Synthesis and Optical Properties of Poly(hydroxyphenylbenzoxazole): A Colorimetric and Fluorescent Sensor for Ionic Species

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Abstract

We synthesized a poly[2-(2'-hydroxyphenyl) benzoxazole] under the two step procedures of Suzuki coupling polymerization with corresponding monomers followed by the deprotection of benzyl group. The polymer in DMF solution is applicable to colorimetric sensing fluoride anion, which shows a color change from colorless to yellow. High sensitivity to fluoride anion compared to other anions such as phosphate, chloride, and sulfate is ascribed to the high coordination ability of the 2-(2'-hydroxy phenyl)benzoxazole moiety in the polymer chain. Emission shift by metal cations, which can be applied to fluorescent sensing was also observed in the polymer solution.

Introduction

Recently, optical sensors for anionic species received a great deal of attention mainly upon the supramolecular chemistry of receptor design. The binding is typically monitored by changes in absorption and fluorescence intensity from a chromophore mainly covalently attached to the receptors.[1,2] However, simple and easily prepared anion optical sensors are rare because signal transduction can be limited by many factors.[3] Recent efforts in detecting anion binding by "colorimetric anion sensors" which allow the so-called "naked-eye" detection may provide important results.[4] Among optical chemosensors for anionic analytes, fluoride anion sensing is of particular interest because of the important role in dental care and environmental pollutants.[5] Though some sensor compounds for fluoride anions have been reported,[6] there is still a need for good anion sensors with an improved specific response. Detection of metal cations is also received a considerable attraction because of their potential importance in environmental, physiological, and related fields.
Conjugated polymers show unique electrical and optical properties due to the extended π-conjugation in the main chain. The localized electronic structure of these polymers is responsible for the electrical conductivity, luminescence, photoconductivity, and nonlinear optical properties. Furthermore, functionalized conjugated polymers with receptor group can detect, transduce, and amplify chemical information into an optical signal. Thus conjugated polymer-based chemosensor have such advantages over small molecular sensors.
Herein we are reporting a new conjugated polymer-based chemosensor containing 2-(2'-hydroxyohenyl)benzoxazole units in the main chain. 2-(2'-Hydroxyphenyl)benzoxazole has been widely studied from the view point of photophysics due to its two emissions through the excited-state intramolecular proton transfer (ESIPT). In this paper, we will describe the synthesis of the polymer and demonstrate its optical sensing for various ions.

Results and Discussion

A polymer containing 2-(2'-hydroxyphenyl) benzoxazole groups was synthesized via the Suzuki coupling reaction from the dibromo-terminated benzyl-protected monomer and the dialkoxyphenylene diboronic acid monomer. The synthetic route for the polymer from the precursor polymer **1** is shown in Scheme 1. At first we tried to synthesize polymer **2** from the direct reaction from dibromo compound with free hydroxyl group and corresponding diboronic aicd. We, however, found that the free hydroxyl group played a role in inhibiting the Suzuki coupling reaction and failed to synthesize **2**. Thus we synthesized a benzyl group-protected monomer to circumvent the hydroxyl group inhibition and the benzyl groups were deprotected from precursor polymer **1** after polymerization to obtain **2**.
The polymers **1** and **2** are grayish white powders and have good solubility in conventional organic solvents such as chloroform, THF, and *N,N*-

dimethylformamide (DMF). The good solubility is presumed to be attributed to the two *n*-hexyloxy side-chains attached on the phenylene units. Well-defined polymer structures of **1** and **2** were identical to the expected structures, which were characterized with FT-IR and ^{1}H NMR spectroscopy. Degree of benzyl group deprotection from **1** to **2** was found to be of 47%, which was calculated from the ratio between peak at 5.4 ppm (benzyl $-OC\underline{H}_2$-Ph) and reference peak at 4.0 ppm ($-OC\underline{H}_2C_5H_{11}$) before and after deprotection. Molecular weight of **2** was revealed by GPC and measured of 5090 as a number average molecular weight (M_n) and of 7950 as a weight average molecular weight (M_w). The optical properties of polymers **1** and **2** were studied using UV-visible spectrophotometer. The absorption maxima (λ_{max}) of the precursor polymer **1** and deprotected polymer **2** in chloroform solution were not significantly changed from 329 nm to 331 nm implying that the electronic effect of hydroxyl group is negligible. However, upon excitation at 330 nm, two polymers in chloroform showed completely different fluorometric behaviors. The polymer **1** solution emitted at 418 nm on the while polymer **2** solution exhibited an additional band at 518 nm along with the normal blue one at 414 nm (Fig. 1). It is presumed that this different fluorometric results are attributed to the occurrence of the ESIPT process of the hydroxyl form and he excited state of a polar tautomeric form. Transparent thin film of **2** is readily prepared from chloroform solution by spin-casting method. The film exhibited a strong fluorescence with maximum at 516 nm, which indicated the tautomeric form was preferred energetically regardless of virtually frozen state of isomers. This result complied well with that of the previous research work on polyquinoline.[7]

The ability of polymer **2** to coordinate with anions (in the form of their tetrabutylammonium salts) in DMF was investigated using UV-visible absorption method. In the presence of phosphate or fluoride anion, the original absorption band at 333 nm decreased and new long-wavelength peaks around 420 nm formed. The λ_{max} intensity of the new absorption is largest for the most basic fluoride ion, modest for phosphate ion, and absent for the least basic anion chloride ion. Furthermore the color in DMF solution changes from colorless to yellow in the presence of fluoride anion. Therefore we can conclude that the polymer **2** can be used as a colorimetric sensor for a detection of fluoride anion conveniently.

References

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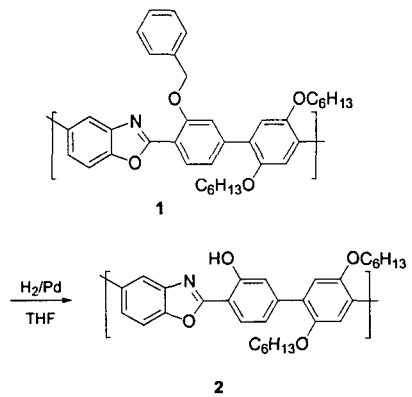

Figure 1. Chemical structure of polymer.

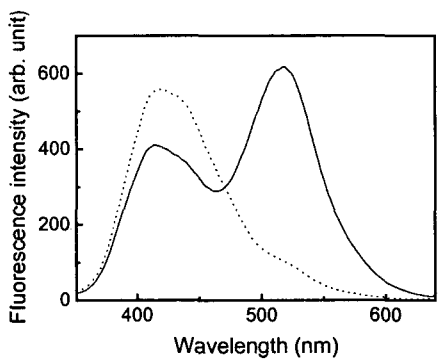

Figure 2. Emission spectra of **1** (dotted line) and **2** (solid line) in chloroform (excitation wavelength 330 nm).