Sensing of polymeric sensor-based rhodamine B derivative for metal cations in complete aqueous solution

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Abstract. The water-soluble polymeric chemosensor poly(AM-GRBD) has been synthesized by precipitation copolymerization with the functional monomer, GRBD, which was made of N″-(rhodamine B-yl) diethylenetriamine and glycidyl methacrylate (GMA) and a hydrophilic co-monomer acrylamide (AM). The chemical sensor behaved as a fluorescent and chromogenic sensor towards various heavy metal cations and transition metal cations; particularly, Cr^{3+}, Fe^{3+} and Hg^{2+} ions in completely aqueous media. The fluorescence of poly(AM-GRBD) was enhanced by Cr^{3+}, Fe^{3+} and Hg^{2+} metal ions. Moreover, during titration of Cr^{3+}, Hg^{2+} or Fe^{3+} to the aqueous solution of poly(AM-GRBD), the visual colour changed from colourless to pink or brown yellow under visible light.

Keywords. Fluorescent sensor; water-soluble polymer; rhodamine B; diethylenetriamine; acrylamide.

1. Introduction

The development of fluorescent sensors for the detection of environmentally and biologically relevant heavy metal and transition metal cations, such as Cr^{3+}, Fe^{3+}, Hg^{2+}, and so on [1–3], is currently of great interest because these metal ions are pollutants in environment or involved in a variety of fundamental biological processes in organisms [4–9]. A variety of fluorescent cation sensors have been developed based on small molecules as cation receptors [10–12]. Nevertheless, these materials have shown several problems such as low mechanical and thermal stability, weak chemical union with the metals, poor removal efficiency, high cost, etc. In contrast with small molecular sensors [13], it is well known that polymer-based systems have advantages over low-molecular-weight system in terms of stability, easy handling and reuse. When the fluorescent probes were covalently bonded to the polymer chain, they generally show very similar effect as monomeric fluorophore [14,15]. The copolymers of traditional monomers with some polymerizable fluorescent units display intensive fluorescence. For many acrylic monomers bearing chromophore, Li *et al* [16] and Cui *et al* [17] found that the fluorescent intensity of the polymerizable fluorescent monomer is dramatically lower than those of its polymer or copolymer in the same chromophore concentration, due to the 'structural self-quenching effect' [18]. Moreover, the covalent bonding of the fluorophores to the polymer chain provided good stability to solvents and migration, improving their environmental behaviours [19]. Stomphorst *et al* [20,21] indicated that the use of polymer matrices

can avoid clustering of the dye molecules to aggregate the chromophores such as chlorophylls or porphyrins, often displayed in water and organic solvents. In the past decade, there is considerable interest in the field of chemosensor in the design of polymeric sensors for cation and anion recognition [22,23].

Although many polymers containing recognition chromophore are designed and investigated, most of them are applied in organic solution which limited their application in biological condition [18]. In order to be used as a matrix for fluorescent chemosensor purposes in aqueous solution, the polymer must be water-soluble [24]. Among the water-soluble polymer utilized, polyacrylamide (PAM) has been quite appropriate for the purpose, because it is water-soluble with attractive properties for applications in water-soluble polymeric sensors [13,15,25,26].

Rhodamine dyes are widely used as fluorescent probes and sensors owing to their high absorption coefficient and broad fluorescence in the visible region of the electromagnetic spectrum, high fluorescence quantum yields and photostability after complexes with metal ions by activating a carbonyl group in a spirolactone or a spirolactam moiety [27–30]. The mechanism is based on the switch off/on of the spirocyclic moiety mediated by guests.

In general, spirolactam formation of rhodamine derivatives is non-fluorescent, whereas its ring-opened amide system by guests gives rise to a pink colour and strong fluorescence emission. Recently, rhodamine-based sensors for cations and other analytes have received ever-increasing interest in areas such as sensors for Hg^{2+}, Fe^{3+}, Cr^{3+}, NO and OCl⁻ [9,13,27,28,31,32]. In this article, we design the functional monomer, GRBD, which is made of N″-(rhodamine B-yl)

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diethylenetriamine and glycidyl methacrylate (GMA) and its copolymer poly(AM-GRBD) with the water-soluble monomer acrylamide (see scheme 1). The response of the copolymer to the presence of different metal cations in aqueous solutions has been investigated as well.

2. Experimental

2.1 *Instrumentation*

The ^{1}H NMR spectra were measured on a DRX 400 Bruker spectrometer (AVANCE AV 400, Bruker Corporation, Switzerland) at 298 K in CDCl$_3$ or D$_2$O with TMS as internal standard. FTIR spectra were recorded on a Nicolet Neus 8700 FTIR spectrophotometer (Thermo Scientific Instrument Co. USA) with KBr compressing tablet. Elemental analyses (C, H and N) were carried out on a VarioELIII analyzer (Elementar Corporation, Germany) for the monomer GRBD. All pH measurements were made with a Model pHS-3C pH meter (Shanghai, China). Fluorescence spectra were acquired on a RF5301PC fluorescence spectrophotometer (Shimadzu Corporation, Japan). The viscosity average molecular weight (M_η) was estimated for PAM and poly(AM-GRBD) from intrinsic viscosity of the polymer in aqueous solution at a constant temperature of 30°C with Ubbelohde viscometer ($\Phi = 0.51$ mm).

2.2 *Material*

Rhodamine B, glycidyl methylacrylate (GMA) and 2,2′-azo bis(2-methylpropionitrile) (AIBN, 98%) were purchased from Sigma-Aldrich Trading Co. Ltd (Shanghai, China). Diethylenetriamine and natrium sulphuricum were purchased from Sinopharm Chemical Reagent Co. Ltd (Shanghai, China) and used without further purification.

Acrylamide (AM) was supplied by Aladdin Chemistry Co. Ltd (Shanghai, China); N$_2$ gas, sulphuric acid, sodium hydrate and sodium chloride were obtained from commercial suppliers and all were analytically pure. Anhydrous methanol and ethanol, dichloromethane, chloroform, ethyl acetate, petroleum ether and tetrahydrofuran (THF) were obtained from commercial suppliers. Rhodamine B-yl diethylene-triamine (RBD) was prepared according to the literature method [33–38].

2.3 *Synthesis of monomer GRBD*

A quantity of 0.142 g (1.0 mmol) of GMA mixed with 10 ml of trichloromethane was added dropwise from an addition funnel to 0.528 g (1.0 mmol) of RBD in 10 ml of trichloromethane at 60°C for about 50 min under stirring. The mixture was refluxed for an additional 15 h after complete addition of GMA. The reactions were monitored by change of epoxide number or FT-IR. The obtained liquid was rotate and vacuum evaporated for removing the solvent to get a violet-red residue, which was purified by silica-gel column chromatography with ethyl acetate-petroleum ether (2:1, v/v) as eluent, affording 0.544 g of GRBD (yield: 81.15%) [33,34]. FT-IR of GRBD (KBr), ν cm^{-1}: 3363.64 (s,ν_{-NH}); 3084.95 (m, $\nu_{-C=C-H}$); 2966.46 (s), 2933.54 (s), 2872.10 (s), [$\nu_{C-H(CH2,CH3)}$]; 1731.04 (s, $\nu_{C=O}$, –CO–O–); 1673.98 (s, $\nu_{C=O}$, –CO–NH–); m 1616.93 (s, $\nu_{ArC=C}$); 1507.21 (s, δ_{N-H}), 1467.71 (m, $\nu_{ArC=C}$), 1353.61 (m, $\nu_{ArC=C}$), 1217.55, 1110.03 (C–O). ^{1}H NMR of GRBD (400 MHz, CDCl$_3$), δ: 0.969 (s, H$_2$C=C–CH$_3$), 1.030–1.188 (s, –CH$_2$–CH$_3$), 1.869 (s, HO–CH–CH$_2$–NH–); 2.398–2.732 (–CH$_2$–NH–CH$_2$–); 2.826 (–CH–OH); 3.108–3.117 (d, NH$_2$–CH$_2$–CH$_2$–NH–); 3.412–3.36 (COO–CH$_2$–CH–OH); 3.622–3.675 (s, CH$_3$–CH$_2$–N–); 4.488–4.567 (s, –CH–OH); 5.15 (d, H$_2$C=C–CH$_3$); 5.645 (s, =CH$_2$); 6.204–6.367 (m, –Φ–H); 7.021
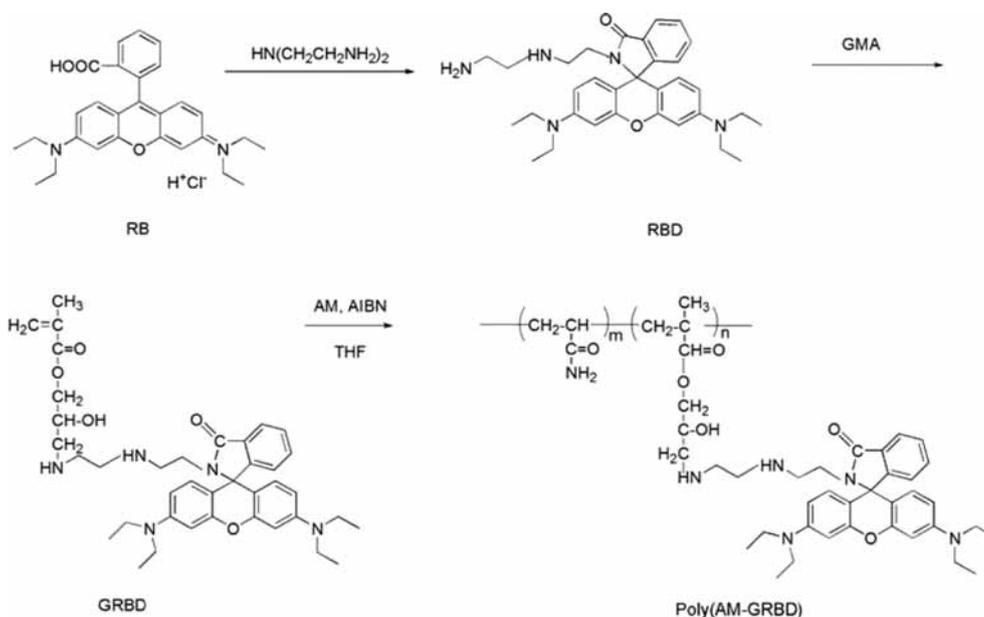
Scheme 1. Synthesis of poly(AM-GRBD).

(s, –Φ–H); 7.370–7.409 (s, –Φ–H); 7.813 (s, –Φ–H). Anal. calc. for $C_{39}H_{51}N_5O_5$ (%): C, 69.82; H, 7.74; N, 10.45. Found (%): C, 69.87; H, 7.87; N, 10.35.

2.4 *Synthesis of PAM and poly(AM-GRBD)*

A solution of AM (0.7108 g, 10.0 mmol) and AIBN (0.0657 g, 0.04 mmol) in 25 ml of dry THF was introduced into a dry three-neck round-bottomed flask. The solution was deoxygenated by purging with purified N_2. The three-neck round-bottomed flask was sealed and placed in a regulated thermostat bath at 65°C for 12 h. The mixture was cooled to room temperature. The obtained white precipitate was collected by filtration, washed two times with chloroform (5 ml × 2) and dried at 50°C under vacuum to a constant weight (0.6773 g, yield: 95.29%) [35–42].

The poly(AM-GRBD) was prepared by similar methods as the polymerization of AM. The recipes were as described. AM: 1.3962 g (19.6 mmol) and GRBD: 0.2679 g (0.4 mmol). The poly(AM-GRBD) was dissolved in double distilled water (5 ml) and again precipitated into absolute ethyl alcohol. The above dissolution-precipitation cycle was repeated three times. The copolymers were purified with a Soxhlet extractor for 12 h with chloroform and absolute ethyl alcohol, respectively. The final products were dried at 50°C under vacuum to produce poly(AM-GRBD) as purple powders (1.4544 g, yield: 89.36%) [15,43–45]. FTIR (KBr) of poly(AM-GRBD), ν cm^{-1}: 3394.36, 3199.06 (–$CONH_2$); 2929.15, 1450.16 (–CH_2–); 2856.74 (–CH–); 1667.40 (C=O); 1627.90, 1518.18, 1419.44 (Ar); 1121.06 (C–O). ^{1}H NMR of poly(AM-GRBD) (400 MHz, D_2O), δ: 1.046–1.092 (m, –CH_3); 1.593 (d, –CH_2–); 1.682–1.736 (CHOH–C$\underline{H}_2$–NH–); 1.394–1.408 (–CH_3); 2.158–2.176 (m, –CH–); 2.277 (–NH–C$\underline{H}_2$–C$\underline{H}_2$–NH–); 2.394–2.406 (–NH–); 3.467–3.488 (s, –N–C$\underline{H}_2$–CH_3); 3.547 (C$\underline{H}$–OH); 3.689 (s, –NH–); 4.908 (m, –COO–C$\underline{H}_2$–CHOH); 5.976 (s, –CH–O$\underline{H}$); 6.133–6.226 (s, –Φ–H); 6.57–7.19 (m, Φ–H); 7.605–7.013 (s, –Φ–H).

2.5 *Measurement procedures*

The poly(AM-GRBD) stock solution (1.00 mg ml^{-1}) was prepared in an aqueous solution. The pH was adjusted from 2.25 to 10.82 by the addition of H_2SO_4 or NaOH to the copolymer aqueous solution with a digital pH controller. The effects of the metal cations on the fluorescent intensity were examined by adding a few microlitre of the metal cations solution (the concentration of metal cations was 0.10 mol l^{-1}) to a known volume of the copolymer solution (2.00 ml). The total volume of the addition metal cations solution was limited to 0.10 ml, so that the dilution of the copolymer solution remained insignificant. The metal ions are nitrate salts of Ag^+, Ba^{2+}, Cd^{2+}, Co^{2+}, Cr^{3+}, Cu^{2+}, Fe^{2+}, Fe^{3+}, Hg^{2+}, K^+, Mg^{2+}, Mn^{2+}, Na^+, Ni^{2+}, Pb^{2+} and Zn^{2+}, whose solutions were prepared in distilled water. For all fluorescent measurements, excitation wavelength was 500 nm with the emission recorded over the wavelength range of 520–650 nm

[46]. The detection limit was calculated using the following equation:

$$\text{Detection limit} = 3S/\rho,$$

where S is the standard deviation of blank measurements and ρ the slope between intensity *vs.* sample concentration [27,46–48]. The viscosity average molecular weight (M_η) of PAM and poly(AM-GRBD) was estimated from intrinsic viscosity of the polymers in distilled water at a constant temperature of 30°C, using the Mark–Houwink–Sakurada (MHS) equation [49]:

$$[\eta] = kM_\eta^\alpha (k = 9.33 \times 10^{-3}, \alpha = 0.75).$$

3. Results and discussion

3.1 *Molecular design and syntheses of sensors poly(AM-GRBD)*

Based on the selective host–guest design for metal cation sensors, we utilized the glycidyl methacrylate-rhodamine-yl diethylenetriamine ligand (GRBD) as a host, which could provide seven binding sites to metal cation via favourable electrostatic interactions of metal cations to the nitrogen and oxygen atoms [34,35,50]. The nitrogen in the diethylenetriamine linker and the carbonyl oxygen can provide binding unit for metal cations [51,52]. It was expected that the copolymer poly(AM-GRBD) would sense more than one metal ions.

The synthetic strategy of the monomer and copolymers is shown in scheme 1. The sensor was readily synthesized by employing shorter synthetic routes and economy of starting materials [50]. First, RBD was facilely synthesized through amidation of diethylenetriamine with rhodamine B in ethanol, which can be prepared in high yield [33,52]. Then, the polymerizable monomer GRBD was prepared by ring-opening reaction between RBD and the epoxide functional group of GMA [46]. Finally, the water-soluble copolymer poly(AM-GRBD) was prepared by conventional free radical precipitation polymerization of GRBD with AM. As is well known, PAM has the advantage of excellent water-solubility, so AM is quite appropriate to be selected as monomer [46].

The structures of the monomer GRBD and copolymer poly(AM-GRBD) were confirmed by FTIR and ^{1}H NMR. The characteristic FTIR spectra of the polymeric sensor showed aromatic rhodamine peaks (1622 and 1510 cm^{-1}) and acid amides peak (3394–3199 cm^{-1}), and the wide absorption band at 3480 cm^{-1} was indicative of the –NH and –OH functional groups. The prominent peak at 1667 cm^{-1} was attributed to the stretching vibration of an amide carbonyl [46]. Typical ^{1}H NMR spectra of the poly(AM-GRBD) showed the characteristic signals of –CH_2 and –CH groups in the region of 1.0–2.1 and 2.2–2.6 ppm and aromatic protons at 7.8–5.5 ppm, respectively. The characteristic NMR signals corresponding to the vinyl groups of the monomer (d(H) 5.77 and 5.32) disappeared completely in the copolymer, and the signals corresponding to the xanthene and benzene

rings of GRBD (d(H) 6.0–8.0) appeared in the ^{1}H NMR spectra of poly(AM-GRBD). This observation confirmed that the hydrophobic functional monomer GRBD had been successfully incorporated into the polymer [9]. The average molecular weights of PAM and poly(AM-GRBD) were 5.72 $\times$ 10^4 and 6.18 $\times$ 10^3 g mol^{-1}, respectively, which were designed to be reasonably low to ensure the water solubility of the material [9].

3.2 *Effects of pH on fluorescent intensity of poly(AM-GRBD)*

The chemosensor containing spirolactam ring and nitrogen donors was highly sensitive to environmental pH, as the protonation degree of nitrogen was strongly dependent on the pH [52]; hence, for practical applicability of the poly(AM-GRBD), a proper pH range of 2.25–10.82 was determined. Figure 1 shows variations of the fluorescence intensity of poly(AM-GRBD) (C_p = 0.2 mg ml^{-1}, λ_{ex} = 500 nm) with pH in the absence of the metal ion in aqueous solution [53]. The poly(AM-GRBD) had a weak fluorescence emission within the pH range 5.43–10.82 and the solution colour could hardly be observed due to the presence of the ring-closed spirolactam structure. With the increase in solution acidity, the fluorescence of poly(AM-GRBD) in aqueous solution was gradually enhanced along with clear colour changes from colourless to pink, which implied that the spirolactam ring of poly(AM-GRBD) was opened up due to protonation. Considering that higher pH range could lead to hydrolysis for transition metal ions, the proper pH span for poly(AM-GRBD) to sense metal ions in aqueous solution was selected to be under near-neutral pH conditions, which was a physiological pH value too [52,54].

3.3 *Sensitivity of poly(AM-GRBD)*

Concentration effects of Cr^{3+}, Fe^{3+} and Hg^{2+} ions on the emission spectra of the poly(AM-GRBD) (0.2 mg ml^{-1},
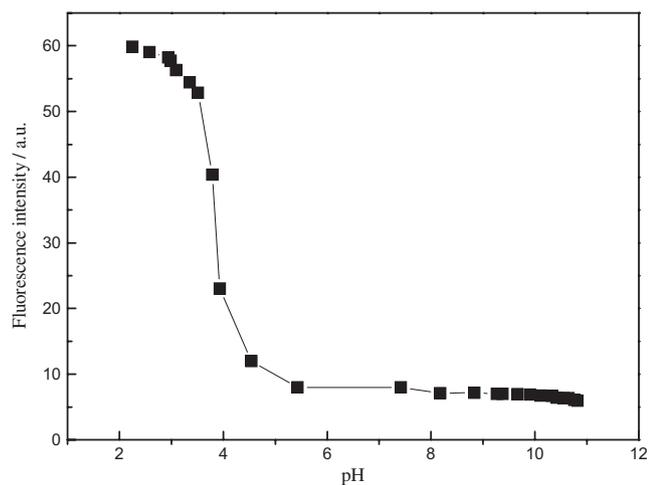
Figure 1. Fluorescent intensity of poly(AM-GRBD) in aqueous solution (C_p = 0.2 mg ml^{-1}, λ_{ex} = 500 nm) at different pH.

λ_{ex} = 500 nm) are given in figure 2a–c, respectively. Inset of figure 2 shows the relationship of relative fluorescent intensity (I/I_0) of poly(AM-GRBD) in aqueous solution with ion concentration of Cr^{3+}, Fe^{3+} and Hg^{2+}. Here I is the fluorescence emission intensity of poly(AM-GRBD) actually
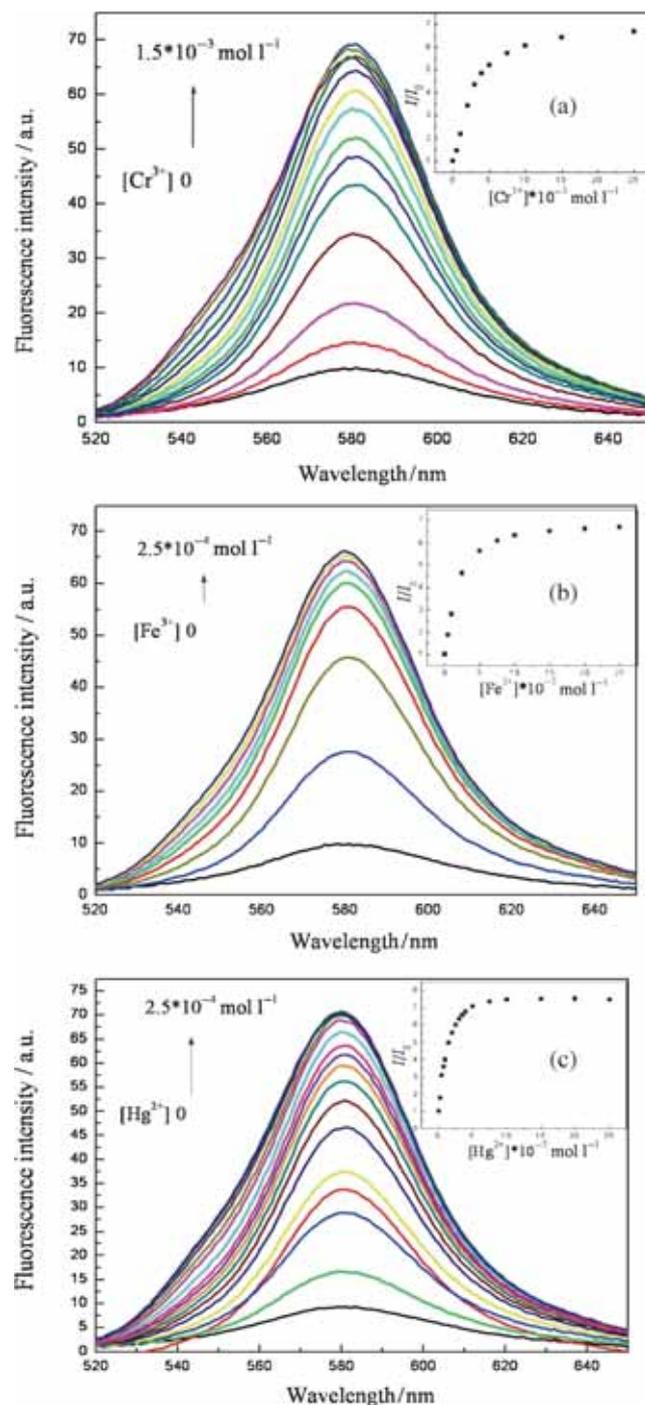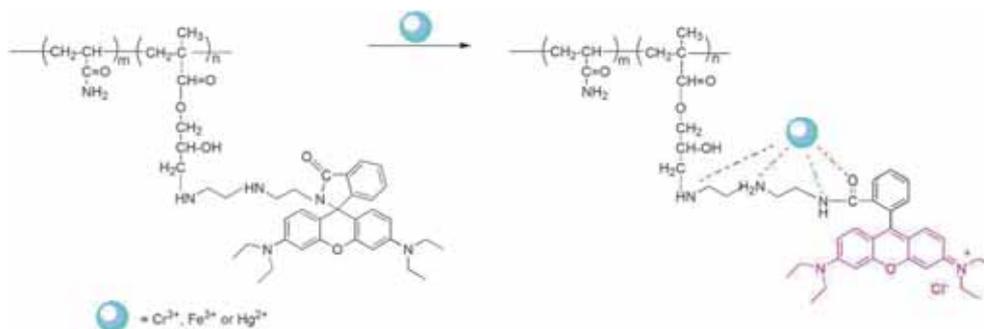
Figure 2. Fluorescence spectra of poly(AM-GRBD) (C_p = 0.2 mg ml^{-1}, λ_{ex} = 500 nm) in the presence of increasing concentrations of (**a**) Cr^{3+} (0 to 1.5 $\times$ 10^{-3} mol l^{-1}), (**b**) Fe^{3+} (0 to 2.5 $\times$ 10^{-4} mol l^{-1}) and (**c**) Hg^{2+} (0 to 2.5 $\times$ 10^{-4} mol l^{-1}). Inset: the relative fluorescent intensity (I/I_0) changes of poly(AM-GRBD) upon gradual addition of Cr^{3+}, Fe^{3+} and Hg^{2+}.

Scheme 2. Possible mechanism of Cr^{3+}-, Fe^{3+}- and Hg^{2+}-induced ring opening of rhodamine moiety on poly(AM-GRBD).

Table 1. Equation of I/I_0 of poly(AM-ARBD) to the concentrations of Cr^{3+}, Fe^{3+} and Hg^{2+} cations.

Metal cations	Equation	Regression coefficient (R)	Concentration range of metal cations (mol l^{-1})	Detection limit (mol l^{-1})	Equation number
Cr^{3+}	$I/I_0 = 0.9907 + 1.1476 \times 10^5\ [Cr^{3+}]$	0.9971	0 to 3×10^{-5}	2.61×10^{-11}	1
Fe^{3+}	$I/I_0 = 1.1366 + 1.4405 \times 10^5\ [Fe^{3+}]$	0.9941	0 to 2.5×10^{-5}	4.16×10^{-11}	2
Hg^{2+}	$I/I_0 = 0.1001 + 3.6339 \times 10^5\ [Hg^{2+}]$	0.9874	0 to 7.5×10^{-6}	8.25×10^{-12}	3
Hg^{2+}	$I/I_0 = 3.8887 + 7.9764 \times 10^4\ [Hg^{2+}]$	0.9858	1.5×10^{-5} to 3.5×10^{-5}	3.76×10^{-11}	4

measured at a given metal concentration, I_0 is the fluorescence emission intensity of the poly(AM-GRBD) with free ions, and $[Cr^{3+}]$, $[Fe^{3+}]$ and $[Hg^{2+}]$ represented the concentration of Cr^{3+}, Fe^{3+} and Hg^{2+} added. When no metal ion was added to the solution of poly(AM-GRBD), only weak fluorescence signal in the range from 520 to 650 nm could be observed, because the spirocyclic form of rhodamine prevailed. However, upon treating with Cr^{3+}, Fe^{3+} or Hg^{2+}, significant enhancement of I/I_0 emerged quickly, which were reasonably assigned to the delocalized xanthene tautomer of the rhodamine group [51,55–61] and the colour changes from colourless to pink (Cr^{3+} and Hg^{2+}) or brown-yellow (Fe^{3+}) were observed simultaneously [57,59]. Further addition of Cr^{3+}, Fe^{3+} or Hg^{2+} cations hardly had any effect upon the relative fluorescence intensity that was indicative of an entirely fluorescent complex formed between poly(AM-GRBD) and Cr^{3+}, Fe^{3+} or Hg^{2+} cations, respectively [62], and about 6.89-, 6.76- or 7.46-fold enhancement in the fluorescent intensity was noted [46]. The possible mechanism was described as shown in scheme 2. The GRBD units of poly(AM-GRBD) containing carbonyl (–CO–), imino groups (–HN–) and lactam could selectively chelate with metal ions by using N of imino and O atoms in structure to form more stable pentabasic or heptabasic rings. The spirolactam ring-closed form could be transformed to ring-opened amide form with high fluorescent caused by conjugation enhancement [63,64].

Supplementary figure S5a–c shows the plots of the emission intensity of poly(AM-GRBD) *vs.* the concentration of added Cr^{3+}, Fe^{3+} and Hg^{2+} cations, and a good linearity relationship was obtained in certain range and could be expressed by the following equations (1–4) of the calibration line (table 1) [15,46]. The detection limit was found to be 10^{-11} to 10^{-12} mol l^{-1} (calculated as three times standard
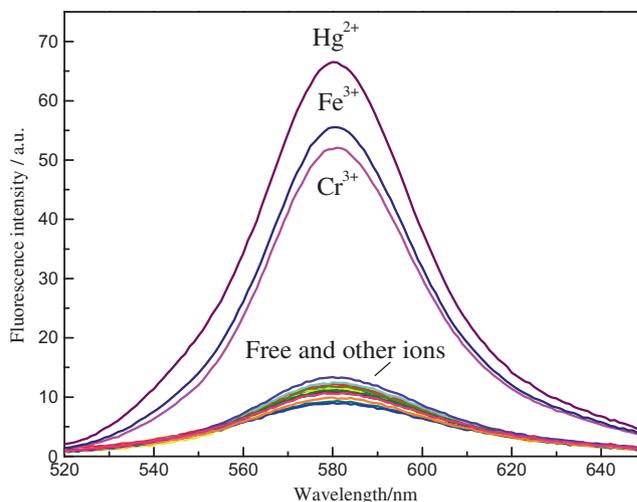

Figure 3. Fluorescence spectra of poly(AM-GRBD) ($C_p = 0.2$ mg ml^{-1}) upon addition of 5.0×10^{-5} mol l^{-1} of diverse metal cations.

deviation of blank solution). Therefore, poly(AM-GRBD) was sensitive enough to detect Cr^{3+}, Fe^{3+} and Hg^{2+} cations in complete water media [46].

3.4 *Selectivity and competitiveness of poly(AM-GRBD)*

The influences of various metal cations (5.0×10^{-5} mol l^{-1}) on the relative luorescent intensity (I/I_0) of the poly(AM-GRBD) were investigated in neutral aqueous solution (figure 3). The poly(AM-GRBD) had no obvious response for fluorescence spectra upon additions of Ag^+, Ba^{2+}, Cd^{2+}, Co^{2+}, Cu^{2+}, Fe^{2+}, K^+, Na^+, Ni^{2+}, Mg^{2+}, Mn^{2+}, Pb^{2+} and Zn^{2+}, respectively, but had great fluorescence enhancement for
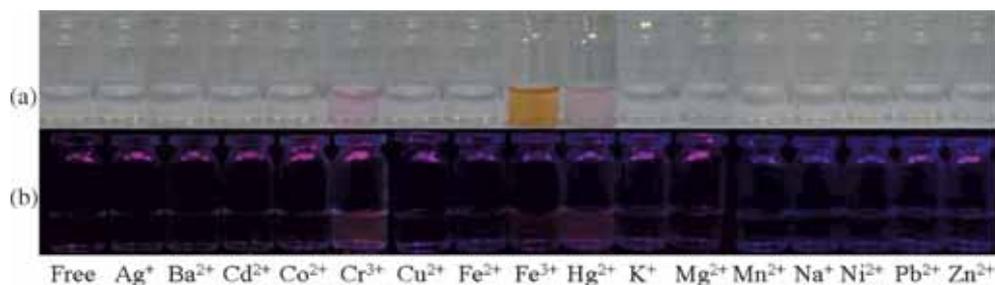
Figure 4. Photographs recorded under (**a**) visible light and (**b**) UV light at 365 nm for aqueous solutions of poly(AM-GRBD) (0.2 mg ml^{-1}) in the presence of different metal ions (2.5 × 10^{-5} mol l^{-1}).

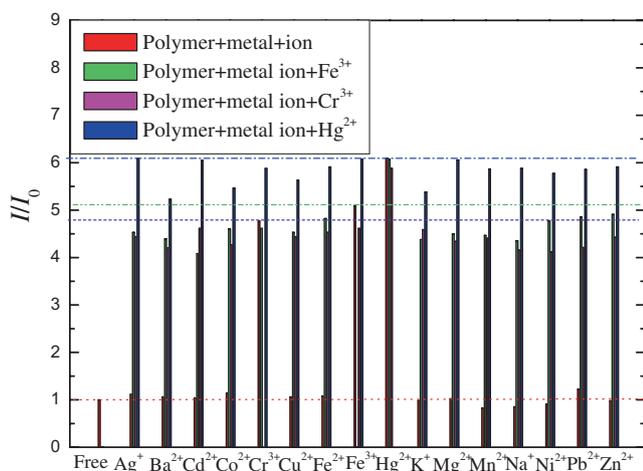**Figure 5.** Selectivity of poly(AM-ARBD) (C_p = 0.2 mg ml^{-1}) for Cr^{3+}, Fe^{3+} and Hg^{2+} in the presence of other metal ions (2.5 × 10^{-5} mol l^{-1}) in neutral aqueous solution, red bars represent polymer + ion. Green, magenta or blue bars represent the subsequent addition of Fe^{3+}, Cr^{3+} or Hg^{2+} (2.5 × 10^{-5} mol l^{-1}) to the solution, respectively.

Cr^{3+}, Fe^{3+} and Hg^{2+} [19,62,65]. The selectivity for Cr^{3+}, Fe^{3+} and Hg^{2+} was probably due to the cooperation of several combined influences, such as the suitable coordination geometry, the proper radius and charge density of the Cr^{3+}, Fe^{3+} and Hg^{2+} ions, and the amide deprotonation ability of Cr^{3+}, Fe^{3+} and Hg^{2+} [46] (see scheme 2).

The colour and fluorescence changes of poly(AM-GRBD) on the addition of various cations are shown in figure 4. Upon addition of Cr^{3+}, Fe^{3+} or Hg^{2+}, a visible colour change occurred from colourless to pale pink (Cr^{3+} and Hg^{2+}) or brown-yellow (Fe^{3+}) under visible light (figure 4, top). Under UV light at 365 nm, the poly(AM-GRBD) in the presence of Cr^{3+}, Fe^{3+} and Hg^{2+} emitted orange red fluorescence (figure 4, bottom) [9,13,43,46,66–68].

The competition experiments were also carried out by adding Cr^{3+}, Fe^{3+} or Hg^{2+} into the solution of poly(AM-GRBD) (0.2 mg ml^{-1}, excited at 500 nm) in the presence of other metal ions (2.5 × 10^{-4} mol l^{-1}) as shown in figure 5. The results indicated that the sensing of Cr^{3+}, Fe^{3+} or Hg^{2+} by poly(AM-GRBD) was hardly affected by these common interfering ions [13,46].

4. Conclusions

A functional monomer bearing a rhodamine B derivative, GRBD, which was made of N″-(rhodamine B-yl) diethylene-triamine and GMA group, was synthesized in this work. The radical precipitation copolymerization of the new monomeric fluorophore with the hydrophilic co-monomer AM was carried out. By means of fluorescence spectroscopy, we studied the sensibility and selectivity of poly(AM-GRBD) for metal cations in completely aqueous solution. The results showed that poly(AM-GRBD) was an efficient 'off-on' switcher for Cr^{3+}, Fe^{3+} and Hg^{2+} metal ions. The titration of Cr^{3+}, Hg^{2+} or Fe^{3+} to the aqueous solution of poly(AM-GRBD) led to the visual colour changes from colourless to pale pink or brown orange.

Electronic Supplementary Material

Supplementary material pertaining to this article is available on the *Bulletin of Materials Science* website (www.ias.ac.in/matersci).

Acknowledgement

References

[1] Wang S and Chang Y T 2006 *J. Am. Chem. Soc.* **32** 10380

[2] Ojida A, Nonaka H, Miyahara Y, Tamaru S I, Sada K and Hamachi I 2006 *Angew. Chem. Int. Ed.* **45** 5518

[3] Baruah M, Qin W, Vallée R A, Beljonne D, Rohand T, Dehaen W and Boens N 2005 *Org. Lett.* **20** 4377

[4] Xu Z C, Xiao Y X, Qian X H, Cui J N and Cui D W 2005 *Org. Lett.* **7** 889

[5] Majzoub A E, Cadiou C, Olivier I D, Tinant B and Chuburu F 2011 *Inorg. Chem.* **50** 4029

[6] Sarkar M, Banthia S and Samanta A 2006 *Tetrahedron Lett.* **47** 7575

[7] Jung H S, Kwon P S, Lee J W, Kim J I, Hong C S, Kim J W, Yan S H, Lee J Y, Lee J H, Joo T and Kim J S 2009 *J. Am. Chem. Soc.* **5** 2008

[8] Fan L J and Jones W E 2006 *J. Am. Chem. Soc.* **128** 6784

[9] Wang Y, Wu H Q, Luo J and Liu X Y 2012 *React. Funct. Polym.* **72** 169

[10] Silva A P, Gunatatne H Q N, Gunnlauggson T, Huxley A J M, McCoy C P, Radmancher J T and Rice T E 1997 *Chem. Rev.* **97** 1515

[11] Basheer M C, Alex S, Thomas K G, Suresh C H and Das S 2006 *Tetrahedron* **62** 605

[12] Ramachamdram B, Sankaran N B, Karmakar R, Saha S and Samanta A 2000 *Tetrahedron* **56** 7041

[13] Noi N, Chatthai K, Weerapol S, Banchob W, Buncha P and Thawatchai T 2013 *Polym. Chem.* **4** 3039

[14] Rurack K 2001 *Spectrochem. Acta Part A* **57** 2161

[15] Wang B Y, Guan X L, Hu Y L and Su Z X 2008 *J. Polym. Res.* **15** 427

[16] Li F M, Ga Q Y, Wang L and Zhang J X 1997 *J. Polym. Sci. Part A*: *Polym. Chem.* **35** 1087

[17] Cui Y C, Liu C Y and Gao Q Y 2000 *Polym. Adv. Technol.* **11** 172

[18] Liu Y H, Meng L Z, Lu X J, Zhang L F and He Y B 2008 *Polym. Adv. Technol.* **19** 137

[19] Wang B Y, Liu X Y, Ding S L and Su Z X 2011 *J. Polym. Res.* **18** 1315

[20] Stomphorst R G, van der Zwan G, van Zandvoort M A M J, Sieval A B, Zuilhof H, Vergeldt F J and Schaafsma T J 2001 *J. Phys. Chem. A* **105** 4235

[21] Wang B Y, Guan X L, Hu Y L and Su Z X 2007 *Polym. Adv. Technol.* **18** 529

[22] Huang H M, Wang K M, Tan W H, An D L and Yan X H 2004 *Angew. Chem. Int. Ed.* **43** 5635

[23] Tang Y L, He F and Yu M H 2006 *Macromol. Rapid. Commun.* **27** 389

[24] Serrano B, Baselga J and Piérol I F 2002 *Polym. J.* **34** 905

[25] Kim S R, Yuk S H and John M S 1997 *Eur. Polym. J.* **33** 1009

[26] Risbud M V and Bhonde R R 2000 *Drug. Deliv.* **7** 69

[27] Chen X Q, Pradhan T, Wang F, Kim J S and Yoon J 2012 *Chem. Rev.* **112** 1910

[28] Antonio B, Estefanía D P, Enrique G E, Claudia G and Fernando P 2014 *Coord. Chem. Rev.* **260** 156

[29] Kim H N, Guo Z, Zhu W, Yoon J and Tian H 2011 *Chem. Soc. Rev.* **40** 79

[30] Beija M, Afonso C A M and Martinho J M G 2009 *Chem. Soc. Rev.* **38** 2410

[31] Kim H N, Lee M H, Kim H J, Kim J S and Yoon J 2008 *Chem. Soc. Rev.* **37** 1465

[32] Lee S, Anand H P and Schanze K S 2013 *Macromol. Rapid Commun.* **34** 791

[33] Xie P H, Guo F Q, Yang S, Yao D H, Yang G Y and Xie L X 2014 *J. Fluoresc.* **24** 473

[34] Jua H, Lee M H, Kim J, Kim J S and Kim J 2011 *Talanta* **83** 1359

[35] Lee M H, Wu J S, Lee J W, Jung J H and Kim J S 2007 *Org. Lett.* **9** 2501

[36] Lee M H, Kim H J, Yoon S, Park N and Kim J S 2008 *Org. Lett.* **10** 213

[37] Chai M M, Zhang D, Wang M, Hong H J, Ye Y and Zhao Y F 2012 *Sens. Actuators B Chem.* **174** 231

[38] Xiang Y and Tong A J 2006 *Org. Lett.* **8** 1549

[39] Liu T, Joseph M D S and Roberts G W 2006 *Polymer* **47** 4276

[40] Liu T, Garner P, Desimone J M *et al* 2006 *Macromol.* **39** 6489

[41] Bunyakan C and Hunkeler D 1999 *Polymer* **40** 6213

[42] Bunyakan C, Armanet L and Hunkeler D 1999 *Polymer* **40** 6225

[43] Geng T M, Huang R Y and Wu D Y 2014 *RSC Adv.* **86** 46332

[44] Geng T M, Wu D Y and Huang W 2015 *J. Polym. Res.* **22** 40

[45] Geng T M, Wang X, Jiang H, Song W, Ni R F, Chen J and Wang Y 2016 *J. Fluoresc.* doi:10.1007/s10895-016-1785-4

[46] Luo J, Jiang S S, Qin S H, Wu H Q, Wang Y, Jiang J Q and Liu X Y 2011 *Sens. Actuators B Chem.* **160** 1191

[47] Zhou Z G, Yu M X, Yang H, Huang K W, Li F, Yi T Y and Huang C H 2008 *Chem. Commun.* **29** 3387

[48] Kumar K S, Ramakrishnappa T, Balakrishna R G and Pandurangappa M 2014 *J. Fluoresc.* **24** 67

[49] Hill A, Candau F and Selb J 1993 *Macromol.* **26** 4521

[50] Wanichacheva N, Praikaew P, Suwanich T and Sukrat K 2014 *Spectrochim. Acta A* **118** 908

[51] Mao J, Wang L N, Dou W, Tang X L, Yan Y and Liu W S 2007 *Org. Lett.* **9** 4567

[52] Chereddy N R, Suman K, Korrapati P S, Thennarasu S and Mandal A B 2012 *Dyes Pigm.* **95** 606

[53] Wang X M, Iqbal M, Huskens J and Verboom W 2012 *Int. J. Mol. Sci.* **13** 16822

[54] Anindita S, Sujit S P, Partha B and Roy S 2012 *J. Fluoresc.* **22** 443

[55] He G J, Zhang X L, He C, Zhao X W and Duan C Y 2010 *Tetrahedron* **66** 9762

[56] Yang Z, She M Y, Yin B, Cui J H, Zhang Y Z, Sun W, Li J L and Shi Z 2012 *J. Org. Chem.* **77** 1143

[57] Ko S K, Yang Y K, Tae J S and Shin I J 2006 *J. Am. Chem. Soc.* **128** 14150

[58] She M Y, Yang Z, Yin B, Zhang J, Gu J, Yin W T, Li J L, Zhao G F and Shi Z 2012 *Dyes Pigm.* **92** 1337

[59] Chatterjee A, Santra M, Won N, Kim S, Kim J K, Kim S B and Ahn K H 2009 *J. Am. Chem. Soc.* **131** 2040

[60] Zhang X L, Xiao Y and Qian X H 2008 *Angew. Chem. Int. Ed.* **47** 8025

[61] Grabchev I, Dumas S and Chovelon J M 2008 *Polym. Adv. Technol.* **19** 316

[62] Li N J, Xu Q F, Xia X W, Wang L H, Lu J M and Wen X W 2009 *Mater. Chem. Phys.* **114** 339

[63] Tang R R, Lei K, Chen K, Zhao H and Chen J W 2011 *J. Fluoresc.* **21** 141

[64] Duan Y L, Shi Y G, Chen J H, Wu X H, Wang G K, Zhou Y and Zhang J F 2012 *Tetrahedron Lett.* **53** 6544

[65] Kaya İ and Kamacı M 2013 *J. Fluoresc.* **1** 115

[66] Gao W, Yang Y T, Huo F J, Yin C X, Xu M, Zhang Y B, Chao J B, Jin S and Zhang S P 2014 *Sens. Actuators B Chem.* **193** 294

[67] Song J H, Huai M X, Wang C C, Xu Z H, Zhao Y F and Ye Y 2015 *Spectrochim. Acta Part A* **139** 549

[68] Hu Z Q, Du M, Zhang L F, Guo F Y, Liu M D and Li M 2014 *Sens. Actuators B Chem.* **192** 439