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Synthesis of Polymeric Fluorescent Chemosensor for the Recognition of Fe^{3+} Ion

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We have synthesized a polymer with acridine group in its main chain and found that the polymer solution showed spectrometric and fluorometric changes upon addition of ferric ion (Fe^{3+}) specifically indicating that the polymer would be a useful sensing material for ferric ion.

Keywords: polymeric fluorescent chemosensor; acridine; ferric ion sensing; molecular recognition

INTRODUCTION

Currently highly sensitive and selective molecular sensory materials have received considerable attention [1-3]. In particular, a lot of researches on design and construction of chemosensory systems that are capable of detecting metal ions in both a real-time and reversible fashion are performed [4,5]. Among these researches on chemosensors polymers containing molecular recognition sites have also been studied as high sensitive chemosensors. Recently conjugated polymers having coordination sites were synthesized for application to fluorescent sensors for metal ion sensing, nonlinear optics, and organic light emitting diodes. In the conjugated polymer systems, introduction of long side chain into their molecular backbone is needed to be soluble in solvents.

Acridine is a well-known luminophore and has interacting sites with metal ion. We, therefore, thought that acridine moiety could be

introduced into a main chain via simple condensation polymerization [6]. In this paper, we are reporting the synthesis of fluorescent polymer containing acridine moiety in the main chain and sensing ability (selectivity and sensitivity) of the polymer toward metal ion.

EXPERIMENTAL

Polymer-metal complex solutions used for absorption and fluorescence measurements were prepared from a polymer solution (3ml, 3.66×10^{-5}M (based on acridine unit) in DMF) plus small amount of HCl (5μl) and aqueous metal salt solutions at ambient temperature.

RESULTS AND DISCUSSION

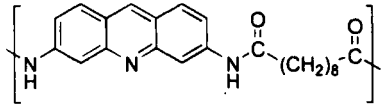

FIGURE 1. Chemical structure of the polymer.

The polymer with acridine units in its main chain was synthesized via solution polymerization in NMP (FIGURE 1). FT-IR spectrum of the polymer showed characteristic bands of functional groups such as carbonyl group (C=O) at 1650cm^{-1} and C-N at 1404cm^{-1} implying the polymerization was successfully accomplished. The molecular weight of the polymer was found to be 10,000 (M_n) and 25,500 (M_w) according to GPC measurement.

The polymer shows two absorption maxima (λ_{max}) at 296 and 386nm in DMF before addition of small amount of HCl as shown in FIGURE 2. We, however, found that the λ_{max} at 386nm was shifted to 422nm upon addition of HCl (5μl into 3ml polymer solution). Clearly the polymer exhibits substantial red-shift in absorption spectra when small amount of

HCl is added. More interestingly, in the case of Fe^{3+} ion as an analyte, new absorption maximum at 368nm was observed. Therefore according to this ion-dependent responsive optical properties it seems possible to detect ferric ion specifically by using the polymer we synthesized. We also have investigated ion-responsive property with other metal ions such as Cu^{2+}, Ca^{2+}, Ba^{2+}, K^{+}, Eu^{3+}, and UO_2^{2+} and found these ions did not have any significant effect on the absorption of the polymer. However addition of trace amount of Fe^{3+} causes a changes in absorption of the polymer solution.

Ion-responsive properties of the polymer recorded by fluorescence emission spectra are also informative. Some representative results are illustrated in FIGURE 3. It is apparent that the ferric ion causes

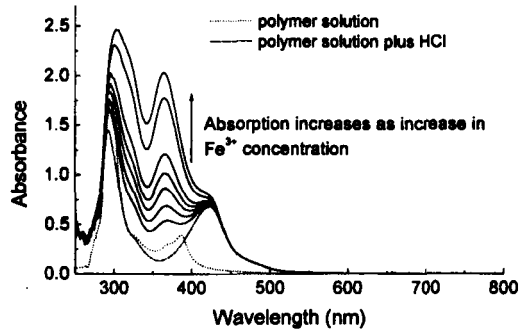

FIGURE 2. Absorption changes upon addition of ferric ion.

quenching the fluorescence of the polymer. Linear relationship between fluorescence intensity and ferric ion concentration is clearly shown. In contrast the addition of Cu^{2+} and UO_2^{2+} to the solution of the polymer led to non-efficient quenching. The fluorescence quenching of the polymer

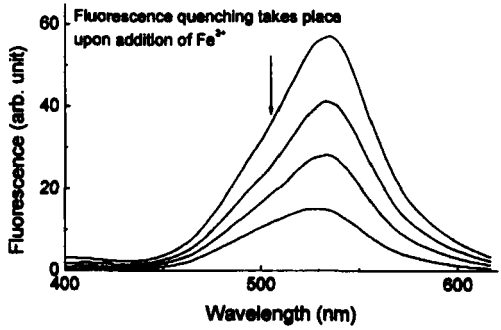

FIGURE 3. Fluorescence emission spectra recorded in DMF solution with ferric ion. Polymer concentration is 3.66×10^{-5}M and ferric ion concentration is 0, 0.033, 0.067, 0.133mM (up to down). Excitation wavelength is 366nm.

with Fe^{3+} ion is thought to be caused by an electron or energy transfer reaction between the metal complexes and the polymer backbone.

CONCLUSION

A novel polymer containing acridine segments in the main chain was synthesized and its ability to sense metal ion was investigated by the absorption and fluorescence emission spectra. The fluorescence of the polymer solution was quenched by the addition of Fe^{3+} ion. We can conclude that the polymer as synthesized is a good fluorescent sensing material for ferric ion.

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