A Novel Colorimetric Sensing Material, Poly(γ-Glutamic acid)-*graft*-3, 4-Dihydro-3-(2′-ethyl hydroxyl)-6-Ethyl-1,3,2*H*-Benzoxazine (γ-PGA-*graft*-ethyl-Bx), for Iron(III) Ions

(Bahan Pengesan Kolorimetri Baru, Poly(γ-Asid Glutamic)-*graf*-3, 4-Dihidro-3-(2′-etil hidroksil)-6-Etil-1,3,2*H*-Benzoksazin (γ-PGA-*graf*-etil-Bx) untuk Iron Ferum (III))

Nu-Orn Choothong, Attaphon Kaewvilai, Apirat Laobuthee* & Amornrat Lertworasirikul

ABSTRACT

A novel rapid ion colorimetric sensing material for iron(III) ions was developed from poly(γ-glutamic acid) and 3,4-dihydro-3-(2′-ethyl hydroxyl)-6-ethyl-1,3,2H-benzoxazine (ethyl-Bx). The benzoxazine as an ionophore segment was grafted into γ-PGA backbone via the esterification reaction, which is a simple and effective reaction. The structure of γ-PGA-graft-ethyl-Bx was characterized by using FT-IR and ¹H-NMR. The most attainable degree of conversion was 25%. The γ-PGA-graft-ethyl-Bx showed a highly selective and sensitive recognition toward iron(III), which was clearly observable with the naked eye. The iron(III) ions sensing property of γ-PGA-graft-ethyl-Bx was further examined by using photometric titration method. After the interaction between the γ-PGA-graft-ethyl-Bx and iron(III) ions was formed, the solution of the polymer in dimethyl sulfoxide was changed from clear and colorless to red color, resulting in the shift of the maximum wavelength from UV to visible range.

Keywords: Benzoxazine; colorimetric sensing materials; photometric titration method; transition metal ion; γ-PGA

ABSTRAK

Bahan sensor kolorimetrik ion pantas yang baru untuk ion ferum(III) telah dihasilkan daripada asid poli(γ-glutamat) dan 3,4-dihidro-3-(2′-etil hidroksil)-6-etil-1,3,2H-benzoksazin (etil-Bx). Benzoksazin yang bertindak sebagai segmen ionofor telah digabungkan dengan struktur utama γ-PGA melalui tindak balas esterifikasi, yang merupakan tindak balas mudah dan berkesan. Struktur γ-PGA-graf-etil-Bx dikelaskan dengan menggunakan FT-IR dan ¹H-NMR. Perubahan yang paling tinggi boleh dicapai adalah 25%. γ-PGA-graf-etil-Bx menunjukkan keserasian yang sangat memilih dan sensitif terhadap ferum(III), yang boleh diamati dengan mata kasar. Sifat penderiaan ion ferum (III) bagi γ-PGA-graf-etil-Bx telah dikaji dengan lebih lanjut menggunakan kaedah pentitratan fotometri. Setelah interaksi antara γ-PGA-graf-etil-Bx dan ion ferum (III) terbentuk, larutan polimer dalam dimetil sulfoksida telah berubah daripada jernih dan tidak berwarna kepada warna merah, lantas menghasilkan perubahan gelombang yang maksimum daripada UV kepada julat yang boleh dilihat.

Kata kunci: γ-PGA; bahan sensor kolorimetrik; benzoksazin; ion logam transisi; kaedah titrasi fotometri

Introduction

Iron is a common contaminant often present in the waste water from the industrial sites or iron smelter industries. In nature, iron is usually found in its oxidized form as an iron(III) oxide, which is insoluble and non-degradable. The ingestion or consumption of iron is especially harmful to human. After ingestion, the iron passes deeper into the body and damages the internal organs, particularly the brain and the liver. The body goes into shock and death from liver failure. Despite the numerous water treatments, iron is still present in the water due to the dissolution of pipes and the solder in older buildings. Thus, many independent and government organizations are concerned and set the permissible limit of iron(III) level in waste water and drinking water. These factors demonstrate the need for the development of a rapid, simple and easily handled equipment for detecting iron(III) ions in residential and environment water samples.

The sensor technology is much simpler in an instrument and sample preparation. Many sensors for iron detection have been investigated (Hassan et al. 2009; Wang et al. 2010) but the selective colorimetric sensor has been attracted due to the excellent sensitivity, rapid response, the ability to do the detection in a non-destructive manner and cost-effective. The sensing method of colorimetric detection has been widely utilized for quantifying various molecules (Liang et al. 2007; Maity & Govindaraju 2011). Most of the generated colorimetric sensors are based on the complex formation between the heavy metals and the ligand as a substrate (Sun et al. 2011).

Benzoxazines, heterocyclic compounds consisting of benzene and oxazine rings, were synthesized from *p*-substituted phenolic compounds, primary amines and para-formaldehyde via Mannich reaction (Holly & Cope 1944). Benzoxazines could form complex with rare earth metal (Veranitisagul et al. 2011), alkali, alkali earth and transition metals (Panushkin et al. 2007; Rungsimanon et al. 2008) at nitrogen and oxygen positions. Due to their chemical structures, many researches have been focused on their supramolecular structures and interactions with metal ions. Laobuthee et al. (2003) found that intermolecular hydrogen bonding plays an important role and the host-guest formation was occurred via molecular assembly. It was noted that although the type of metal ion was changed, the host always interacted at the same position. Phongtamrug et al. (2006) confirmed the host-guest property of benzoxazine via the inclusion phenomenon. The results suggest that the nitrogen atom and oxygen atom play an important role in interaction with heavy metal by sharing their lone pair electrons. Therefore, benzoxazines are attractive for the development of sensing material for metal ions.

Additionally, non-toxic and biodegradable materials have been applied for use in the field of bio-sensor during the past decade (Gu et al. 2011). Poly(γ-glutamic acid) is a natural components existing in a natto, a traditional Japanese food. It is produced by fermentation of soy bean by *Bacillus subtilis*. The properties of the poly(γ-glutamic acid) are water soluble, biodegradable and non-toxic. It is very useful in many fields such as drug delivery carrier and tissue engineering material (Takami et al. 2005). High proportion of carboxylic functional group in γ-PGA provides binding properties for metal ions. A number of studies using this polymer for the removal of metal ions from waste water have been reported (Shih et al. 2003; Taniguchi et al. 2005, 2005a). Cross-linked poly(γ-glutamic acid) was found to be able to form the interaction with iron(III) ions (Taniguchi et al. 2005).

This work attempted to develop a novel sensing material for iron(III) ions by combining a chelating property of γ-PGA with the supramolecular and ion extraction properties of benzoxazine monomer. Here, 3,4-dihydro-3-(2′-ethyl hydroxyl)-6-ethyl-1,3,2*H*-benzoxazine is grafted into the poly(γ-glutamic acid) main chain via the esterification reaction. The selectivity and sensitivity as a colorimetric sensor for iron(III) ions was qualitatively and quantitatively studied by a photometric titration method.

Experimental Details

MATERIALS

γ-PGA (poly(γ-glutamic acid), M_w = 170,000) was supplied from Wako (Japan). Ethyl-benzoxazine (3,4-dihydro-3-(2′-ethyl hydroxyl)-6-ethyl-1,3,2*H*-benzoxazine) was synthesized as reported elsewhere (Attaphon et al. 2012). Acetonitrile (CH_3CN) was provided from Labscan

(Thailand). Sulfuric acid from Carlo Erba was used as a catalyst. Dimethyl sulfoxide (DMSO) was purchased from Sigma-Aldrich (Germany). Iron(III) nitrate salts ($Fe(NO_3)_3 \times 9H_2O$) was obtained from Ajax (New Zealand). All chemicals used in this work were of analytical grade and used without further purification.

INSTRUMENTS

Fourier transform infrared (FTIR) spectra were recorded on an Alpha FTIR spectrometer instrument from Bruker within the frequency range of 4000-600 cm^{-1} and resolution of 4 cm^{-1}. Proton nuclear magnetic resonance (^{1}H-NMR) spectra were measured on a varian mercury-400 spectrometer working at 400 MHz. Deuterated dimethyl sulfoxide (DMSO-d6) was used as a solvent and tetramethylsilane (TMS) was used as an internal reference. UV-visible spectra and maximum absorbance were recorded on a Shimadzu UV-1700 spectrophotometer from 190 to 800 nm.

PREPARATION AND CHARACTERIZATION OF γ-PGA-*GRAFT*-ETHYL-BX

γ-PGA-*graft*-ethyl-Bx was prepared from γ-PGA and ethyl-benzoxazine monomer via esterification reaction. The synthesis schematic of the grafted copolymer is shown in Figure 1.

γ-PGA (1.0 g, 2.0 mmol) dispersed in CH_3CN (100 mL) was prepared in a two-necked round bottoms flask equipped with a magnetic stirring bar, a condenser and a dropping funnel. A catalytic amount of H_2SO_4 was added to the solution. The slurry was refluxed and stirred at 80°C for 1 h. The ethyl-Bx (1.5 g, 7.75 mmol) dissolved in CH_3CN (80 mL) was then drip-fed into the slurry. The mixture was further refluxed at 80°C for 2 h. Then, the yellow solid product was filtered, washed several times with distilled water and acetone and dried overnight in an oven at 60°C.

The grafted copolymer product was characterized by FT-IR and ^{1}H-NMR. The degree of grafting was calculated by ^{1}H-NMR.

INVESTIGATION ON IRON(III) IONS RESPONSIVE PROPERTIES OF γ-PGA-*GRAFT*-ETHYL-BX

The iron(III) ions responsive behavior were investigated in aqueous solution. The γ-PGA-*graft*-ethyl-Bx powder (2.0 mg) was added in to the aqueous solution of iron(III) nitrate (5 mM). The mixture was dramatically shaken for 5 min. After that the solution was detected by naked eye and UV-visible spectrophotometer.

The iron(III) ions responsive properties were qualitatively and quantitatively studied with the photometric titration method in a DMSO solution. Different volumes of 0.008 mM of γ-PGA-*graft*-ethyl-Bx in DMSO solutions (0.100, 0.200, 0.300, 0.400, 0.500, 0.600, 0.800, 1.000, 1.200, 1.400, 1.600, 1.800, 2.000, 2.500, 3.000, 3.500, 4.000, 4.500 and 5.000 mL) were prepared and then each solution was added into 5.000 mL of DMSO solutions of the iron(III) nitrate (0.40 mM). The mixed solutions
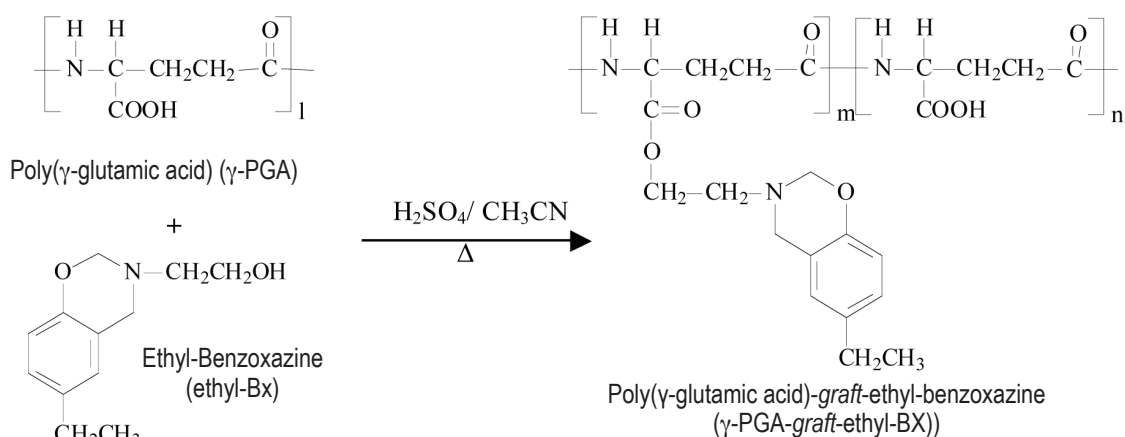
FIGURE 1. Synthesis schematic of γ-PGA-*graft*-ethyl-Bx

were adjusted with DMSO to attain to a total volume of 10.000 mL. After the mixed solutions were left at room temperature for 30 min, their absorbances were detected by UV-visible spectrophotometer.

RESULTS AND DISCUSSION

PREPARATION AND CHARACTERIZATION OF γ-PGA-*GRAFT*-ETHYL-BX

FTIR spectra of γ-PGA, ethyl-Bx and the product are shown in Figure 2. γ-PGA showed the characteristic peaks at 3283, 1640 and 1730 cm^{-1} (Figure 2(a)). The first two positions related to the amide bond and the last position referred to a carbonyl group. Figure 2(b) shows the absorption peaks of ethyl-Bx at 1504, 1120 and 871 cm^{-1} referred to an oxazine ring (trisubstituted on benzene), ether aromatic

(Ar-O-C) and benzene ring out of plane, respectively (Attaphon et al. 2012). It was found that the characteristic peaks of the product appeared at 1733, 1517, 1164 and 901 cm^{-1} which correspond to the carbonyl bond, oxazine ring (trisubstituted on benzene), ether aromatic (Ar-O-C) and benzene ring out of plane, respectively (Figure 2(c)).

The ^{1}H-NMR spectrum of γ-PGA-*graft*-ethyl-Bx is shown in Figure 3. The signals of methylene protons (4H), methine proton (1H) and -NH amide proton (1H) from the γ-PGA backbone are shown at δ_H = 1.46-2.11, 2.11-2.41 and 8.04-8.28 ppm, respectively, while the signals of ethyl proton (5H), oxazine ring protons (2H) and aromatic protons (3H) from the ethyl-Bx attached to the carboxyl group of the γ-PGA backbone were shown at δ_H 0.97-1.21, 2.90-2.92 and 6.58-7.31 ppm, respectively. These results implied that the ethyl-Bx was successfully grafted into the γ-PGA backbone.
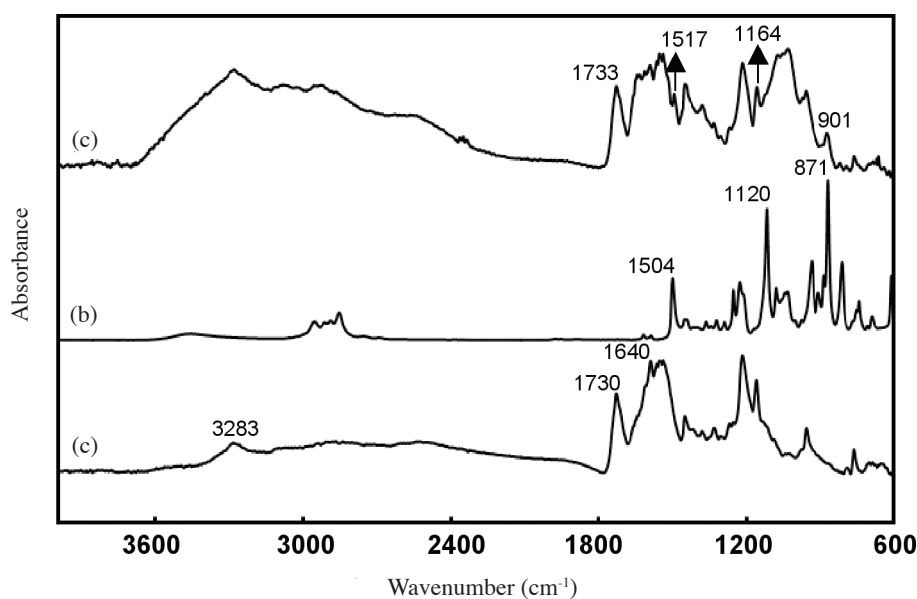

FIGURE 2. FT-IR spectra of (a) γ-PGA, (b) Bx and (c) γ-PGA-*graft*-Bx

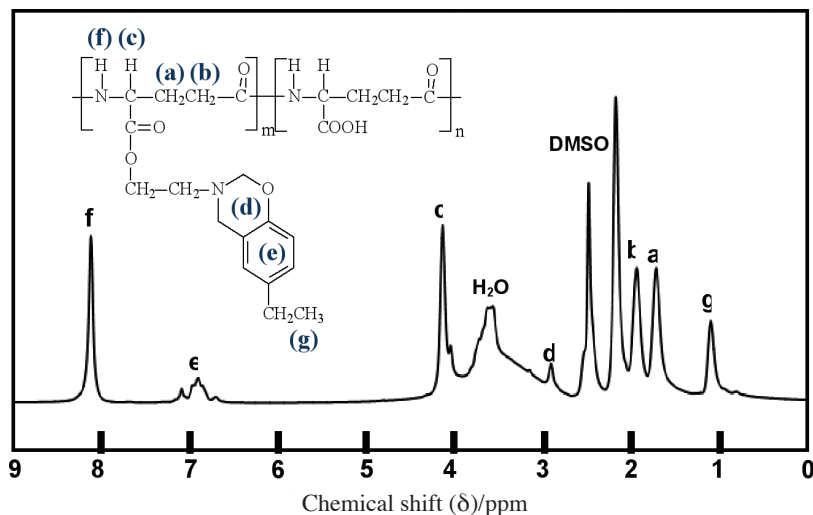FIGURE 3. ¹H-NMR spectrum of γ-PGA-*graft*-ethyl-Bx in DMSO-d6

The integration ratio of the amide proton (8.04-8.28 ppm) of γ-PGA and the aromatic proton (6.58-7.31 ppm) of ethyl-Bx was evaluated in the order to calculate the degree of grafting. The degree of ethyl-Bx grafting was found to be 25%. The characterization results of γ-PGA, ethyl-Bx and the product are summarized as follows:

Ethyl-Bx: FT-IR (KBr, cm^{-1}): 3600-2900 (br, OH), 2877 (s, CH), 1501 (oxazine ring), 1226 (s, CN), 1126 (s, CO), 1027 (s, Ar-O-C), 871 (s, CH) ;¹H NMR (400 MHz, CDCl$_3$, ppm): δ$_H$ 2.21 (3H, s, Ar-**CH$_3$**), 2.93 (2H, t, **CH$_2$**CH$_2$OH J_2 = 3.11 Hz), 3.84 (2H, t, CH$_2$**CH$_2$**OH J_2 = 3.11 Hz), 4.33 (2H, s, Ar-**CH$_2$**-N), 4.83 (2H, s, O-**CH$_2$**-N), 6.70 (H, d, **Ar-H**, J_3 = 2.34 Hz), 6.71. (H, s, **Ar-H**), 6.77 (H, d, **Ar-H**, J_3 = 2.34 Hz).

γ-PGA: FT-IR: 3283 (br, OH), 3000-2200 (br, CH), 1730 (s, C=O (carboxy)), 1640 (s, C=O (amide)), 1225 (s, C-O); ¹H NMR (400 MHz, DMSO-d$_6$, ppm): δ$_H$ 1.75, 1.95 (2H(diastereotropic hydrogens), t, CH$_2$CH$_2$C=O J_2 = 6.90 Hz), 2.20 (2H, t, CH$_2$CH$_2$C=O J_2 = 6.90 Hz), 4.14 (H, s, NHCHCH$_2$), 8.13 (H, d, NH, J_3 = 5.91 Hz).

γ-PGA-*graft*-ethyl-Bx: FT-IR: 3600-3200 (br, OH), 2978-2450 (br, CH), 1727 (s, C=O (carboxy)), 1613 (s, C=O (amide)), 1494 (oxazine ring), 1225 (s, C-O), 1073 (s, CO), 878 (s, CH); ¹H NMR (400 MHz, DMSO-d$_6$, ppm): δ$_H$ 1.78 (2H, t, CH$_2$CH$_2$C=O J_2 = 5.84 Hz), 2.00 (2H, t, CH$_2$CH$_2$C=O J_2 = 5.84 Hz), 2.12 (3H s, Ar-CH$_3$), 4.23 (H, d, NHCHCH$_2$ J_3 = 7.88 Hz), 2.94 (2H, s, O-CH$_2$-N), 6.87 (H, d, Ar-H, J_4 = 12.6 Hz), 7.09 (H, d, Ar-H, J_4 = 12.6 Hz), 7.16 (H, s, Ar-H), 8.16 (H, d, NH, J_5 = 7.35 Hz).

INVESTIGATION ON IRON(III) IONS RESPONSIVE PROPERTIES OF γ-PGA-*GRAFT*-ETHYL-BX

The iron(III) ions responsive properties of γ-PGA-*graft*-ethyl-Bx were investigated with naked eye (Figure 4). After the γ-PGA-*graft*-ethyl-Bx was added into the aqueous solution of iron(III) nitrate, color of the solution has changed from clear to purple. This color transition phenomenon was further examined by using UV-visible spectrophotometer.

Figure 5(a) shows the UV spectrum of an aqueous solution of iron(III) nitrate. The maximum absorbance was observed at 294 nm. The maximum absorption peak was shifted to 520 nm after the γ-PGA-*graft*-ethyl-Bx was added into the solution Figure 5(b). This result indicated that γ-PGA-*graft*-ethyl-Bx formed complex with the iron(III) ions resulting in color transition of the solution.

γ-PGA-*graft*-ethyl-Bx   Aqueous solution of   γ-PGA-*graft*-ethyl-Bx-iron(III) complex
                                iron(III) nitrate   in an aqueous solution
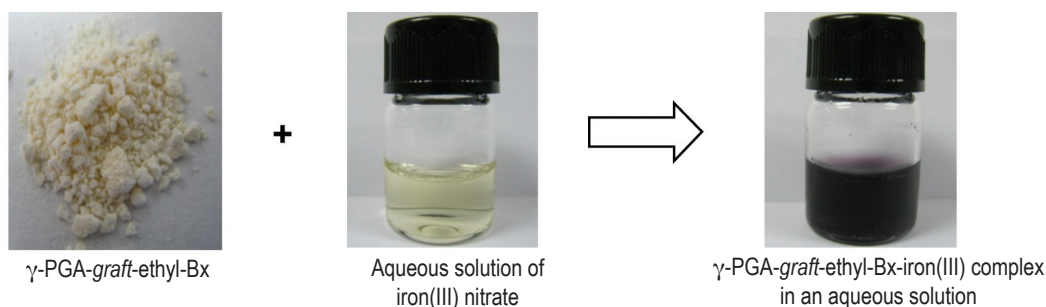
FIGURE 4. The color transition of aqueous solution of iron(III) nitrate
after mixing with γ-PGA-*graft*-ethyl-Bx

Iron(III) ions responsive properties of γ-PGA-*graft*-ethyl-Bx was additionally observed in DMSO solution. The solution of γ-PGA-*graft*-ethyl-Bx in DMSO solution was mixed with iron(III) nitrate in DMSO solution. Then the color of the mixture was immediately changed from clear to red (Figure 6). This color transition phenomenon was further confirmed by using UV-visible spectrophotometer.

Figure 7 shows the UV spectra of solution of γ-PGA-*graft*-ethyl-Bx in DMSO, iron(III) nitrate in DMSO and the mixed solution of γ-PGA-*graft*-ethyl-Bx and iron(III) nitrate in DMSO. The maximum absorption peak shifted to 501 nm after the complex between the γ-PGA-*graft*-Bx and iron(III) ions was formed. The results indicated that γ-PGA-*graft*-ethyl-Bx showed sensitivity to iron(III) ions in both aqueous and DMSO solutions. It is surmised that the interaction between γ-PGA-*graft*-ethyl-Bx and iron(III) ions occurred at oxygen and nitrogen atoms of the benzoxazine since these two positions of the benzoxazine are the active sites for forming the complex with metal ions (Chirachanchai et al. 2000; Phongtamrug et al. 2006).

The qualitative analysis to determine a ratio of the polymer to iron(III) ions in the complex was carried out by using a photometric titration method. The solution of the γ-PGA-*graft*-ethyl-Bx and iron(III) ions were prepared by using DMSO as a solvent. In this study, different amount of the polymer solution was added into the iron(III) ions solution. The ratio of γ-PGA-*graft*-ethyl-Bx complexed with iron(III) ions was evaluated from the absorbance at the maximum wavelength (λ_{max}) of the complex at 501 nm. Figure 8 shows the result obtained from the photometric titration method. It was found that the absorbance increase as quantity of the polymer in the solution increased at the beginning and then it started to be constant after the polymer solution was added with more than 1.63 mL. Calculation based on these result and revealed that the ratio of γ-PGA-*graft*-ethyl-Bx to the iron(III) ions was 1:154.

CONCLUSION

The color transition based sensor for iron(III) ions was developed in this study by grafting 3,4-dihydro-3-(2′-ethyl hydroxyl)-6-ethyl-1,3,2*H*-benzoxazine (ethyl-Bx) into γ-PGA backbone. The grafting degree was approximately 25%. This grafted copolymer showed
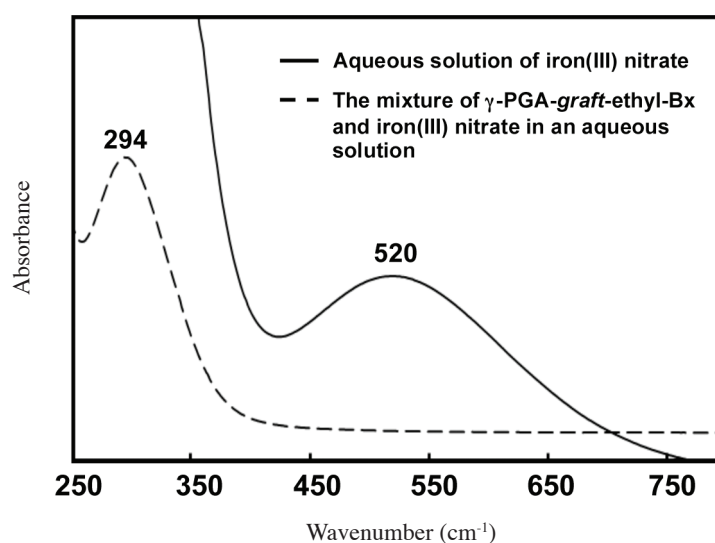

FIGURE 5. UV-visible absorption spectra of an aqueous solution of iron(III) nitrate mixture of γ-PGA-*graft*-ethyl-Bx and iron(III) nitrate in an aqueous solution
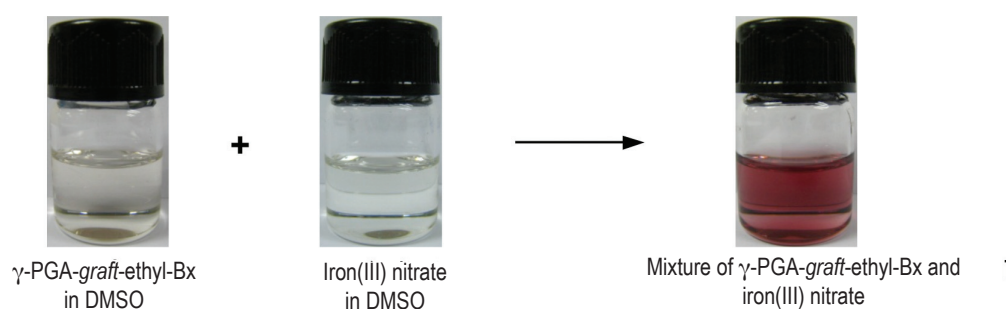

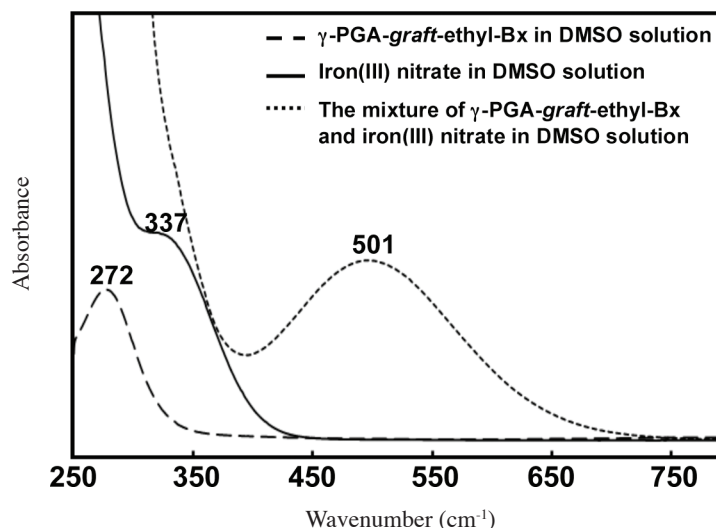FIGURE 6. Color transition of the DMSO solution of the iron(III) ions after γ-PGA-*graft*-ethyl-Bx solution was added

FIGURE 7. UV-Vis absorption spectra of solution of γ-PGA-*graft*-ethyl-Bx in DMSO, iron(III) nitrate in DMSO and mixture of γ-PGA-*graft*-ethyl-Bx and iron(III) nitrate in DMSO solution
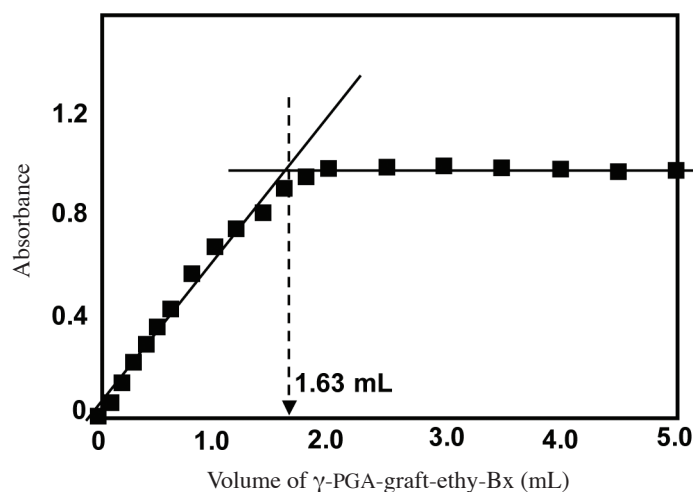

FIGURE 8. Relationship between absorbance at 501 nm and volume of γ-PGA-*graft*-ethyl-Bx solution (0.008 mM) from photometric titration method

sensitive response toward iron(III) ions in both aqueous and DMSO solutions. The response of the γ-PGA-*graft*-ethyl-Bx to iron(III) nitrate can be observed from the color transition. The color changed from clear to purple in aqueous solution and clear to red in DMSO solution. The stoichiometric ratio of γ-PGA-*graft*-ethyl-Bx to the iron(III) ions estimated from the photometric titration method was found to be 1:154.

REFERENCES

Attaphon, K., Sawittree, R., Worawat, W., Chatchai, V., Songwut, S., Nattamon, K. & Apirat, L. 2012. The effect of alkali and Ce(III) ions on the response properties of benzoxazine supramolecules prepared via molecular assembly. *Molecules* 17: 511-526.

Chirachanchai, S., Laobuthee, A., Phongtamrug, S., Siripatanasarakit, W. & Ishida, H. 2000. A novel ion extraction material using host-guest properties of oligobenzoxazine local structure and benzoxazine monomer molecular assembly. *Journal of Applied Polymer Science* 77: 2561-2568.

Gu, T., Zhang, Y., Deng, F., Zhang, J. & Hasebe, Y. 2011. Direct electrochemistry of glucose oxidase and biosensing for glucose based on DNA/chitosan film. *Journal of Environmental Sciences* 23: 66-69.

Hassan, A.Z., Mohammad, R.A. & Mohammad, R.G. 2009. Monitoring of iron(III) ions with a Fe^{3+} PVC membrane sensor based on 4,4'-dimethoxybenzil bisthiosemicarbazone. *Journal of the Chilean Chemical Society* 54: 186-190.

Holly, F.W. & Cope, A.C. 1944. Condensation products of aldehydes and ketones with o-aminobenzyl alcohol and o-hydroxybenzylamine. *Journal of the American Chemical Society* 66: 1875-1879.

Laobuthee, A., Ishida, H. & Chirachanchai, S. 2003. Metal ion guest responsive benzoxazine dimers and inclusion phenomena of cyclic derivatives. *Journal of Inclusion Phenomena and Macrocyclic Chemistry* 47: 179-185.

Liang, Z.Q., Wang, C.X., Yang, J.X., Gao, H.W., Tian, Y.P. Tao, X.T. & Jiang, M.H. 2007. A highly selective colorimetric chemosensor for detecting the respective amounts of iron(II) and iron(III) ions in water. *New Journal of Chemistry* 31: 906-910.

Maity, D. & Govindaraju, T. 2011. Highly selective colorimetric chemosensor for Co^{2+}. *Inorganic Chemistry* 50: 11282-11284.

Panushkin, V.T., Apenysheva, T.E., Sokol, V.I., Sergienko, V.S., Pushkareva, K.S., Bolotin, S.N., Kolokolov, F.A., Gromachevskaya, E.V., Borogavko, A.A. & Kosulina, T.P. 2007. The copper(II) acetate complex with 2-(2-hydroxyphenyl)-4,4-diphenyl-1,2-dihydro-4H-3,1-benzoxazine. *Russion Journal of Inorganic Chemistry* 33: 674-679.

Phongtamrug, S., Chirachanchai, S. & Tashiro, K. 2006. Supramolecular structure of N,N-Bis(s-hydroxybenzyl) alkylamine: From hydrogen bond assembly to coordination network in guest acceptance. *Macromolecular Symposium* 242: 40-48.

Rungsimanon, T., Laobuthee, A., Miyata, M. & Chirachanchai, S. 2008. [1+1] and [2+2] crown ethers derived from N,N-bis(2-hydroxyalkylbenzyl) alkalamine and their inclusion phenomena with metal ions. *Journal of Inclusion Phenomena and Macrocyclic Chemistry* 62: 333-338.

Shih, I.L., Van, Y.T. & Sau, Y.Y. 2003. Antifreeze activities of poly(γ-glutamic acid) produced by *Bacillus licheniformis*. *Biotechnology Letters* 25: 1709-1712.

Sun, J., Ge, J., Liu, W., Fan, Z., Zhang, H. & Wang, P. 2011. Highly sensitive and selective colorimetric visualization of streptomycin in raw milk using Au nanoparticles supramolecular assembly. *Chemical Communications* 47: 9888-9890.

Takami, A., Tatsuo, K., Toshiyuki, K. & Mitsuru, A. 2005. Preparation and characterization of biodegradable nanoparticles based on poly(γ-glutamic acid) with L-phenylalanine as a protein carrier. *Journal of Controlled Release* 108: 226-236.

Taniguchi, M., Kato, K., Shimauchi, A., Ping, X., Nakayama, H., Fujita, K.I., Tanaka, T., Tarui, Y. & Hirasawa, E. 2005. Proposal for wastewater treatment by applying flocculating activity of cross-linked poly-γ-glutamic acid. *Journal of Bioscience and Bioengineering* 99: 245-251.

Taniguchi, M., Kato, K., Matsui, O., Nakayama, H., Usuki, Y., Ichimura, A., Fujita, K.I., Tanaka, T., Tarui, Y. & Hirasawa, E. 2005a. Flocculating activity of cross-linked poly-γ-glutamic acid against bentonite and *Escherichia coli* suspension pretreated with $FeCl_3$ and its interaction with Fe^{3+}. *Journal of Bioscience and Bioengineering* 100: 207-211.

Veranitisagul, C., Kaewvilai, A., Sangngern, S., Wattanathana, W., Suramitr, S., Koonsaeng, N. & Laobuthee, A. 2011. Novel recovery of nano-structured ceria (CeO_2) from Ce(III)-benzoxazine dimer complexes via thermal decomposition. *International Journal of Molecular Sciences* 12: 4365-4377.

Wang, B., Hai, J., Liu, Z., Wang, Q., Yang, Z. & Sun, S. 2010. Selective detection of iron(III) by rhodamine-modified Fe_3O_4 nanoparticles. *Angewandte Chemie* 49: 4576-4579.

Department of Materials Engineering
Faculty of Engineering
Kasetsart University, Bangkok 10900
Thailand

*Corresponding author; email: fengapl@ku.ac.th