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Synthesis of Magneto-Optically Active Polyanilines

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Abstract

We report preparation of polyaniline (PANI) with radicals on the *N*-positions. Chirality of a PANI having optically active substituent is retained even upon oxidation by *m*-chloroperoxybenzoic acid in chloroform to generate spin species. Electron spin resonance and circular dichroism spectroscopy measurements suggest that the chiral paramagnetic properties of PANIs are derived from the combination of chiral side chains and oxy-radicals in the structure of the polymer. This report focuses on a new synthetic approach for obtaining magneto-optically active polyanilines.

Keywords: circular dichroism, paramagnetism, polyaniline

1. Introduction

Synthesis and application of electrically conducting polymers is a basis for “plastic” electronic devices such as photovoltaics [1], organic transistors [2,3], and batteries [4–6]. The conducting polymers consist of a π -conjugated sequence main chain. Recently, interest in the chemistry and physics of π -conjugate polymers has extended from electro-conductivity to chirality and magnetism.

Organic magnetic materials based on π -conjugated skeletons have been reported [7–9]. Synthesis of π -conjugated polymers with high spins has been achieved [10]. Furthermore, non-conjugated polymers bearing radical groups have been successfully prepared as electrodes for polymer batteries [11], and novel photovoltaic cells have been developed [12].

Many helical conjugated polymers have been successfully prepared by introducing optically active side-chains [13–15]. Optically active polyaniline (PANI) as a π -conjugated polymer can be prepared in the presence of optically active camphor sulfonic acid in a polymerization reaction [16]. Optically active camphor sulfonic (CSA) acid is electrostatically introduced onto the positions of the nitrogen atoms of PANI, inducing predominantly one-handed helicity [17]. Alternatively, introduction of an optically active substituent into polyaniline via covalent bonding for obtaining

helical PANI is possible [18]. However, these studies have not focused on optical activity and magnetism of the main chains.

Multiple functionalities, such as magnetism and chirality, can be achieved through the introduction of both a radical moiety and an optically active compound into π -conjugated polymers.

In a previous study, optically active polythiophene derivatives were synthesized with a new asymmetric polymerization method using a cholesteric liquid crystal (CLC) medium derived from achiral monomers [19]. Although the polymers synthesized in the CLC do not bear asymmetric carbon atoms, the polymers display consistent chirality due to the formation of chiral aggregates under the influence of the CLC medium. The chirality is maintained by the molecular construction of the chiral aggregate.

In the present study, we prepared chiroptically active PANI with electrochemical polymerization and chemical polymerization. The PANI prepared with electrochemical polymerization is carried out in the presence of an excess amount of optically active CSA. The PANI thus prepared has CSA in the substituent via static interaction. Subsequent reduction releases CSA from PANI, and oxidation yields radicals at the *N*-position of PANI. In the next approach, PANI having both an optically active substituent and oxy-radicals is prepared for obtaining magneto-optically active π -conjugated polymers. Electron magnetic resonance (ESR) and circular dichroism (CD) are used to evaluate functionality of the polymer in this study. Note that oxidation of PANI with *m*-chloroperoxybenzoic is based on the oxidation reaction of diphenylamine (Scheme 1) [20].

2. Experimental

2.1. Instruments

Optical absorption spectra were obtained at room temperature using a HITACH U-3500 spectrometer with a quartz cell. CD spectra were obtained using a JASCO J-720 spectrometer. ESR measurements were carried out using a JEOL JES TE-200 spectrometer with 100 kHz modulation. Spin concentrations of the samples were obtained with $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ as a standard.

2.2. Chemicals

Aniline (Wako Chemical, Japan) was purified by distillation. High-purity chloroform (Wako) was used without purification for optical measurements of the polymer. (+)-(*S*)-camphorsulfonic acid ((+)-CSA, Kanto Chemical, Japan), *m*-chloroperoxybenzoic acid (Wako Chemical), hydrazine (Tokyo Chemicals, TCI)

were used as received.

Synthesis of PANI with no optical activity and generation of radicals

Chiroptically active polyaniline was prepared by the previously reported method [17,18]. Quantity used: aniline (1.0 g, 10 mmol), HCl (1.0 g, 27 mmol), water (25 mL), ammonium persulfate (APS, 1.0 g, 3.5 mmol) in 5 mL of distilled water. After the polymerization, the resultant polymer was treated with ammonia (28 % solution, 20 mL), and hydrazine monohydrate (20 mL). Next, *m*-chloroperoxybenzoic (1.85 g, 10 mmol) was added to the reduced PANI in chloroform solution. After 1 h, the solution was filtered off, and the product was dried in vacuum to afford 0.11 g of polyradicals. This polymer is abbreviated as NA-PANI-oxyl (NA = not optically active).

2.3. *Electrochemical polymerization of aniline in the presence of optically active camphor sulfonic acid and generation of radicals*

Polyanilines deposited on ITO were prepared by the previously reported method (as-prepared polyaniline is abbreviated as PANI-S). PANI-S was treated with hydrazine to yield a reduced form of polyaniline (abbreviated as PANI-RE). The synthetic routes are described in Scheme 2. Next, the PANI-RE prepared by electrochemical polymerization was treated with *m*-chloroperoxybenzoic acid in chloroform solution to generate oxyradicals at the *N*-position. The polyaniline thus obtained is abbreviated as PANI-oxyl.

Scheme 2.

2.4. *Synthesis of PANI with optically active substituents and generation of radicals*

PANI with optically active substituents (C-PANI, Scheme 3) was prepared by the previously reported method [18]. Subsequently, *m*-chloroperoxybenzoic acid (10 mg, 0.05 mmol) was added to the PANI with optically active substituents in 1 mL of chloroform solution. After stirring for 1 h, the solution was poured into a large volume of methanol, filtered, and dried in vacuum to yield optically active polyradicals (abbreviated as C-PANI-oxyl).

Scheme 3.

3. Results and Discussion

3.1. ESR

ESR measurements of NA-PANI-oxyl were carried out at room temperature. A *g*-value of 2.00459 was observed. Relaxation of the ESR signals of the PANI-oxyl

resulted in one broad signal due to the radicals. The unimodal signals ($\Delta H_{pp} = 0.68$ mT, spin concentration = 8.27×10^{18} spin/g) is suggestive of a locally high-spin concentration within the molecules [17]. This result indicates oxidation of PANI with *m*-chloroperoxybenzoic acid produces polyradicals specifically, according to the method reported for preparation of diaryl nitroxides [20].

Fig. 1 shows ESR spectra of PANI-S (prepared with electrochemical polymerization) and PANI-oxyl. PANI-S, as prepared, displays a *g*-value of the center signal of 2.00217 (2.7×10^{18} spins/g) with asymmetric Dysonian line-shape. Radicals of the PANI-ES are derived from radical cations (polarons, conduction species) on the main chain generated by the doping. This is due to the fact that, as prepared, PANI is doped with the APS and CSA during the polymerization reaction. The Dysonian line-shape of the PANI-S comes from the conduction species. In this case, microwave signals can not intrude inside of the sample, resulting in an asymmetric pattern. On the other hand, PANI-oxyl shows a broad signal ($g = 2.00378$, spin concentration is 4.7×10^{18} spin/g). Changes in *g*-value, line shape, and spin concentration suggest that the spin species of PANI-oxyl (oxy-radicals) is different from that of PANI-S (polarons). However, surface treatment of hydrazine followed by treatment of *m*-chloroperoxybenzoic acid for the polymer does not affect the interior of the film on ITO glass. Therefore, the PANI-oxyl may have both oxy-radicals and polarons.

C-PANI-oxyl having chiral substituents shows triple signals with a *g*-value of the center signal at 2.00516 ($\Delta H_{pp1} = 0.49$ mT, $\Delta H_{pp2} = 0.48$ mT, spin concentration = 7.69×10^{17} spin/g) in the ESR measurements, as shown in Fig. 2. The spectrum form of the triple signal confirms generation of nitroxyl radicals of the PANI [21,22]. The spin concentration is somewhat low because treatment of the polyaniline after oxidation in air decreases spins at the main chains, while radicals were specifically produced at the *N*-position of the polyanilines. The *g*-values of the C-PANI-oxyl ($g = 2.00516$) in bulk indicates that the ESR signal of the C-PANI-oxyl is not derived from the charged species on the main chain.

Fig. 1.

Fig. 2.

3.2. Optical measurements

PANI-S shows an absorption maximum at 416 nm in UV-vis absorption spectrum. Broad absorption at long wavelengths of the doping band (polarons) was observed. PANI-RE displays an absorption band at around 600 nm (shoulder) [23]. No intense

absorption at long wavelengths is observed. PANI-oxyl shows broad-band absorption centered around 430 nm. This absorption may be due to the oxy-radicals. The PANI-S is dark green, but the color is turned to gray with treatment of hydrazine, and to brown by the oxidation.

Fig. 3 displays CD spectra of PANI-S, PANI-RE. PANI-S exhibits a sharp negative signal at 468 nm, and a broad positive signal at long wavelengths. PANI-RE shows a positive signal at 346 nm, a weak negative signal at 478 nm, and a broad negative signal at long wavelengths. Intensity of the CD signals after reduction is weakened. This can be due to the reduction process removing the CSA from the main chain, with helicity of the main chain depressed. PANI-oxyl shows no Cotton effect in the CD, resulting in no maintenance of helical structure after oxidation.

Fig. 3.

On the other hand, for C-PANI-oxyl a positive signal at 441 nm and a negative signal at 654 nm are observed in the CD (Fig. 4). The Cotton effect indicates that the chirality of the polymers was maintained upon oxidation with *m*-chloroperoxybenzoic acid and that the polymers are inherently chiral. The results from the ESR and the CD suggest that the C-PANI-oxyl shows chiral paramagnetic properties, which derive from a combination of chirality and paramagnetism. The sign of the Cotton effect of the C-PANI-oxyl changes from positive to negative at around 590 nm. The peak (shoulder) of the absorption spectrum is located at the inflection point observable in the CD. The ESR, the CD and the optical absorption spectroscopy results suggest that the nitroxyl radicals of C-PANI-oxyl are arranged in helical manner accompanied by the helical structure of the main chain.

Fig. 4.

4. Plausible structure

Fig. 5 shows a plausible structure of PANI bearing chiral substituents. Chiral side chains induce main-chain helical structure of the PANI. Each nitroxyl radical (spin), as a diphenyl nitroxyl radical unit, distributes along the main chain. The spins of the polymer exist along the helical structure of the main chain. As a consequence, the polymer shows macroscopic paramagnetism.

5. Conclusions

We attempted synthesis of magneto-optically active polyanilines via a newly proposed method. The polymer displays Cotton effect in the CD measurements. The

ESR and the CD results indicate that the radicals of C-PANI-oxyl can be arranged in a helical manner.

The polymer thus synthesized in this study is magneto-optically active, although chiroptical activity is weak in the present stage. However, this can be the first example of helical polyaniline-bearing radicals. An introduction of chiral compounds having several stereogenic centers (i.e., natural optically active compounds) should enhance the helicity of the PANI. The present preparation method for generation of nitroxyl radicals from chiroptically active PANIs is a new approach for the synthesis of chiral organic polymers with magnetic properties.

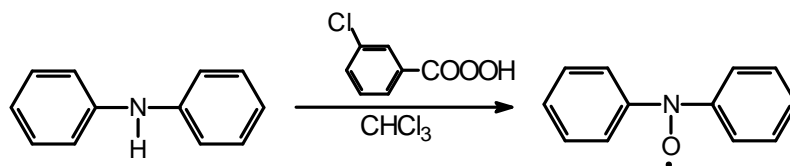
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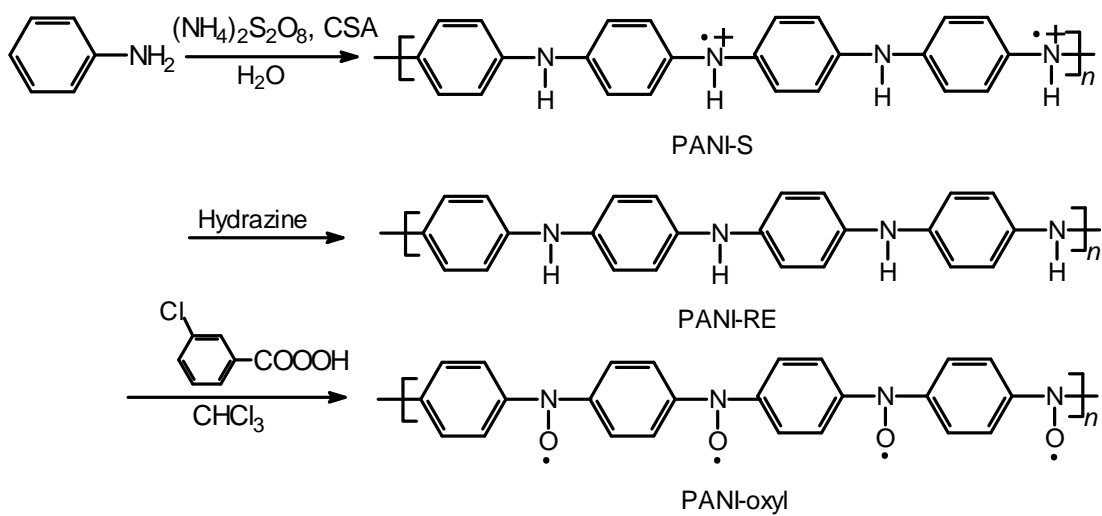
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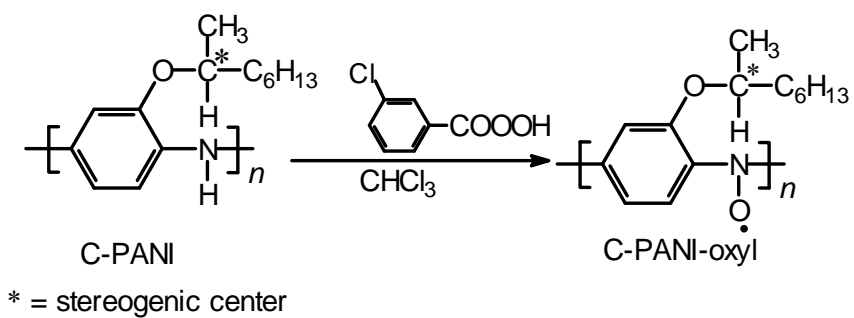
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21. Charge carriers such as polarons (radical cations distributed on the main chain) show no triple signals in the ESR.
22. All of the N-H in the PANI might not be inverted into nitroxyl radicals with the oxidation because of the polymer reaction.
23. The polymer films on ITO are fragile. Therefore, the oxidation process requires careful treatment in order to obtain optical spectra.



Scheme 1. Generation of nitroso radical from diphenylamine



Scheme 2. Oxidation of polyaniline and chiral polyaniline to generate radicals. CSA = (+)-(*S*)-camphorsulfonic acid.



Scheme 3. Oxidation of chiral a PANI to generate radicals.

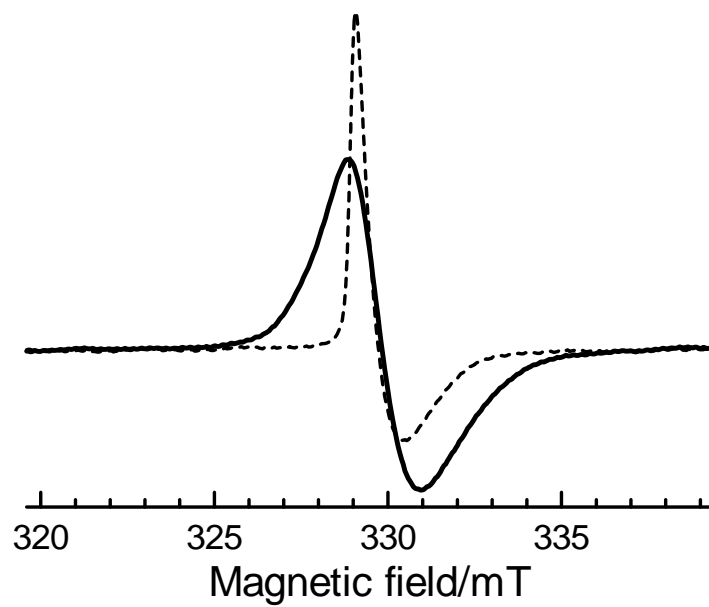


Figure 1. ESR spectra of PANI-S (dashed line) and PANI-oxyl (solid line).

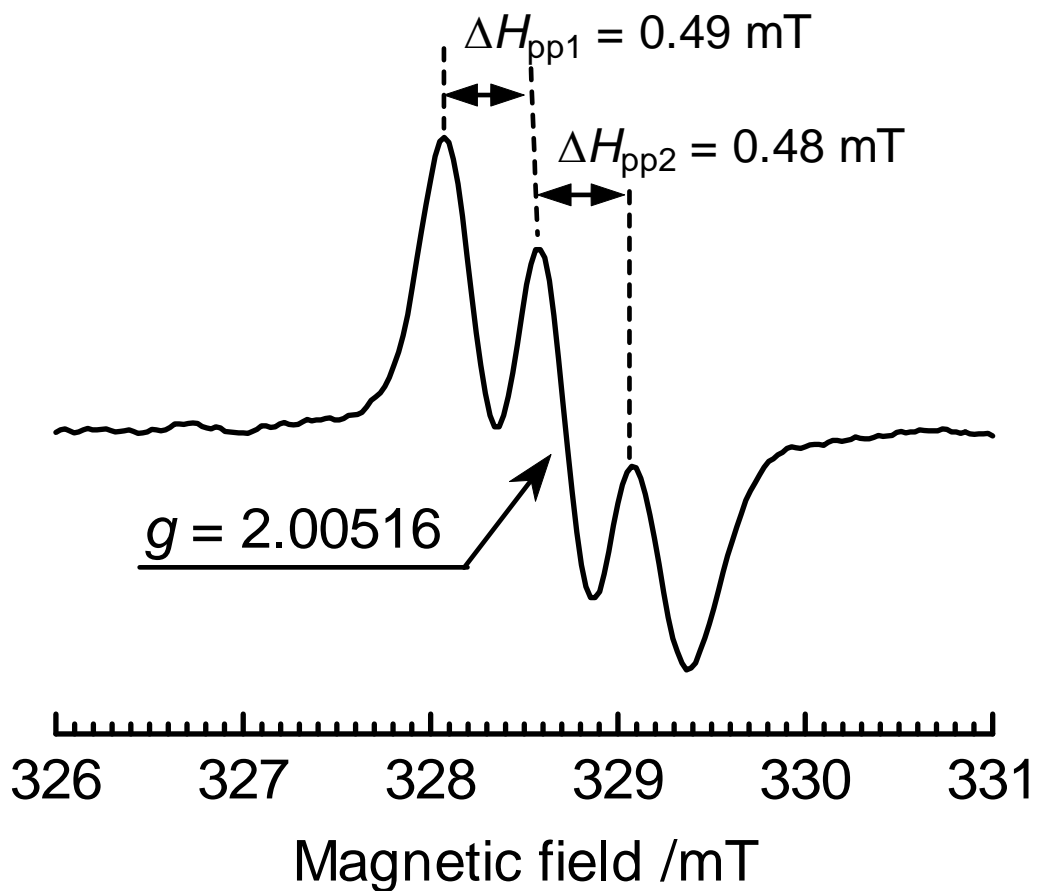


Figure 2. ESR spectrum of C-PANI-oxyl in chloroform.

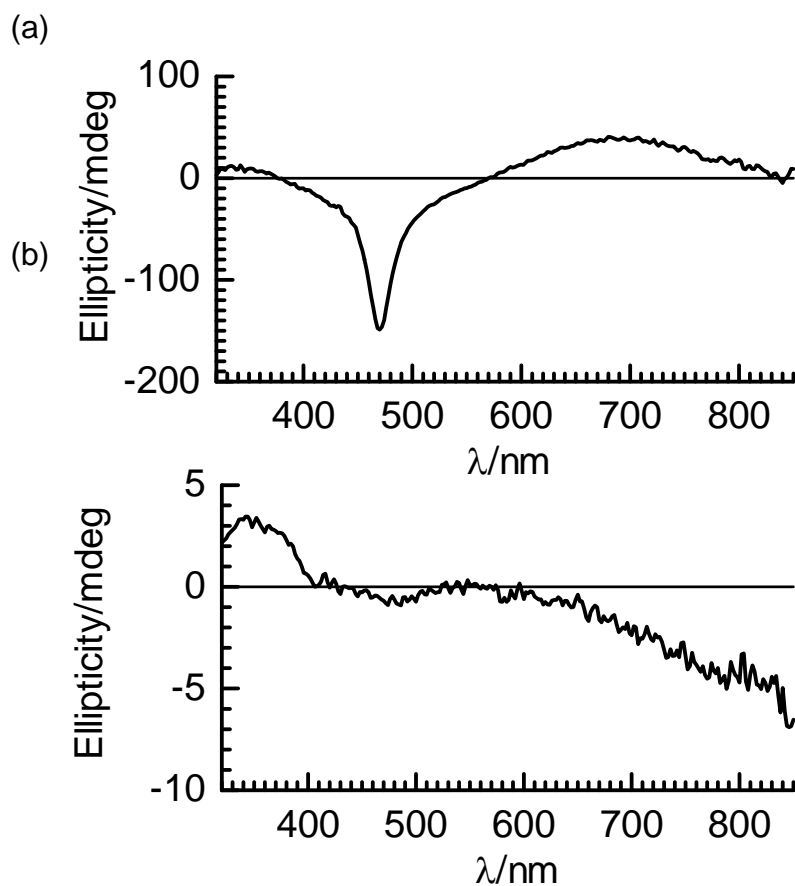


Figure 3. CD spectra of PANI-S prepared with the electrochemical polymerization method (a) and PANI-RE (b). The spectra are obtained from polymer films on indium-tin-oxide (ITO) glass electrodes.

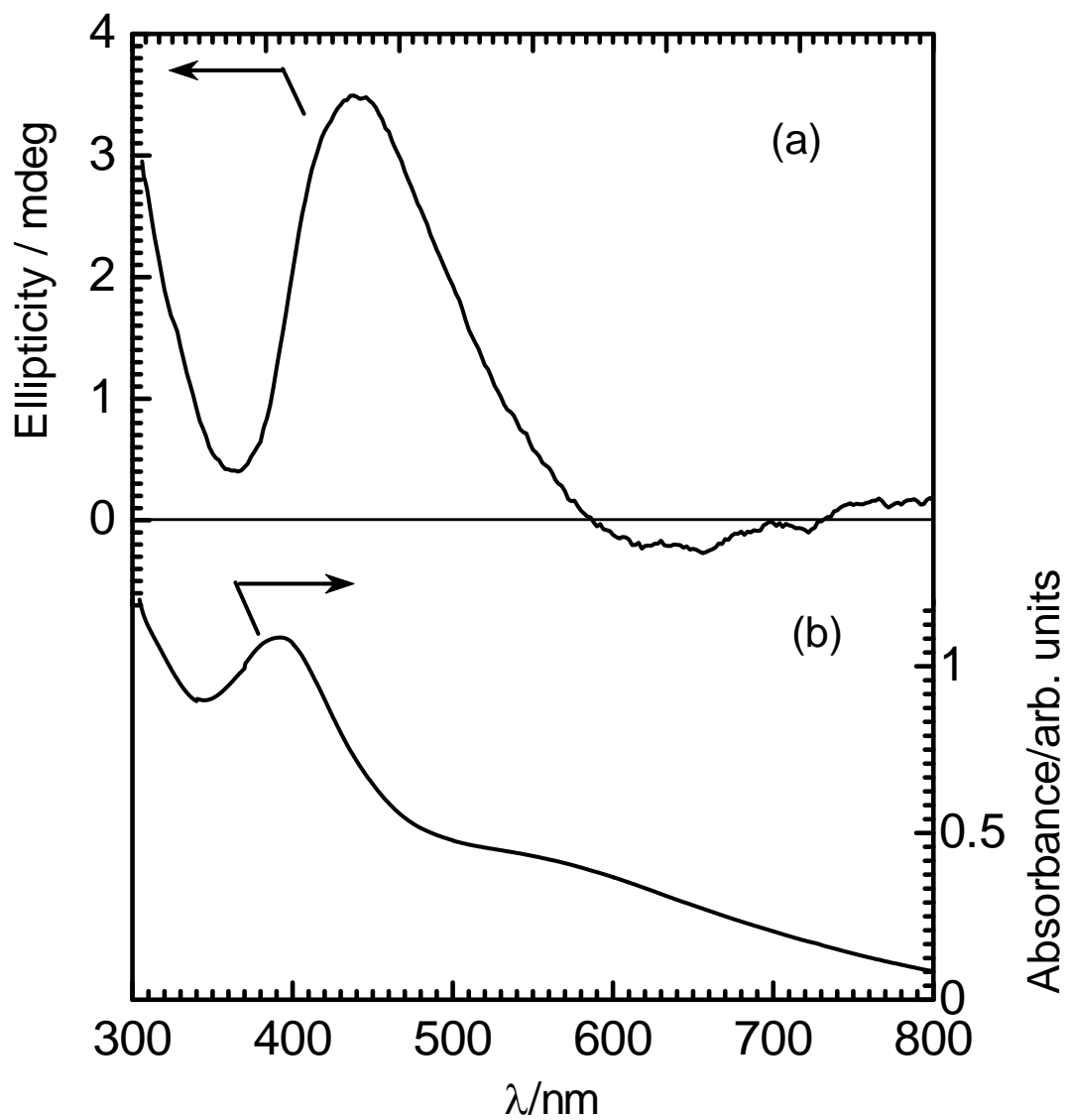


Figure 4. (a) CD spectrum of C-PANI-oxy in chloroform solution. (b) UV-Vis absorption spectrum of C-PANI-oxy in chloroform solution.

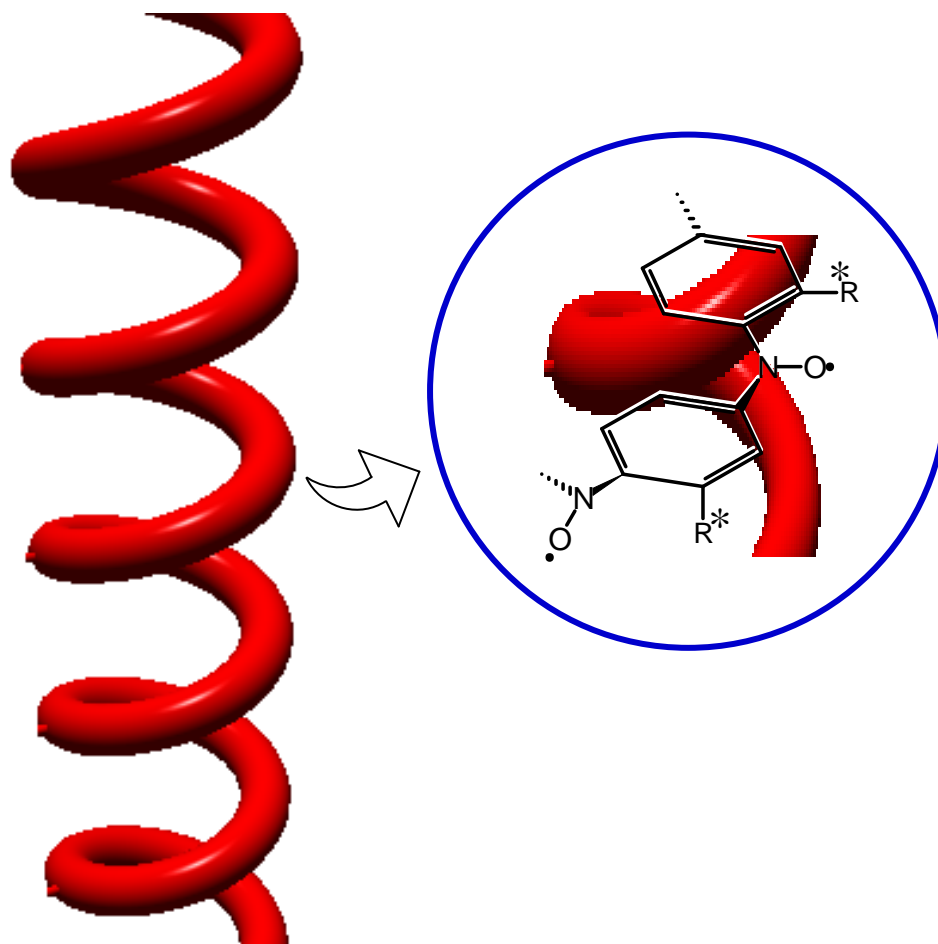


Figure 5. Plausible structure of helical polyaniline with paramagnetism. R^* = chiral substituents.