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Polymer 44 (2003) 5501–5504
polymer
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Polymer Communication

Helical polyaniline induced by specific interaction with biomolecules in neutral solution

Guo-Li Yuan, Noriyuki Kuramoto*

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

Received 17 March 2003; received in revised form 4 June 2003; accepted 10 June 2003

Abstract

Some kinds of sugar and amino acid are used to interact with polyaniline emeraldine base in neutral aqueous solution. PANI complexed with these molecules shows interesting induced circular dichirom (ICD) spectra, which indicates that excess one-handed helical structure is induced on PANI. Furthermore, opposite ICD spectra are observed for PANI while it is interacted with L- and D-amino acid, respectively. It is presumed that H-bonding interaction plays a central role in such a helical induction. This is the first example to prepare optically active PANI in neutral solution by one step without protonating EB into polycation in advance.

Keywords: Helical polyaniline; Biomolecules; Induced circular dichirom

1. Introduction

Polyaniline (PANI), a low-cost inherently conducting polymer, is also an optically inactive polymer in nature. Nevertheless, it can show an induced circular dichroism (ICD) if it is doped with some chiral acids as dopants, because a preferred one-sense helical screw was induced on PANI backbone [1–6]. In all the above cases, either post-protonating PANI emeraldine base (EB) or in situ doping PANI with chiral acid, two steps have been involved. The first step is to protonate PANI to radical cation structure. Subsequently, chiral anion is incorporated into main chain of PANI as couterionic dopant through electrostatic interaction. Therefore, excess one-handed helical structure is induced on the main chain of PANI due to the induction of chiral anion along its main chain. Kane-Maguire et al. [7–9] emphasized that the deprotonation of PANI to its neutral form made it completely lose optical activity in solution because the induction of helical structure on PANI depended on the electrostatic bonding chiral anion along its chain. For preparing optically active PANI, it seems to be necessary to protonate PANI to radical cation in strongly acidic condition, and then electrostatically incorporate chiral dopant along its chain. Without the electrostatic interaction between PANI and chiral counterion, it may become very difficult to induce a helical structure on PANI. So, it is a challenge to prepare a helical PANI in neutral condition to avoid protonating it in strongly acidic condition.

Most recently, a lot of interest has been focused on studying the interaction between some conjugated polymers and biomolecules due to the possible applications [10,11]. Significantly, a preferred one-handed helical structure has been induced on these conjugated polymers due to the interaction with these structure-ordered biomolecules, which has been proved by defined ICD spectra.

Herein, we report that a preferred one-sense helical screw is induced on the main chain of PANI EB (emeraldine base, neutral form of PANI) by interaction with some sugars and amino acids in neutral solution, which is studied on the basis of ICD spectra.

2. Experimental section

2.1. Materials and methods

EB was prepared via oxidation of aniline with ammonium persulfate (APS) in 1.0 mol dm^{-3} at 0 °C,

* Corresponding author. Tel./fax: +81-238-26-3051.
E-mail address: kuramoto@dip.yz.yamagata-u.ac.jp (N. Kuramoto).

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doi:10.1016/S0032-3861(03)00503-2

followed by dedoping with NH_4OH and washing as previously reported method [12]. The average molecular weight was determined to be ca. 30 000 on TOSOH HLC-8120 GPC (column, TOSOH KD80M) at 25 °C using 0.01 mol L^{-1} LiBr/DMF as eluent. The weight-average (M_w) molecular weight was determined by standard procedures using polystyrene standards. The sugars and amino acids, such as D-(+)-glucose, D-(+)-galactose, D-(+)-tryptophan, L-(−)-tryptophan, D-(−)-alanine and L-(+)-alanine were the products of Tokyo Chemical Industry Co., Ltd. (Japan). Hydroxypropyl cellulose (HPC 150–400 cps) is the product of Wako (Japan).

2.2. Preparation of the PANI-biomolecules complex

Some biomolecules, such as D-(+)-glucose, D-(+)-galactose, D-(+)-tryptophan, L-(−)-tryptophan, D-(−)-alanine and L-(+)-alanine, were respectively complexed with EB to prepare EB-biomolecule complexes in the mixed-solvent of NMP and water (1:10). Typically, 2 ml of EB (0.1 wt.% in NMP) was slowly added to D-(+)-glucose aqueous solution (0.1 g in 20 ml water) with vigorous stirring, and a blue EB-(D-(+)-glucose) solution was obtained, which was used for the measurement of spectra.

2.3. Spectroscopic studies

UV–vis and CD spectra of polymers were recorded by JASCO V-570 UV–vis-NIR spectrophotometer and JASCO V-720 WI spectropolarimeter, respectively. The spectra measurement was performed in 10 nm quartz cells.

3. Results and discussion

As shown in Fig. 1, the complex of EB with amino acids, such as D-(+)- and L-(−)-tryptophan, exhibit interesting ICD spectra with defined bands. EB-(D-(+)-tryptophan) shows almost opposite ICD spectra to that of EB-(L-(−)-tryptophan). Similar result has also been found for EB-(D-(−)-alanine) and EB-(L-(+)-alanine). Based on these CD spectra, it is understood that excess one-handed helical structure has been induced on EB because tryptophan does not show any CD bands in this region. In addition, opposite ICD spectra indicates opposite excess one-handed helical structure is induced on PANI main chain while respectively interacting with D-(+)- and L-(−)-tryptophan.

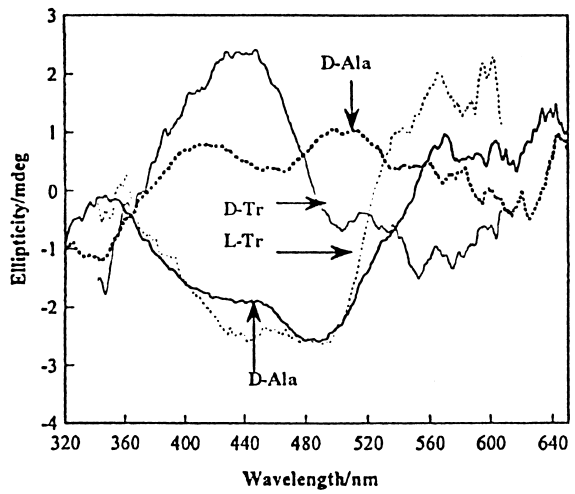

Fig. 1. ICD spectra of EB-(D-tryptophan), EB-(L-tryptophan), EB-(D-alanine), and EB-(L-alanine) in mixed-solvent of NMP/water (1:10).

Undoubtedly, the induction of helical structure on EB arises from the interaction with tryptophans. Because protonation of PANI is a function of the pH ($-NH_2^+-$ p K a 2.5 and $=NH^+-$ p K a 5.5) [13], it is almost impossible to protonate EB into polyelectrolyte in such neutral solution. So, the electrostatic interaction between EB and tryptophan was limited. It is reasonable to presume that the interaction between EB and tryptophan mainly arose from H-bonding rather than electrostatic interaction, although further work is needed to confirm it. In detail, the H-bonding interaction probably arose from carbonyl and amine group in tryptophans to amine and imine in EB. As suggested in previous reports, bidental structure in dopants seemed to be necessary to induce and hold the helical structure on PANI [14]. Undoubtedly, the structure in tryptophans possesses such a structure motifs although the interaction herein is H-bonding rather than that of electrostatic bonding interaction. Of course, it has to be considered that the hydrophobic interaction between PANI and tryptophan may contribute the complexation to them in aqueous solution. However, it is almost impossible for such a hydrophobic interaction to contribute stereo arrangement to PANI backbone because the interaction groups are not defined, especially in the case of alanine. In addition, it is not in keep with the requirement of the bidental structure in holding the helical structure on PANI [14].

Most interestingly, it is found that the specific interaction between EB and carbohydrates is also effective to induce a helical structure on EB. Fig. 2 shows the ICD spectrum of EB-(D-(+)-glucose) and EB-(D-(+)-galactose). The defined bisignated ICD bands indicate excess one-handed helical structure has been induced on EB main chain, at least partially. The similar ICD spectrum in EB-galactose suggests that PANI also predominantly adopted one-handed helical structure similar to that of EB-glucose. The concentration of EB was changed in EB-glucose aqueous solution. There is no obvious change in CD spectra except the intensity of it due to the change of concentration. At high concentration, blue EB precipitated from solution owing to the absence of complexing with glucose.

In this case, the exclusively possible interaction for helical induction presumably attributed to H-bonding interaction between EB and sugars because there are no charged groups in either EB or sugars. The interaction was considered mainly arising from the H-bonding between hydroxy group in sugars and imine (or amine) in the main

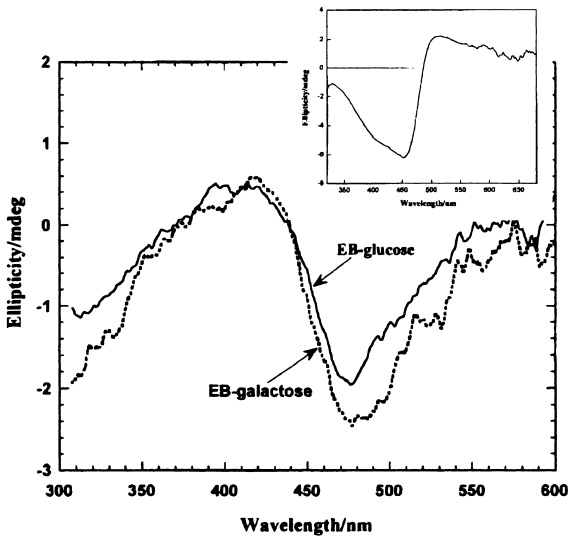

Fig. 2. ICD spectra of EB-(D-(+)-glucose), EB-(D-(+)-galactose), and EB-HPC (insert figure) in mixed-solvent of water/NMP (1:10).

chain of EB. Although such H-bonding interaction in water has not yet been clearly confirmed and may be very weak, the result clearly indicates that EB interacted with carbohydrates through it even in water. Similar result has also been reported by Yashima et al. [15]. In addition, excess one-handed helical structure is induced on EB, while it was interacted with hydroxypropyl cellulose, but it is opposite to that of EB-(D-glucose) (Fig. 2). Fig. 3 shows the possible interaction model of glucose with the backbone of EB. It is presumed that the multivalent hydrogen bonding interaction, which is attributed to the special structure in glucose, may make such weak interaction to be effective and sensitive.

The UV–vis spectra of EB, EB-(D-(+)-glucose), and EB-(D-(+)-galactose) complex are shown in Fig. 4. EB shows its characteristic bands at visible region. After complexed with D-(+)-glucose, the band shows an obvious red-shift. Furthermore, a small shoulder at ca. 420 nm is observed after the complexation, which is found not arising from the change of polarity in solvents by a control experiment. The change and shift of bands in spectra indicate the complexation of EB with sugars. In the case of

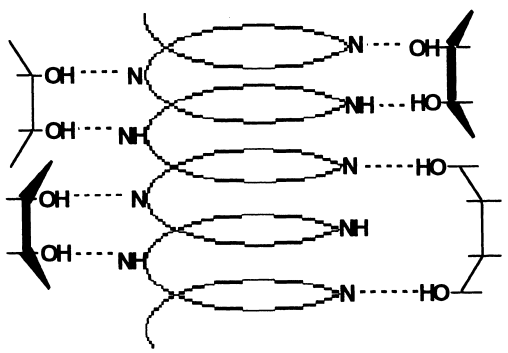

Fig. 3. Possible interaction models between glucose and polyaniline emeraldine base (EB).

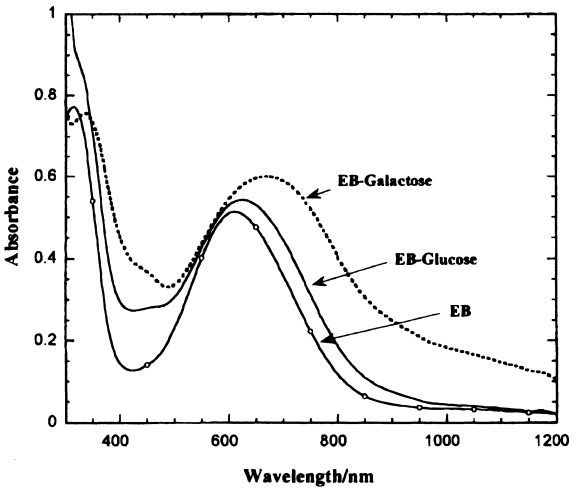

Fig. 4. UV–vis spectra of EB, EB-(D-(+)-glucose), and EB-(D-(+)-galactose) in mixed-solvent of water/NMP (1:10).

D-(+)-galactose, similar change in electronic spectra is observed as shown in Fig. 4.

4. Conclusion

Excess one-handed helical structure has been induced on PANI by interacting with some sugars and amino acids, which was confirmed by ICD spectra. It is first example that helical structure was induced on PANI EB in neutral solution rather than reported that of strongly acidic condition. The opposite ICD spectra respectively induced on PANI by enantiomers of amino acid indicates that PANI shows high potential to be used as receptor for biomolecular recognition. Although further work is needed, it is exclusively presumed that H-bonding interaction played a central role in inducing helical structure on PANI. The result also clearly confirmed that H-bonding interaction is sensitive and effective.

Acknowledgements

G.-L. Yuan is grateful to the Ministry of Education, Culture, Sports, Science and Technology, Japan, for scholarship.

References

[1] Majidi MR, Kane-Maguire LAP, Wallace GG. Polymer 1994;35:3113.
[2] Majidi MR, Kane-Maguire LAP, Wallace GG. Polymer 1995;36:3597.
[3] Havinga EE, Bouman MM, Meijer EW, Pomp A, Simenon MMJ. Synth Met 1994;66:93.
[4] Egan V, Bernstein R, Hohmann L, Tran T, Kaner KB. Chem Commun 2001;801.
[5] Yuan GL, Kuramoto N. Chem Lett 2002;544.

[6] Yuan GL, Kuramoto N. Macromolecules 2002;35:9773.
[7] Kane-Maguire LAP, MacDarmid AG, Norris ID, Wallace GG, Zheng W. Synth Met 1999;106:171.
[8] Norris ID, Kane-Maguire LAP, Wallace GG. Macromolecules 2000; 33:3237.
[9] Nagarajan R, Liu W, Kumar J, Tripathy SK, Bruno FF, Samuelson LA. Macromolecules 2001;34:3921.
[10] Saito MA, Maeda K, Onouchi H, Yashima E. Macromolecules 2000; 33:4616.
[11] Ho HA, Boissinot M, Bergeron MG, Corbeil G, Doré K, Boudreau D, Leclerc M. Angew Chem Int Ed 2002;41:1548.
[12] Rannov P, Gawlicka A, Berner D, Pron A, Nechtschein M. Macromolecules 1998;31:3007.
[13] Shoji E, Freund M. J Am Chem Soc 2001;123:3383.
[14] Ashraf SA, Kane-Maguire LAP, Majidi MR, Pyne SG, Wallace GG. Polymer 1997;38:2627.
[15] Onochi H, Maeda K, Yashima E. J Am Chem Soc 2001;123:7441.