Cyclodextrin-Induced Fluorescence Enhancement of an Ionic Polyacetylene Having Phenylethylpyridinium Groups

*Sang-Mi Lee, Ji-Seok Lee, Jong-Man Kim**

Summary: A phenylethylpyridinium substituted polyacetylene PA-PEP has been prepared in a straight forward manner by the reaction of 2-ethylnylpyridine with (2-bromoethyl)benzene. The UV-visible maximum of this ionic polyacetylene undergoes a bathochromic shift in the presence of β-cyclodextrin. In contrast, a negligible bathochromic shift is observed in the presence of α- or γ-cyclodextrin. In addition, the most prominent enhancement fluorescence intensity of the polyacetylene was observed with β-cyclodextrin when it interacts with cyclodextrins. It is proposed that the observed fluorescence perturbations are a consequence of the inclusion complex formed between β-cyclodextrin and the polyacetylene side-chain.

Keywords: chemosensor; cyclodextrin; fluorescence; ionic polyacetylene

Introduction

The development of efficient sensors based on conjugated polymers has been the central focus of recent investigations.[1–3] Certain conjugated polymers undergo changes in their physical properties, such as absorption, emission, conductivity and redox potential, in response to environmental perturbations. Conjugated polymers, in which these changes take place in response to specific ligand-receptor interaction, should have a broad range of applications. Consequently, a variety of conjugated polymers have been probed as potential biological and chemical sensors.[4–13]

Since most biologically interesting target molecules, including proteins, carbohydrates, and nucleic acids, are only soluble in water, water solubility is an important criterion that must be taken into account in the design of conjugated polymer sensors. In general, the synthesis of water-soluble conjugated polymers is a tedious procedure since most synthetic methods developed for the preparation of these substances are negatively influenced by polar sidechain functionality. As a result, the use of protecting and deprotecting protocols are required in the synthetic schemes designed to form water soluble polymers. Conjugated, ionic polyacetylenes (PAs) are attractive substances in this regard,[14–17] since often they can be readily prepared by facile reactions of ethynylpyridines and alkyl halides.

Cyclodextrins are known to form inclusion complexes with a variety of organic molecules.[22–33] In addition, their different binding specificities makes α-, β- and γ-CDs attractive model systems for studying ligand-receptor interactions. Thus, the observation that cyclodextrins promote changes in the optical properties of an ionic PA, would establish a foundation for the development of novel chemosensors based on ionic PAs. Although syntheses of ionic PAs have been reported, their application as fluorescence chemosensors has not been described and only one example of an ionic PA as a fluorescence quencher has been reported.[7] As part of a research program targeted at the develop-

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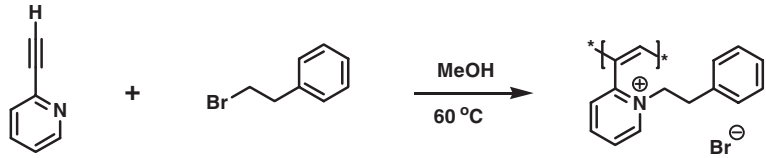
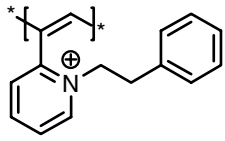


2-Ethynylpyridine (2-Bromoethyl)benzene PA-PEP

Scheme 1.
Synthesis of the ionic polyacetylene PA-PEP.

ment of conjugated polymer-based chemosensors,[18–21] we have prepared a water-soluble ionic polyacetylene (PA-PEP), containing appended phenylethylpyridinium (PEP) groups, and investigated how its absorption and emission properties are effected by interactions with cyclodextrins (CDs). The results of these studies are described below.



PA-PEP

Experimental Part

Preparation of Ionic Polyacetylene PA-PEP

The synthesis of ionic polyacetylene PA-PEP was carried out by employing procedures similar to those described earlier.[15] 2-Ethynylpyridine (0.102 g, 1.0 mmol) was added dropwise to a solution containing (2-bromoethyl)benzene (0.22 g, 1.19 mmol) in MeOH (5 mL). The original light-brown solution turned dark-brown as the polymerization proceeded. The resulting solution was stirred at 60 °C for overnight. The precipitate, formed when the mixture was added dropwise to cold ether (200 mL), was filtered and dried under vacuum to give 200 mg (70%) of the PA-PEP as a dark-brown solid.

Fluorescence Enhancing Experiments

A typical experiment is as follows. To a deionized water solution of PA-PEP (0.1 mM, monomer based) was added α, β, or γ-cyclodextrin (10 mM final concentration). The fluorescence emission spectra of the resulting solutions were measured by using a RF-5301PC series spectrofluorophotometer.

Results and Discussion

The ionic polyacetylene, PA-PEP, is readily prepared by the N-alkylation reaction of 2-ethynylpyridine (2-EP) with (2-bromoethyl) benzene in methanol (Scheme 1). Unlike most conjugated polymers, PA-PEP can be obtained directly by heating in MeOH without the need for initiators or catalysts. PA-PEP, which is precipitated from the reaction mixture by simply adding to cold ether, is produced in yields in the range of 60–70%. Moreover, this ionic polymer is soluble in protic solvents, such as water and MeOH.

The formation of the PA-PEP can be readily monitored by observing the appearance of its dark-brown color. In Figure 1 is

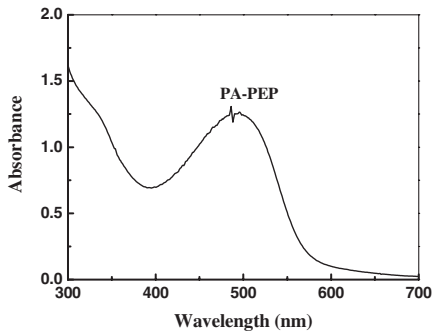


Figure 1.
UV-visible spectra of solutions (MeOH) containing 2-ethynylpyridine (2-EP) and PA-PEP, respectively.

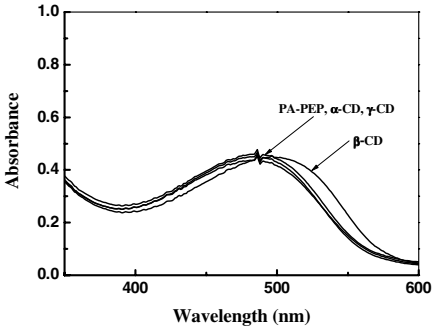


Figure 2.
UV-visible spectra of PA-PEP solutions (0.1 mM) in the presence of cyclodextrins in deionized water.

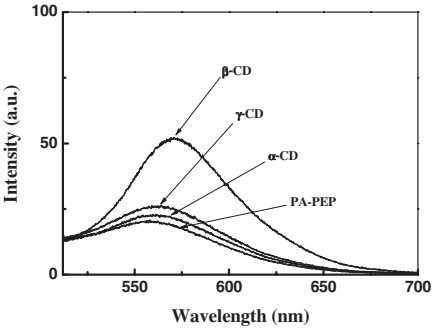


Figure 3.
Fluorescence spectra of solutions containing PA-PEP (0.1 mM) and cyclodextrins (10 mM) in deionized water (excitation at 496 nm).

displayed the UV-visible spectra of PA-PEP which contains an ionic polyacetylene absorption band at *ca.* 500 nm.

The next phase of this effort focused on an investigation of changes in the electronic properties of PA-PEP promoted by interactions with cyclodextrins. UV-visible spectroscopic monitoring of PA-PEP, incubated in aqueous solutions containing cyclodextrins (Figure 2) showed that the absorption maximum of the polymer shifts from 490 to 502 nm in the presence of β-CD. In contrast, α- and γ-CD have little effect on the absorption maximum of this polymer. The bathochromic shift induced by β-CD suggests that effective conjugation length of PA-PEP increases when it interacts with this cyclic polysaccharide. This is likely a consequence of the polymer adopting a more planar conformation when it forms a complex with β-CD.

More interesting results were obtained when interactions between the CDs and PA-PEP were monitored by using fluorescence spectroscopy (Figure 3). An increase in the fluorescence intensity of PA-PEP was observed upon addition of all of CDs. The emission enhancement was most prominent with β-CD which also caused the emission maximum of PA-PEP to shift from 558 to 571 nm.

The cyclodextrin-induced increase of the fluorescence intensity of the polyacetylene containing ionic side chains is a very interesting observation. Since α-, β-, and γ-CDs are structurally very similar except for their cavity sizes, the selective emission enhancement caused by β-CD can be attributed to the selectivity for complex formation with PA-PEP by this cyclic polysaccharide. We speculate that the phenylethyl groups in PA-PEP form inclusion complexes with β-CD as pictured in Figure 4. The detailed mechanism and nature of complex formation are under current investigation.

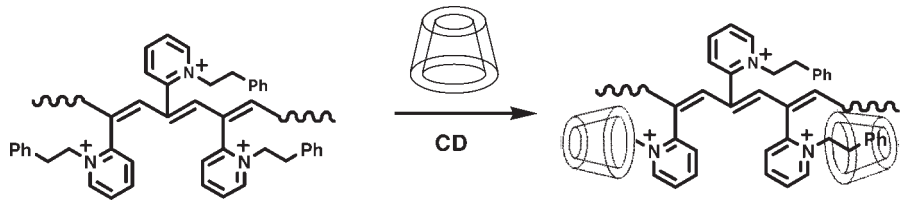


Figure 4.
Schematic representation of possible complexes formed between PA-PEP and cyclodextrin.

Conclusion

We have prepared a water-soluble, ionic polyacetylene that contains phenylethylpyridinium side chains by using the N-alkylation reaction of 2-ethynylpyridine with (2-bromoethyl)benzene in hot MeOH. The process results in direct polymerization of the acetylene without the need for an initiator or catalyst. A bathochromic shift of the absorption maximum as well as an increase in its fluorescence intensity are observed when the ionic polyacetylene is mixed with β-cyclodextrin. The results provide a foundation for the design of new and interesting chemosensors based on ionic polyacetylenes.

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