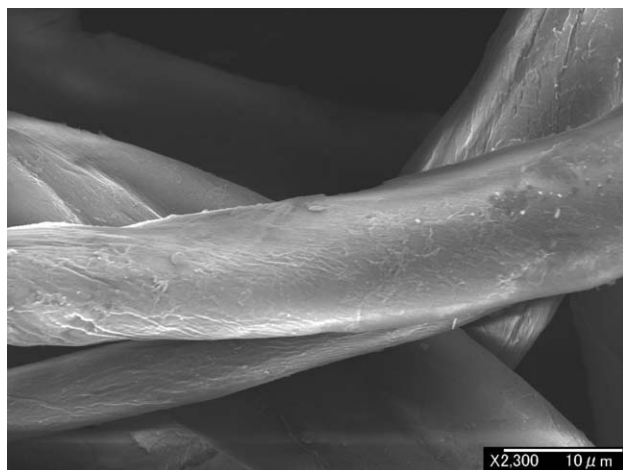
SEM observations were performed using a JSM-7000F (field emission scanning electron microscope, JEOL, Japan) and JSM-521 (JEOL). Diffuse reflectance circular dichroism (DRCD) spectroscopy measurements were performed using a J-720 spectrometer with a DRCD-466 unit (JASCO, Japan). An artifact detection/offset system was used for the measurements. IR spectroscopy measurements were conducted using a FT-IR 550 spectrometer (JASCO). XPS spectroscopy measurements were performed using a JPS-9010TR (JEOL).

## RESULTS AND DISCUSSION

Nitrogen-to-oxygen atom ratio in the PANI/cotton (cellulose) was evaluated using X-ray photoelectron spectroscopy (XPS). The spectral shape is shown in Figure 1. The nitrogen and oxygen signals come mainly from the aniline unit in the PANI and the oxygen in cellulose (Table I, N/O value). The PANI on the cotton is in a form of emeraldine salt (doped state) because the PANI was doped with APS and sulfuric acid during the polymerization. Therefore, the PANI in the composite contains additional oxygen and nitrogen atoms derived from APS and sulfuric acid. The XPS results involve composition of the dopants. Increase of aniline/cotton-feed ratio corresponds to increase of the N/O value. However, the N/O value is not proportional to the aniline/cotton-feed ratio in the polymerization. At the present stage, the N/O values obtained using XPS spectroscopy measurements can be an index of the composition.



**Figure 1.** XPS result for PANI-C3.

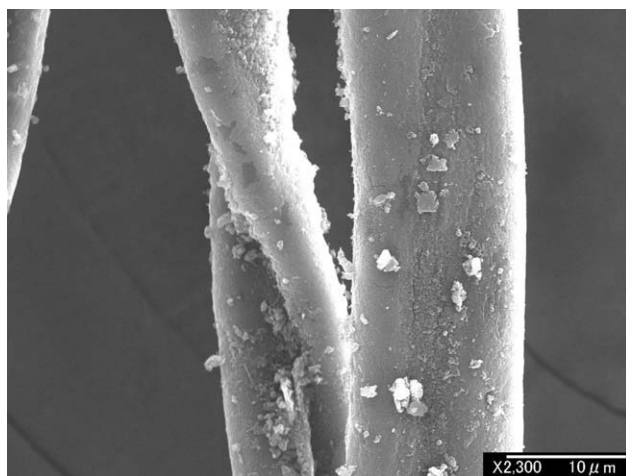


**Figure 2.** Field emission SEM image of the composite fiber surfaces of PANI-C1.

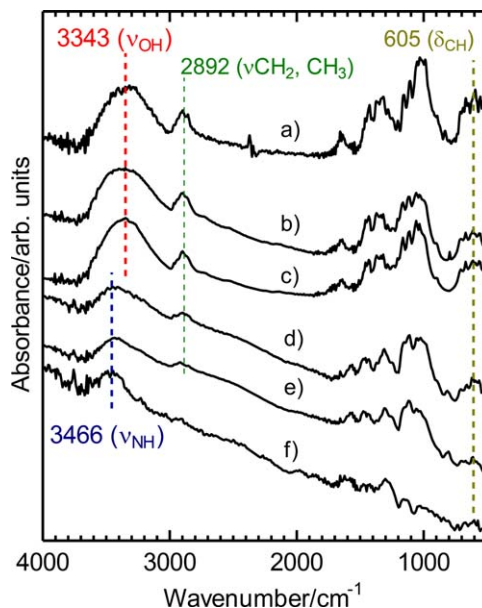
Scanning electron microscopy (SEM) images of the composite surface of PANI-C1, and PANI-C4 are displayed in Figures 2, 3 and Figures S2, S3 (Supporting Information). The smooth fiber surface is observable for PANI-C1 (Figure 2). Increase of composition of PANI in the composite results in a rough surface (Figures 3).

Infrared (IR) absorption spectroscopy measurements with the KBr method are shown in Figure 4. Increase of composition of PANI (increase of aniline/cotton-feed ratio in the polymerization) decreases absorption intensities at  $2892\text{ cm}^{-1}$  due to  $\text{CH}_2$  and  $\text{CH}_3$  stretching vibrations, and  $605\text{ cm}^{-1}$  due to  $\delta\text{CH}$ . The OH-stretching vibration at  $3343\text{ cm}^{-1}$  of the cotton is also decreased with increase of PANI. Conversely, NH stretching absorption intensities at  $3466\text{ cm}^{-1}$  are increased with increase of PANI covering the cotton fibers.

DRCD measurements for the PANI/cotton were performed. The insolubility and infusibility of the composite did not allow measuring the circular dichroism (CD) in solutions. Transmission CD absorption spectroscopy measurements cannot be con-



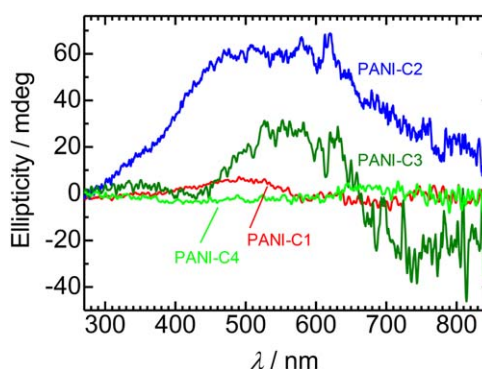
**Figure 3.** Field emission SEM image of the composite fiber surfaces of PANI-C4.



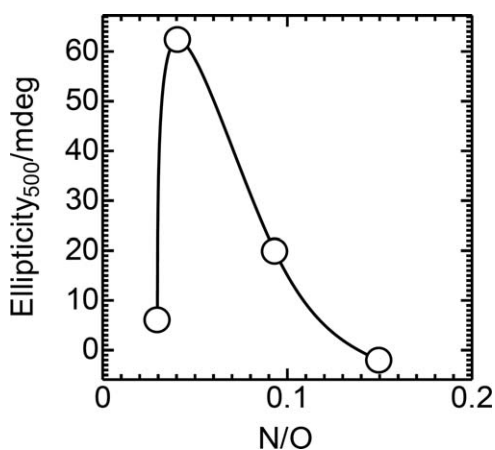
**Figure 4.** IR spectra of the PANI/cotton composite. (a) PANI-C1, (b) PANI-C2, (c) PANI-C3, (d) PANI-C4, (e) PANI-C5, and (f) PANI-C6. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

ducted because the textile composite sample is opaque. The CD intensity of the composites is increased with increase of the PANI deposition amount on the cotton in the first stage (Figure 5). The composite thus prepared shows CD signals in the visible region, indicating the main-chain on the cotton can form an asymmetric structure. Although static interaction between the OH moiety of the cellulose and the N-position of the PANI is weak, the chiral structure of the cellulose produces chiroptically active PANI at the interface of the cotton in the polymerization. Figure 6 summarizes the change in ellipticity at 500 nm as a function of the N/O ratio.

The CD intensities of the PANI/cotton first increased, and then decreased with PANI. A thin polymer layer can contact the surface of the chiral cotton during the polymerization; however, the thick layer could not contact the cotton surface, resulting in no transcription of chirality from the cotton surface. The chirality transcription was achieved for the thin PANI layer on the



**Figure 5.** Results of DRCD spectroscopy. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 6.** Ellipticity at 500 nm in the CD measurements as a function of N/O ratio (N = nitrogen atom, O = oxygen atom).

cotton interface. Linear dichroism (LD) of pure cotton and composites was checked with the LD measurements, as shown in Figure 7 (pure cotton, as an example).

The artifact detection/offset system was combined for the DRCD measurements. The LD elements from the composite are considered to be negligible. Microscopy DRCD measurements for the microsize textile surface is desirable for further investigation. At the present stage, DRCD is valid to confirm chiroptical activity of the composite. Note that pure cotton shows no CD in the visible range because it lacks a chromophore (cotton shows optical activity in the UV range), indicating the composite possesses chiroptical activity provided by the surface transcription from natural cotton.

Figure 8 shows a plausible structure of the PANI/cotton composite. Capillary effect allows efficient absorption of monomer (aniline sulfonic salt) and the APS in the water into the cellulose fiber. Oxidative polymerization affords chirality transcription from the cellulose to the PANI at the interface. As the polymerization progress, additional PANI layers grow epitaxially on the optically active PANI layer, resulting in formation of nonchiroptically active PANI on the chiroptically active PANI layers. Beyond a certain thickness of the PANI contacted with the cotton surface there is no further chiroptical structure. Therefore, only thin PANI layers deposited on the cotton surface show chiroptical activity. Polymerization also progresses toward the inside of the cotton fiber. However, DRCD spectroscopy only detects reflection signals from the surface.

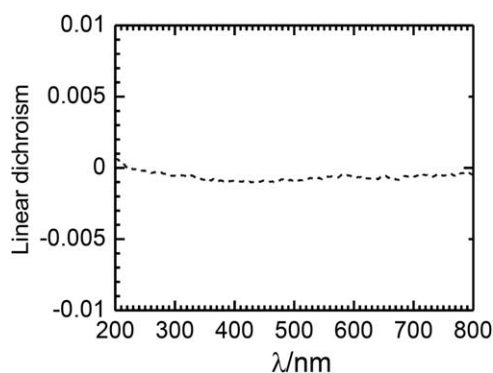
The liquid crystal solvent asymmetric polymerization<sup>17</sup> and asymmetric electrochemical polymerization<sup>18</sup> developed by the author (H.G.) produces chiroptically active polymers from optically inactive monomers. Polymerizations are enhanced in chiral cholesteric liquid crystals to form chiroptical active polymers. The polymers thus obtained show structural chirality because they lack a chiral center in the primary structure. Interfacial chiral conversion of optically inactive polyphenylenevinylene (PPV) precursor at the interface of cholesteric liquid crystals results in production of chiral PPV.<sup>19</sup> Dissolution of optically inactive polymers forms helical structure in optically active limonene as a solvent, demonstrating noncovalent molecular

chirality transfer leading to chiroptical activity in achiral polymers.<sup>20</sup>

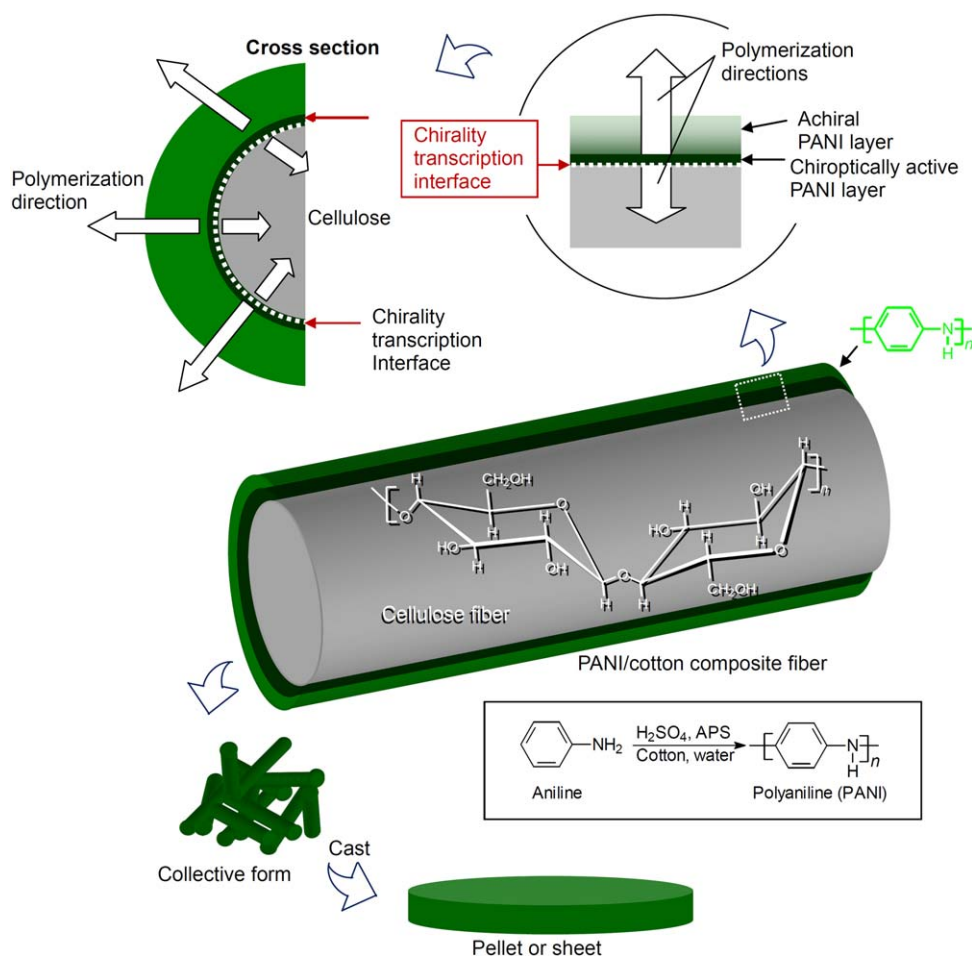
In this study, the polymerization at the cotton textile interface affords chiroptically active PANI via chirality transfer from cellulose to the resultant in the polymerization process.

Cellulose fiber consists of optically active glucose units. The neighboring units form chiral aggregation with fiber structure via hydrogen bonding. Cellulose main chains twist around a central axis in the one-handed helical manner. The PANI grows along the helical structure of cellulose as a helical guide creating a cellulose composite. So, both structural imprinting of secondary structure (main-chain chiroptical structure of cellulose) and tertiary structure (3D helical structure of cellulose) occur in the interfacial polymerization. Also, MIP from the cellulose may occur as well (primary structure imprinting).<sup>21,22</sup> Concentration of monomer, sulfuric acid, and APS in the polymerization reaction change thickness of the optically active layer. Furthermore, diameter, length, surface area, stiffness, and adsorption property of the cellulose fiber as a chiral substrate change the resultant PANI layer thickness. At the present stage, the effective thickness of PANI layer required to show chiroptical activity cannot be estimated. Furthermore, precise control of the optically active layer thickness of PANI on the cotton has not been achieved. However, our results indicate occurrence of chiral transcription from natural chiral polymer (cotton cellulose) to the synthetic polymer at the interface. Polymerizations of aniline in the presence of acrylic fiber (synthetic fiber) were performed. However, the composite thus obtained shows no chiroptical activity. This indicates that interfacial polymerization of aniline on the synthetic textiles produces no optical activities because acrylic fiber has no optical activity.

Individual cotton fiber is composed of concentric structures. The fibers consist of primary cell wall, cuticle area, secondary cell wall, and lumen area.<sup>23</sup> Polymerization occurs at the primary cell wall, cuticle area, and secondary cell wall. Furthermore, cotton cell-hairs and spiral structures were observed on the surface of the primary cell wall.<sup>24</sup> Such morphologies may produce chiral  $\pi$ -stacking or macromolecular spiral structure of the resultant PANI layer on the cotton during transcription. Also, cotton contains small amounts of pectin and fats. Therefore,



**Figure 7.** Linear dichroism (LD) of a pure cotton. LD =  $OD_{//} - OD_{\perp}$ , OD = optical density.



**Figure 8.** Plausible structure and polymerization mechanism on the cotton fiber for obtaining chiroptical activity by the textile-surface interfacial asymmetric polymerization. APS = ammonium persulfate. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

morphologies, structure, and components of cotton substrate affect chirality of the resultant PANI in the composite.

The PANI/cotton composite is stable in the ambient air. Moisture sorption<sup>25</sup> of cotton in the composite can be suppressed by the PANI surface layer. The PANI/cotton can be woven to prepare conducting thread for applications. All fibers have similar coating with PANI after reaction because this reaction proceeded homogeneously on the cotton fibers.

3D composite textile structure can be prepared by polymerization of aniline in the presence of yarn, woven, and knitted products. For example, polymerization on knitted materials yields electrically conducting textile products.

In addition, pulp may be used as a cellulose in place of cotton. The chiral transcription from pulp to aniline during polymerization reaction in the water may well produce a chiral composite.

## CONCLUSIONS

We conducted interfacial polymerization of aniline as a monomer at the natural cotton fiber surface to obtain chiroptical PANI/cotton (cellulose) composites. The major finding of this report is the transcription of chirality from natural chiral

textiles to resultant PANI layers of the composite. Thin layers of PANI on the textile reveal chiroptical activity, while thick PANI on the textile has no chiroptical activity, indicating chiral transcription from the textile to the resultant PANI occurs on the textile surface. The chiroptical activity of the PANI is mainly derived from mechanical transcription of the structural chirality of cellulose. This method allows production of synthetic chiral polymers using natural chiral textiles, a significant innovation.

Furthermore, treatment of cellulose with nitroxy radical creates transparent nanocellulose.<sup>26,27</sup> PANI/cellulose composite using nanocellulose may improve light transparency by suppression of diffuse reflection. A transparent circularly polarized light filter can be prepared with composites consisting of transparent nanocellulose and PANI. Recently, cotton textiles have been applied for organic electronics, such as organic transistors,<sup>28</sup> and organic light-emitting devices.<sup>29</sup> Electro-optically active sheets prepared from PANI/cotton may be applied in organic optoelectronics.

Although further evaluation of the relation between cotton structure and optical activities of resultant composite is required, the mechanism of the interfacial asymmetric polymerization at the cotton interface might be related with enzymatic reactions in biological systems.

## ACKNOWLEDGMENTS

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