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Electrochemical polymerization of helical poly(2-methoxyaniline) doped with β-cyclodextrin sulfate: pH driving the opposition of induced circular dichroism

Guo-Li Yuan[a] (✉), Fang Zou[b], Sheng Yin[b], Noriyuki Kuramoto[c] (✉)

[a] School of the Geosciences and Resources, China University of Geosciences, Beijing, 100083 China
[b] College of Chemistry and Chemical Engineering, Jiangsu University, Zhenjiang, Jiangsu 212013 China
[c] 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
E-mail: yuanguoli@hotmail.com; Fax: +86-10-62559368 (G-L Yuan)
E-mail: kuramoto@dip.yz.yamagata-u.ac.jp; Fax: +81-238-26-3051 (N. Kuramoto)

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Summary

Optically active poly(2-methoxyaniline) (PMOA) was synthesized by electrochemical polymerization of 2-methoxyaniline in the presence of β-cyclodextrin sulfate (CDS). The synthesized PMOA films were characterized by induced circular dichroism (ICD) and UV-vis spectra. PMOA films showed a mirror-imaged ICD spectrum while they were respectively prepared at pH 3 and lower pH values, which suggested that opposite one-perfected helical handedness was induced into PMOA. Nevertheless, post-treatments, such as dedoping, redoping and thermo-treating, seemed no influence on helical handedness of PMOA.

Introduction

Synthesis of helical or optically active macromolecules has received considerable interest in the field of polymer and supramolecular chemistry due to their possible application and academic significance [1-3]. More recently, lots of reports have been focused on inducing helical structure into achiral polymers [4-6]. That is, the helical architecture is induced into the backbone of polymers through non-covalent interaction with other chiral molecules rather than the natural arrangement in the polymer backbone.

Poly(2-methoxyaniline) (PMOA), a derivative of polyaniline (PANI), is one kind of conjugated and achiral polymer in nature. We have reported synthesizing helical PMOA through electrostatic interaction between PMOA backbone and chiral dopant, and the helix-inducting mechanism is same as that of reported PANI [7].

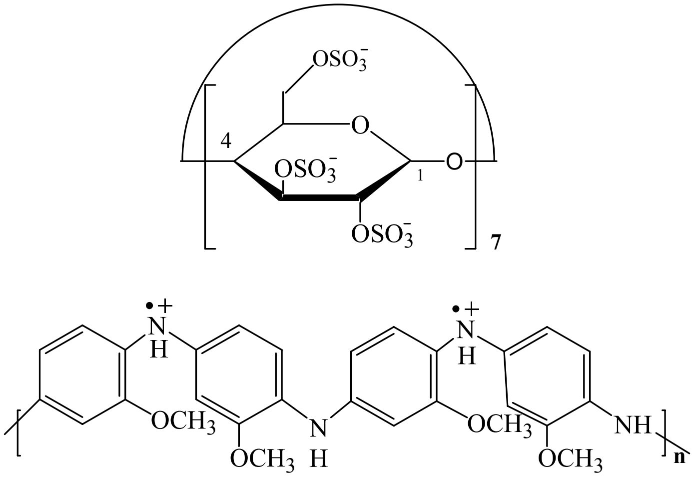
Kane-Maguire et al. reported that two steps had been involved in such a helix-inducing progress [8,9]. The first step was to protonate PANIs into radical cation structure. Subsequently, chiral anion was incorporated into main chain of PANIs as couterionic dopant through electrostatic interaction. Consequently, excess one-handed helical structure was induced on the main chain of PANIs due to the induction of chiral anion along its main chain. So, it is not difficult to understand that such an electrostatic interaction may be very sensitive to synthetic conditions and the helix-holding energy in backbone should be relatively low. Evidently, Wallace et al. has reported temperature-induced helix inversion while electrochemical polymerization of aniline using camphorsulfonic acid (CSA) as chiral dopant [10].

Menardo et al. reported that protonation was a function of the pH ($-NH_2^+-$ pKa 2.5 and $=NH^+-$ pKa 5.5) [11], which indicates that protonation of amine and imine in main chain is affected greatly by pH value of the solution. Freund et al. also reported that the interaction between sugar and polyanilines (amine and imine) was variously affected by pH values in solution [12]. At the same time, it is reasonable to predict that protonated degree greatly affects the electrostatic interaction joint-point between protonated polymer and anionic dopants, which contributes to the helical induction into polyanilines backbone. So, it is an interesting work to study chiroptical properties of PMOA under different pH values.

Although camphorsulfonic acid (CSA) is commonly used as chiral dopant to synthesize helical polyaniline, our group has devoted to synthesize helical polyanilines using some biomolecules as chirality-inducing molecules in aqueous solution, such as saccharide, amino acid and their derivatives [6,13,14]. It has also been found that biomolecules-doped PMOA sometimes showed completely different chiroptical properties to that of PANI [7].

In order to study chiroptical properties of PMOA under different pH values, cyclodextrin sulfonic acid (CDS^-H^+) is an ideally chiral dopant (Scheme 1) for this purpose. Besides it could acts as other chiral dopants, CDSH is a water-soluble doapnt. So, its water-solubility will help to study pHs influence on the chirality of PMOA in aqueous solution. To our knowledge, this report is the first example to use CDS as chiral dopant for PMOA.

Herein, we report electrochemical polymerization of 2-methoxyaniline to prepare helical PMOA using CDS as helix-inducing dopant. Unexpectedly, PMOA films show



Scheme 1 The structure of poly(2-methoxyaniline) (emeraldine salt) and β-cyclodextrin sulfate complex

almost mirror-imaged ICD spectra each other while they were respectively prepared at pH 2 and pH 3. Such a result suggests that PMOA backbone in two films might adsorb an opposite helical screw. To our knowledge, few papers have reported about pH-driving the opposition of ICD for polyanilne derivatives.

Experimental section

Chemicals

The sample of cyclodextrin sulfate sodium salt was the product of Meito (Japan), S 18% corresponding to three sulfate groups per one glucose unit. The Na^+ salt (CDS^-Na^+) (0.2 g of CDSNa dissolved in 200ml of deionized water) was first converted to H^+ forms (CDS^-H^+) by ion exchange, and CDSH was concentrated in 50 ml of aqueous solution by distilling under reduced pressure. The molar acid concentration in the solution was determined by titration with standard NaOH solution (ca. 1.1 mmol CDS in 50ml of solution). The monomers 2-methoxyaniline was purchased from Tokyo Chemical Industry Co., Ltd. (Japan), and used as received.

Potentiostatic Polymerization

Electrochemical polymerizations were carried out in a one-compartment cell using a three-electrode configuration (Hokuto Denko model HA-301 potentiostat). ITO coated glass was employed as the working electrode (2 cm^2), while Pt-plate and Ag/AgCl (3M NaCl) were used as counter and reference electrodes, respectively. Typically, the PMOA-CDSH films were potentiostatically deposited from aqueous solution containing 20 ml aqueous solution containing 0.1ml 2-methoxyaniline and 0.2g CDSH using an applied potential of +0.9 V and passing 120 mC/cm^2 of charge. The polymerization temperature was maintained at 20°C using water bath. The initial pH adjustment was carried by titration with NaOH aqueous solution. The pH value was measured with pH meter and error was controlled between -0.1 and +0.1.

Spectroscopic studies

UV-vis and CD spectra were respectively recorded by JASCO V-570 UV-vis-NIR spectrophotometer and JASCOV-720WI spectropolarimeter.

Results and discussion

Electrochemical polymerization of 2-mothoxyaniline was carried out in the presence of CDS at various pH values. Accompanying the polymerization, PMOA was gradually deposited on ITO glass in aqueous solution containing CDS. It is evidenced by the absorption at 420 and 770 nm in UV-visible spectra (Figure1), which is assigned as the characteristic polaron bands for PMOA emeraldine salt [7]. As shown in UV spectra, the intensity of polaron band at ca. 800nm decreased gradually while pH values changed from 1 to 3.

Nevertheless, PMOA obtained at pH 3 shows a “free carrier tail” spectrum over 800nm. Similar results have also been reported for chiral PANI films [10]. According to previous reports [15,16], the polaron bands corresponding to located electron in main chain, and the “free carrier tail” could be understand as the decrease of located electron or delocalization. While pH value in initial pH in solution is lower than 3, it is difficult to obtain green PMOA film.

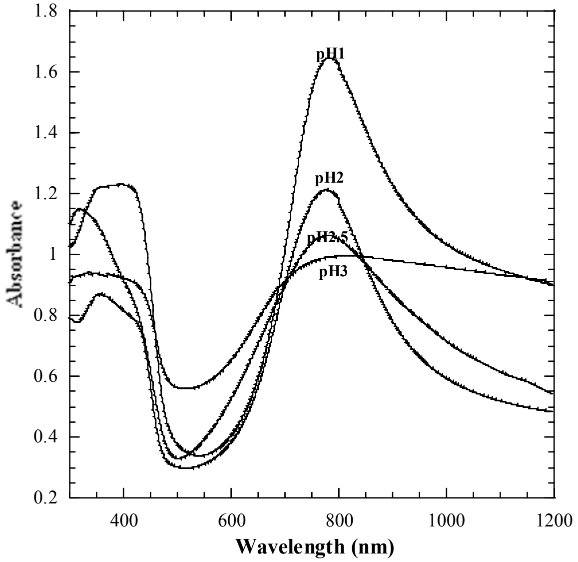


Fig. 1 The UV-visible spectra of PMOA films deposited on ITO glass in conditions of various pH values.

Figure 2 shows the ICD spectra of PMOA films deposited on ITO glasses, which indicates that a preferred one-sense helical screw is induced into PMOA backbones. PMOA films prepared at pH1 and pH 2 show almost similar ICD spectra. They show ICD bands at 330, 400 and 450 nm, which is similar to that of our previous reports [7]. These bands are clearly associated with the macro-asymmetry of the PANI chains,

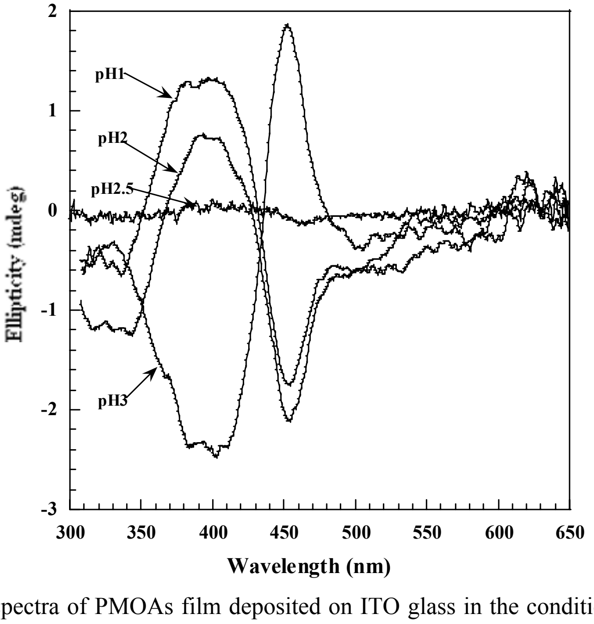


Fig. 2 The CD spectra of PMOAs film deposited on ITO glass in the conditions of various pH values (corresponding to that in Fig.1).

because CDS does not show any ICD bands in this region. The ICD peaks at 450 and 400 nm are tentatively assigned as bisignate, excition-coupling ICD bands associated with the polaron band at 420 nm. Partially overlapping with these is another possible pair of bisignate excition-coupled ICD bands (of which only 330 nm band is observed) that corresponds to the benzenoid π-π* absorption band at 330 nm.

Interestingly, PMOA films prepared at pH 3 shows almost mirror-imaged ICD spectra to that of PMOA prepared at pH 2. Such a mirror-imaged of ICD spectra suggests that opposite handedness has been induced into PMOA. At least, excess one-sense helical handedness induced in one PMOA is opposite to that of the others. That is, PMOAs selectively adsorbed an opposite helical screw while pH was changed from 2 to 3 of polymerization solution. Undoubtedly, such a selectively helical adsorption can be understood as pH-driving behavior. As mentioned above, the main dynamic for helical induction is electrostatic interaction between protonated PMOA cations and CDS anions. However, the density and distribution of cations in PMOA chains depend on the protonating status of amine and imine groups along PMOA backbone. In theory, the density of cations along PMOA backbone decides the distance of electrostatic interaction joint-points as well as the direction of interaction point around backbone of PMOA. As discussed in UV spectra, PMOAs share different degree of located electron in their main chains while they were prepared at pH 2 and pH 3 respectively. In some degree, such a difference is a reflection of protonating degree in PMOA. Consequently, it decides the density and the distribution of ionic interaction along PMOA main chains.

On the other hand, we also reported that only H-bonding can also effectively act as interaction dynamic for helical induction in neutral condition [13]. In this case, H-bonding contribution to helical induction (between SO_3^- and –NH-) should not be neglected although the electrostatic interaction is main dynamic in acidic condition. At least, two kinds of interactions have contributed to helical formation in PMOA although further works are needed to confirm it. One is electrostatic interaction and the other is H-bonding. It could be understood that there exists a balance between electrostatic and H-bonding interaction contributed to helical induction. In strongly acidic condition, electrostatic interaction between polycations and anions dominates the inducing dynamic and the H-bonding interaction could be neglected. In weak acidic condition, electrostatic interaction is not so strong and the H-bonding interaction contributes to helical induction in PMOA.

On basis of above discussion, it could be proposed that opposite handedness induced PMOA resulted from the dynamic-inducing transfer from mainly electrostatic interaction to partially electrostatic interaction combining with H-bonding interaction. Due to the dynamic-inducing transfer, the automatic adjustment of interaction points and direction between PMOA and CDS resulted in the change of helical handedness in PMOA. Evidently, ICD spectum of pH 2.5 supported our opinions. Although the bisignate bands seem to be similar to that of pH 2, ICD bands of pH 2.5 are very weak. According to above discussion, it can be understand that two kinds of interactions contributed to helical handedness reached an equal balance and one-perfected helical handedness can not be reflected by ICD spectrum at pH 2.5.

Although the images are not been shown here, the morphology of PMOAs films were checked by scanning electron micrographs (SEM), helical structure in PMOAs can not been observed by SEM. The chiral films have also been re-dissolved in chroloform, and the solutions show almost similar CD spectra comparing to that in films. These results suggest that a perfected one-handed helix was induced in PMOA backbones.

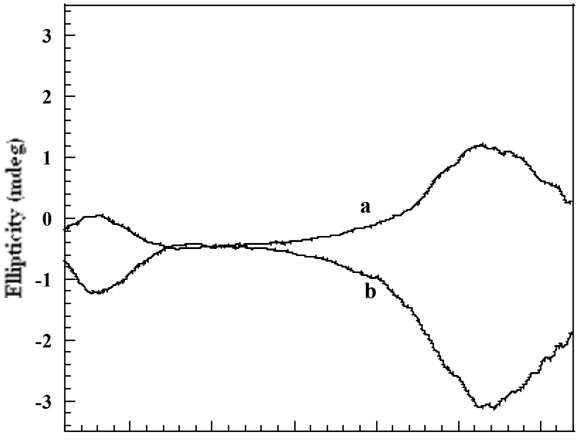


Fig. 3 The CD spectra of PMOA films after treated with 1N NH_4OH: (a) prepared at pH 2, (b) prepared at pH 3.

While chiral aggregation formation of PMOA in films can not been declined, our results don't support it. Because synthetic PMOA is half-protonated and pH values in solutions changed with polymerization progress, more detail pH controlling efforts have been tried and seemed to be rather difficult to operation. The influence of polymerization time to chirality in PMOA was also been checked, the result is that polymerization time was almost no effect to handedness of PMOA films.

In order to remove CDS from films, PMOA-CDS emeraldine salt films were treated with 1.0 mol dm^{-3} NH_4OH and resulted in blue emeraldine base. The UV-vis spectra of films exhibit two absorption bands at 320 and 565 nm, characteristic bands of emeraldine base, which is consistent with our previous reports [7]. Significantly, the ICD spectra (Figure 3) of these PMOA emeraldine base films showed strong bands at about 328 and 570nm. Emeraldine base films prepared at pH2 and 3 expectedly exhibited almost mirror-imaged ICD spectra correponding to that of original prepared films, which indicates that the chiral architecture was well remained in each film after removing CDS. In other words, opposite helical handedness was held in PMOA backbones and not be effected by CDS once it was induced. Also, PMOA films show similar ICD spectra to that of originally prepared PMOA-CDS films after redoped with HCl. After heating and cooling the films, PMOAs also keep their helical handedness except some degree decrease of intensity in ICD spectra due to the partial lose in helical screw.

Conclusions

Excess one-handed helical structure has been successfully induced into PMOA backbone by electrochemical polymerization using CDS as helix-inducing dopant, which was confirmed by ICD spectra. It is found that polymerizing condition, such as pH values, greatly affected the helical handedness of PMOA. In detail, PMOA film prepared at pH 3 selectively adsorbed an opposite handedness comparing to that of PMOA film prepared at lower pH. Although further investigation is needed and now in progress to explore the mechanism of helix-inducing dynamic contributing to handedness of PMOA, the helical handedness of PMOAs in films can be held well after post-treatments.

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