Chemical Synthesis of Optically Active Polyaniline in the Presence of Dextran Sulfate as Molecular Template

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(Received February 4, 2002; CL-020124)

One preferred handed helical structure was induced into the polyaniline main chains by chemical polymerization of achiral aniline in the presence of dextran sulfate as a molecular template, and this affords a novel chemical route for synthesis of chiral conducting polymers.

Template polymerization of aniline in the presence of anionic polyelectrolyte (or polymeric acid) has emerged as a unique simple method to prepare a water-soluble (or dispersible) polyaniline (PANI) chemically,[1] electrochemically[2] and enzymatically.[3] In these processes, the monomers of aniline were aligned onto the molecular template through acid-base interaction prior to polymerization, and the synthesized protonated PANI chain intertwined with the chain of anionic polyelectrolyte template molecule through electrostatic interaction (e.g., between the sites of $HN^{\bullet +}$ in PANI and SO_3^- in polyelectrolyte) to form a molecular complex.[3,4] Besides improving the water-processability of PANI, some workers[1b,c] have tried to induce some properties to PANI by adjusting of polyelectrolyte strand in the molecular complex. Most recently, Nagarajan et al. has found that it was possible for PANI chains to adopt a preferred one-sense helical screw while enzymatic synthesis of PANI in the presence of DNA as template.[5] Nevertheless, there is still no example to induce helical structure into PANI in such intertwined molecular complexes by chemical or electrochemical polymerization of aniline, in which the effect of enzyme on the chirality of PANI could be avoided. However, it has been considered that direct use of a bio-polyeletrolyte template was unsuitable for synthesis of such a molecular complex in these synthetic procedures due to the harsh conditions.[5] So it is a challenge to directly induce a helical structure into PANI chains in chemical or electrochemical polymerization of aniline by selecting a suitable template to complex and intertwine with PANI.

Herein a chemical polymerization of aniline is reported in the presence of dextran sulfate, a synthetic polysaccharide, as molecular template, and PANI chains predominantly adopted one-handed helical structure through complexing and intertwining with such a chiral anionic polyelectrolyte. In addition to the advantage of water-dispersibility, this PANI exhibited almost similar chiroptical properties to those previously reported chiral PANIs. Helical PANI has recently been enantioselectively synthesized by using chiral camphorsulfonic acid (CSA^-H^+) as dopant for PANI, in which the macromolecular asymmetry presumably arose from electrostatic bonding of CSA^- sulfate ion to PANI $HN^{\bullet +}$ centers and H-bonding of CSA^- carbonyl group to HN sites.[6] Also, optically active PANI showed highly potential application in molecular recognition and enantiomeric separation.[7] In this case, the helical structure was induced into PANI backbones resulting from the intertwining with chiral polymeric dopant.

Dextran sulfate (DS) is a linear sulfated polysaccharide containing α-1,6 linked D-glucopyranose units with three sulfate groups per one D-glucose unit and has been employed as chiral selectors in capillary electrophoresis for enantiomer separation owing to its highly ordered structure and chirality.[8] Besides behaving as other anionic polyelectrolyte templates, DS is also a suitable chiral template for anchoring achiral aniline monomers along its chain.

The Na^+ salts of dextran sulfate (DS^-Na^+)[9] were firstly converted to H^+ forms (DS^-H^+) by ion exchange and the molar acid concentration was determined by titration with standard NaOH solution. The monomers of aniline (1 mmol) were added to DS^-H^+ aqueous solution (1.25 mmol in 50 ml) with vigorous stirring. Chemical polymerization of molecular complex of aniline and DSH was initiated by addition of ammonium persulfate aqueous solution dropwisely into monomer solution at ca. 0 °C, and carried out for 20 h. After dialysis of the final solution against deionized water to remove low molecular mass materials, a homogeneous dark green PANI-DS aqueous solution was obtained and showed a characteristic electronic spectrum for PANI emeraldine salt with polaron bands at ca. 420 and 770 nm. PANI-DS complex could be precipitated from the solution while dipped into excess acetone. After collected and dried in air, green powder was obtained, which could be re-dissolved in water.

As shown in Figure 1A, the chiral PANI-DS aqueous solution exhibited characteristic circular dichroism (CD) bands centered at ca. 450, 400 and 327 nm between 300 and 680 nm, which are consistent with that of helical PANI doped with camphorsulfonic acid[6,7] no matter to the direction of the peaks. These observed CD bands are exclusively associated with the chiral architecture of the polyaniline backbones because DS does not show any CD band in this region. This result confirms that PANI chains predominantly adopted one-handed helical structure in the presence of DS as molecular template in polymerization. However, when the polymerization was carried out in the presence of additional excess NaCl, the synthesized PANI lost its optical activity and water-solubility. It is presumed that the presence of Cl^- competitively hindered or "sealed" the binding of protonated aniline (NH_3^+ sites) and PANI ($HN^{\bullet +}$ sites) to DS^- template. As the result, PANI main chain lost its macromolecular asymmetry and solubility without the induction and stabilization of DS. The polymerization of aniline was also found to be template dependent. While the amount of DSH decreased to 0.25 mmol in reaction solution, there was almost no PANI emeraldine salt yielded, which was confirmed by electronic spectra.

We also prepared PANI-DS complex by post-doping PANI emeraldine base with DSH. After addition of emeralidine base in dimethyl sulfoxide (DMSO) to DSH aqueous solution (the volume ratio of DMSO to water is 1 : 10) with vigorous stirring, a stable PANI-DS complex suspension was obtained and showed characteristic polaron bands for PANI emeraldine salt at ca. 776 and 420 nm. No CD bands were observed for this complex in either solution or film in this region. But in such a mixture solvent, PANI-DS complex prepared by in situ polymerization showed identical UV-vis and CD spectra as that in aqueous solution. This result strongly suggests that the induction of one preferred handed helicity in polyaniline chains is the outcome of chemical polymerization.

After evaporation of water on glass substrate, a green PANI-DS film (4 μm) was obtained and showed almost identical CD spectrum as that in aqueous solution (Figure 1B). After thermal decomposition of DS in the film of PANI-DS, the left PANI emeraldine base still remained its optical activity, which was confirmed by CD, UV-vis spectroscopic and TG analysis.

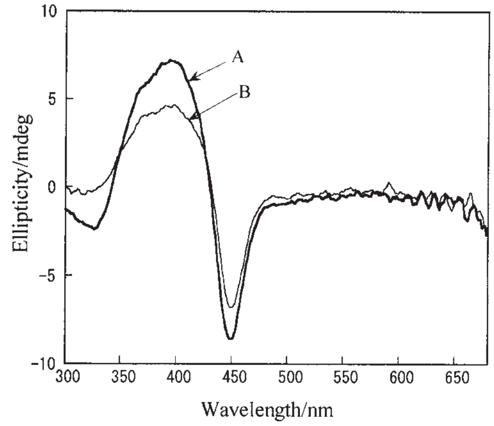

Figure 1. The CD spectra of PANI-DS in aqueous solution (A) and film (B).

While titration of PANI-DS aqueous solution with NaOH, the chiral PANI showed different CD spectra (Figure 2) at various values of pH. As the pH of solution increased, the CD bands at 400 and 450 nm gradually disappeared, and two new intense peaks began to emerge. At a pH of 11, the almost fully dedoped PANI shows CD bands at ca. 327 and 567 nm between 300 and 680 nm, which presumably correspond to the absorption bands of benzenoid π-π^* and quinoid exciton transition respectively. These bands have also been observed in deprotonated chiral PANI-CSA films.[6d,e] Such a change in CD spectra attributes to the special structure of PANI, which showed interesting electronic spectra change at various pHs.[3] The fully deprotonated PANI precipitated gradually from aqueous solution due to the loss of electrostatic interaction with DS chains which imparted the solubility of PANI. The inherent viscosity of the precipitated PANI emeraldine base was measured to be 1.40 dl/g by the previously reported method,[10] which suggests PANI has a rather high average molecular weight. The electrochemical activity was also checked by cyclic voltammetry.

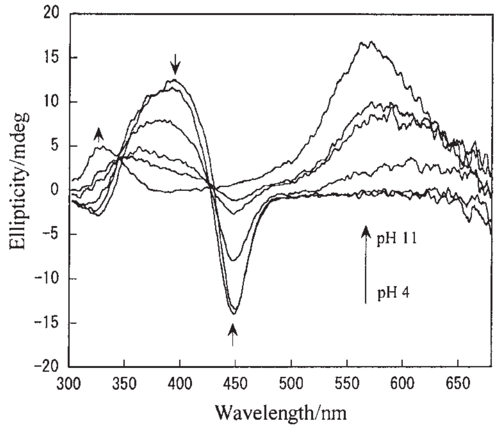

Figure 2. The CD spectral change of PANI-DS in aqueous solution during titration by 0.5 mol dm^{-3} NaOH.

The above-mentioned results indicate that a water-soluble and chiral PANI was prepared by chemical polymerization of aniline in the presence of DS as molecular template. To our knowledge, our work is the first example using chiral polymeric template in chemical polymerization to induce the helical structure into conducting polymer. Further investigation is now in progress for such a template-guided polymerization, involving kinetic study as well as synthesis of other conducting polymers on such chiral template.

The author G.-L. Yuan is grateful to Professor M. Takeishi for his helpful discussions, as well as to the Ministry of Education, Culture, Sports, Science and Technology, Japan for scholarship.

References and Notes

1 a) M. Angelopoulos, M. Patel, J. M. Shaw, N. C. Labianca, and S. A. Rishton, *J. Vac. Sci. Technol., B*, **11**, 2794 (1993). b) J.-M. Liu and S. C. Yang, *J. Chem. Soc., Chem. Commun.*, **1991**, 1529. c) L. F. Sun, H. B. Liu, R. Clark, and S. C. Yang, *Synth. Met.*, **84**, 67 (1997).
2 K. Shannon and J. E. Fernandez, *J. Chem. Soc., Chem. Commun.*, **1994**, 643.
3 W. Liu, J. Kumar, S. Tripathy, K. J. Senecal, and L. Samuelson, *J. Am. Chem. Soc.*, **121**, 71 (1999).
4 P. Chandrasekhar, in "Conducting Polymer, Fundamentals and Applications," Kluwer Academic Publishers, Boston (1997), p 211, and the papers cited therein.
5 R. Nagarajan, W. Liu, J. Kumar, S. K. Tripathy, F. F. Bruno, and L. A. Samuelson, *Macromolecules*, **34**, 3921 (2001).
6 a) M. R. Majidi, L. A. P. Kane-Maguire, and G. G. Wallace, *Polymer*, **35**, 3113 (1994). b) E. E. Havinga, M. M. Bouman, E. W. Meijer, A. Pomp, and M. M. J. Simenon, *Synth. Met.*, **66**, 93 (1994). c) I. D. Norris, L. A. P. Kane-Maguire, and G. G. Wallace, *Macromolecules*, **31**, 6529 (1998). d) L. A. P. Kane-Maguire, A. G. MacDiarmid, I. D. Norris, G. G. Wallace, and W. Zheng, *Synth. Met.*, **106**, 171 (1999). e) S.-J. Su and N. Kuramoto, *Macromolecules*, **34**, 7249 (2001).
7 V. Egan, R. Bernstein, L. Hohmann, T. Tran, and R. B. Kaner, *Chem. Commun.*, **2001**, 801.
8 a) H. Nishi, K. Nakamura, H. Nakai, T. Sato, and S. Terabe, *Eletrophoresis*, **15**, 1335 (1994). b) "The Merck Index," 13th ed., Merck & Co., Inc., Whitehouse Station NJ (2001), p 520.
9 The sample of dextran sulfate sodium salt was kindly provided by JSR Corporation (Japan); Mw 70 000; S 18% corresponding to three sulfate groups per one D-glucose unit.
10 J.-E. Österholm, Y. Cao, F. Klavetter, and P. Smith, *Synth. Met.*, **55**, 1034 (1993).