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Synthesis of Congo Red linked with alkyl amide polymer and its optical ion-sensing property

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Summary

The synthesis and metal ion responsive properties of Congo Red-based polyamide are reported. The polymer was prepared by simple interfacial polymerization between Congo Red and sebacoyl chloride. The polymer showed decrease in electronic absorption when exposed to metal ions. The absorbance tends to decrease linearly in a measurable range according to metal ion concentration. It is found that the polymer showed high sensitivity toward Ca^{2+} and Fe^{3+}.

Introduction

Dyes have been widely used as indicators in analytical technique due to potential availability of dye indication reaction and dye-coupled reaction for analytical measurement (1). Ion-selective chromogenic dyes have been used for colorimetric determination of most commonly found metal ions. These dyes can be used as selective and sensitive photometric reagents and can be used in fabrication of chemical sensors or probes because these dyes bring about changes in specific color or optical absorption when they interact with ions (2-5).

A lot of interest in chemical sensors consisting of immobilized dyes coupled to a spectrometer through fiber optics to determine the concentration of alkali and alkaline earth metals (6-8). Upto now, to our knowledge there has been few reports focused on polymer-based optical chemical sensors (not fluorescent chemosensors (9,10)) for ions. Compared to low molecular weight dyes, polymers can be easily fabricated into transparent films with only a low tendency to recrystallize. Flexible chains or large substituents can be introduced to the polymers to achieve reasonable solubility and thermal properties from a technical point of view (11).

We, therefore, designed a polyamide consisting of indicator dye (Congo Red) and flexible main chain (aliphatic hydrocarbon from sebacoyl chloride) to obtain a suitable properties such as solubility and processability. Ion-responsive optical properties of the polymer were investigated upon exposure to various metal ions in detail.

Experimental

Polymer synthesis

The polymer synthesis is shown in Scheme. The polymerization was carried out via low temperature interfacial polycondensation under vigorous stirring. Congo Red (Acros) was used without further purification Thin layer chromatography (TLC) of Congo Red showed a single spot (developing agent : water/ethanol) (12). Into a 100ml flask 1.0g (1.44mmol) of Congo Red, 0.24ml

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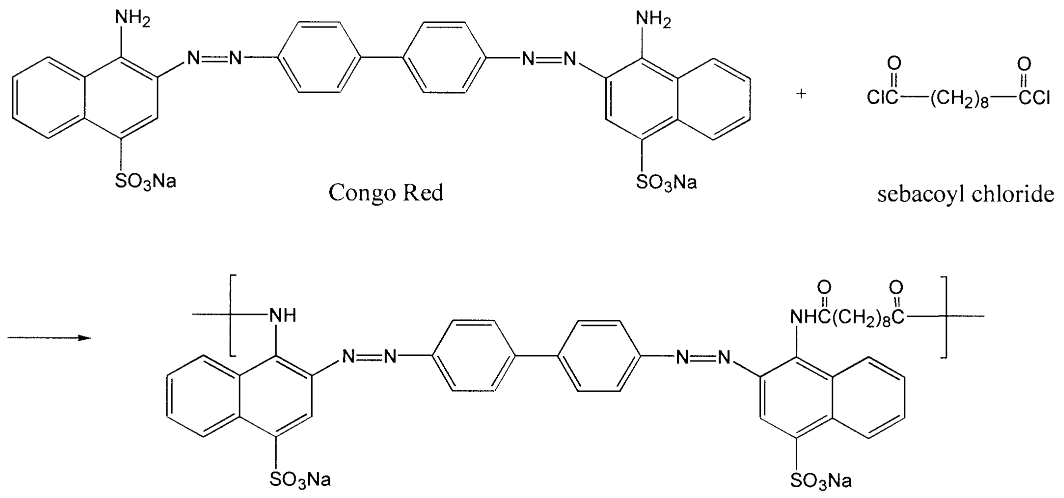

Scheme Synthesis of the polymer

(3.0mmol) of pyridine, and 50ml water were added. After complete dissolution of the monomer 0.30ml (1.44mmol) of sebacoyl chloride (Fluka) in 10ml chloroform was added dropwise while stirring. The color of the mixture changed from red to dark blue after 30min and maintained dark blue until the end of polymerization. The polymerization reaction was carried out with vigorous agitation for 20hr. After the reaction the mixture was poured into 200ml ethanol, changing the color to red and this was evaporated in rotary evaporator. Then the solid was washed with ethanol and collected by filtration. The solid product was washed with ethanol twice and dried in a vacuum oven at 75°C for 24hr. The polymer obtained was dark red powder (0.40g, 40.2% yield).

IR (KBr pellet) : 3382 (m ; N-H), 2930, 2850 (s ; C-H), 1697 (s ; C=O amide), 1370 (s ; C-N), and 1150cm^{-1} (s ; sulfonate). ^{1}H NMR (DMSO and DMF) : δ = aromatic C-*H* : 8.75 (d, 2H), 8.44 (d, 2H), 8.30 (s, 2H), 8.11 (d, 4H), 7.95 (d, 4H), 7.53 (m, 4H) ; N-*H* : 3.6 (s, 2H) ; aliphatic C-*H* : 2.19 (m, 4H), 1.46 (s, 4H), 1.14 (m, 8H).

Characterization

Infrared spectra were recorded on a MAGNA-IR 560 spectrometer using KBr pellets. Absorption spectra were taken on a Hewlett-Packard 8452A spectrophotometer. ^{1}H NMR spectra were taken on a Bruker ARX-300 spectrometer operating at 300MHz. Thermogravimetric analysis (TGA) was conducted with a Perkin-Elmer TGA 7 equipped with TGA 7/3 Instrument Controller with heating rate of 20°C/min under nitrogen. Matrix Assisted Laser Desorption Ionization-Time of Flight (MALDI-TOF) mass spectrometry was performed with a PerSeptive Biosystems Voyager-DE spectrometer using delayed extraction mode with an acceleration voltage of 25keV. Matrix solution used was dithranol in ethanol (10mg/ml).

Ion responsive property measurement

Polymer-metal complex solutions used for optical measurements were prepared from a polymer solution (3ml, 1.0 X 10^{-5}M (based on repeating unit) in ethanol/water 1/9, v/v) and aqueous metal salt solutions at ambient temperature. The metal salt used were cupric sulfate, barium nitrate, ferric nitrate, potassium nitrate, calcium carbonate, and uranyl nitrate. UV/visible spectra of the polymer solutions were recorded upon addition of metal solutions with different concentrations.

Results and Discussion

The polyamide containing Congo Red dye in its main chain was synthesized via interfacial polycondensation. The color of the reaction mixture was changed from red to blue and finally to red. It is well known that the color of Congo Red changes from red to blue when strong acid is added. We, therefore, thought the reaction was accomplished releasing HCl during the polymerization. FT-IR spectra of the polymers showed characteristic bands of the functional groups expected such as carbonyl group (C=O) near 1697cm^{-1} (newly formed) and sulfonate near 1150cm^{-1}. According to MALDI-TOF, the molecular weight of the polymer was found to be 3186. From the TGA data, the polyamide as synthesized has two thermal degradations at 227 and 392°C. It is presumed that the initial decomposition corresponds to the loss of sulfonic acid group and the second thermal degradation is attributed to polymer backbone degradation (13,14). The polymer was found to be soluble in ethanol, DMF, and DMSO.

The polyamide with Congo Red shows an decrease in π - π * transition at 498nm in the azo unit upon exposure to metal ions suggesting that the electrons in the azo groups are affected by metal ions used (Fig. 1 and 2). In the cases of other metal ions such as UO_2^{2+}, Ba^{2+}, Cu^{2+}, and K^+, optical absorption of the polymer solutions decreased in a similar manner. Each solution was maintained neutral to prevent the additional effect of pH on the interaction of polymer with metal ions. It has been observed that even addition of 1.67 μM of Ca^{2+} leads to a noticeable change in the absorbance spectrum. Shifts of the absorption maxima (λ_{max}) were also observed. However we could not observe remarkable instant color changes upon the addition of metal salts to the polymer solutions as shown in Table 1. From these results we thought that conformational changes in azo units (trans to cis) are not involved in this metal-sensing process. We also compared the chromism and absorption changes upon addition of metals between monomeric Congo Red and Congo Red polymer as synthesized. Noticeable difference on the optical properties were not found as we expected. It is also presumed that the dependence of molecular weight on the optical properties was negligible in this report because observed optical properties of monomeric and polymeric Congo Red were similar. Once the polymer interacted with the metal ions, the optical changes such as absorptions and λ_{max} shifts were found to remain unchanged before addition of more metal ions. We, therefore, concluded that the sensing procedure were irreversible.

Table 1. Absorption responses of the polymer upon complexing with metal ions

	ion free	Ca^{2+}	Fe^{3+}	UO_2^{2+}	Ba^{2+}	Cu^{2+}	K^+
absorption (nm)	498	518	500	510	490	494	490

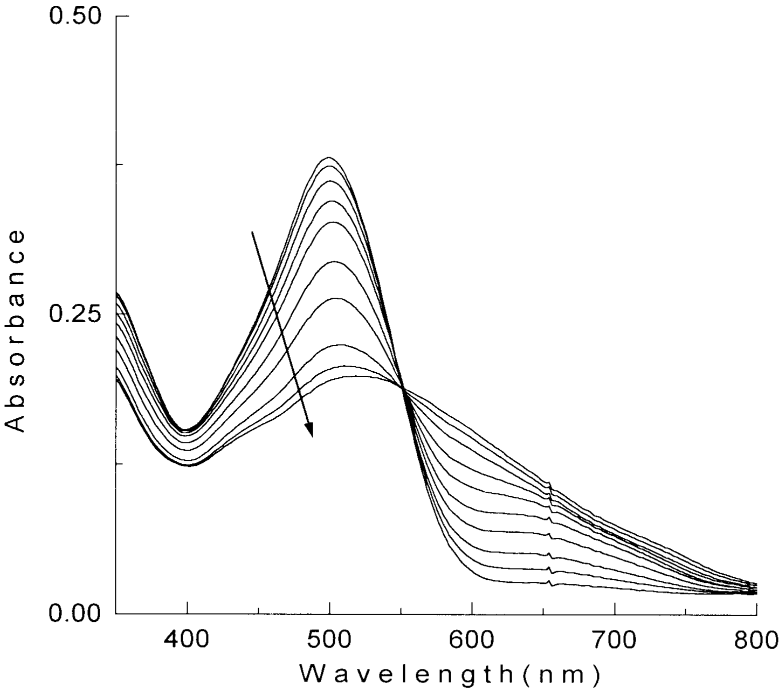

Fig.1. Effect of Ca^{2+} concentration on the absorption spectra of the polymer in ethanol/water ($1.0x10^{-5}M$) ; $[Ca^{2+}]$=0, 1.67, 3.34, 5.01,6.68, 8.34, 10.0, 11.7, 13.3,15.0μM. Arrow represents a direction of the absorption changes.

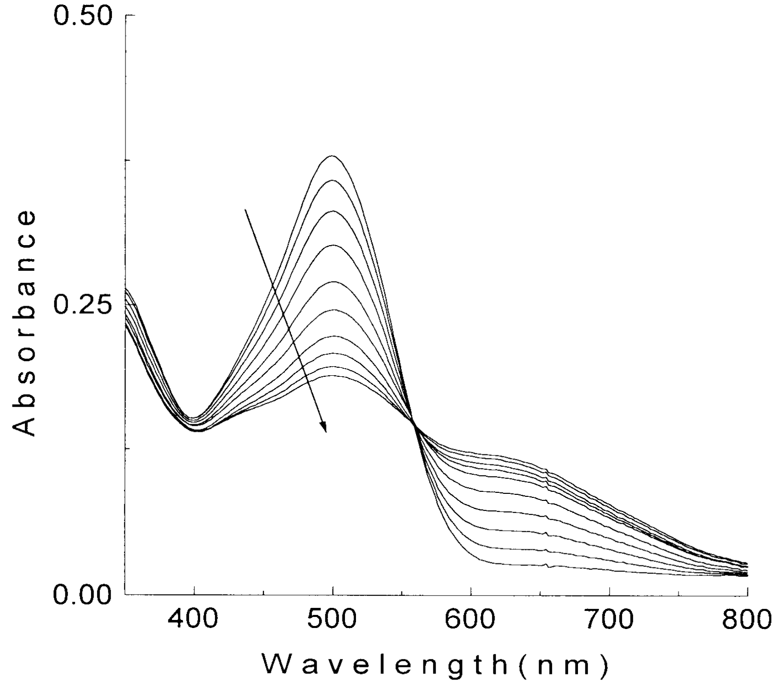

Fig.2. Effect of Fe^{3+} concentration on the absorption spectra of the polymer in ethanol/water ($1.0x10^{-5}M$) ; $[Fe^{3+}]$=0, 3.33, 6.66, 9.99,13.3, 16.6, 19.9, 11.7, 23.3, 26.6, 29.9 μM. Arrow represents a direction of the absorption changes.

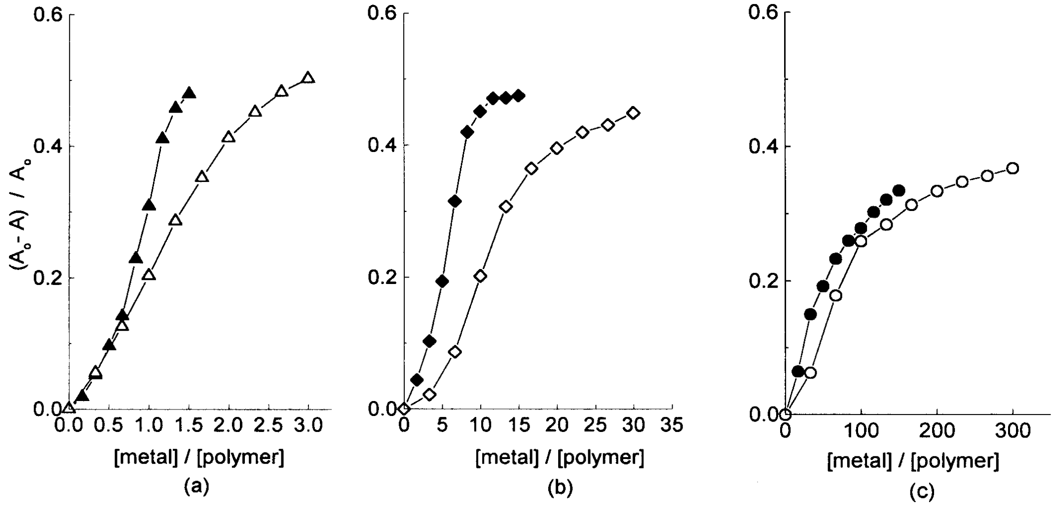

Fig.3. Relationship between absorbance at λ_{max} and metal ion concentrations : (a) ▲;Ca^{2+}, △ ;Fe^{3+}, (b) ◆;UO_2^{2+}, ◇;Ba^{2+}, and (c) ●;Cu^{2+}, ○;K^+. [polymer]=1.0×10^{-5}M
A_o is the absorbance of polymer solution and A corresponds to the absorbance when metal with known concentration is added.

Sensitivity of the polymer toward various metal ions are shown in Fig.3. The sensitivity toward Ca^{2+} and Fe^{3+} ions are about 10 to 10^2 times higher than other metal ions. This encourages us because this material can be used as sensitive sensory material for Ca^{2+} and Fe^{3+}

Conclusion

We synthesized polyamide containing Congo Red dye moieties in the main chain via interfacial polycondensation. We observed that the polymer could act as a visible absorbing material for detecting trace amount of metal cations such as Ca^{2+}, Fe^{3+}, UO_2^{2+}, Ba^{2+}, Cu^{2+}, and K^+ in aqueous media. The polymer showed specific sensitivity to Ca^{2+} and Fe^{3+}. We concluded that this material is promising to use as a sensory material for metal ions, especially Ca^{2+} and Fe^{3+}. We are currently working on thin film formation via self-assembled layer-by-layer deposition (14) between the polyamide as a polyanion and commercially available polycation to use as an optical sensor.

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