PAPER

A polymeric film probe with a turn-on fluorescence response to hydrogen sulfate ions in aqueous media†

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A new kind of hydrophilic copolymer poly(HEMA-*co*-VNP) was designed and synthesized by the radical copolymerization of 2-hydroxyethylmethacrylate (HEMA) and 2-{[2-(4-vinylbenzyloxy)naphthalen-1-yl]methyleneamino}-(*S*)-2-phenylethanol (VNP). The desired copolymer showed a highly selective red-shifted emission and a unique chiroptical response upon HSO_4^- binding in organic solution. UV-vis and ^{1}H NMR spectroscopic studies revealed that the hydrogen bonding between the imine moiety in the VNP repeating units and HSO_4^- is crucial for the high selectivity of the receptor to this anion. As expected, the incorporation of HEMA into the polymer matrix endowed the copolymer excellent hydrophilicity, flexibility and good film-forming properties. Thus, high-quality film sensors could be easily fabricated on quartz plates through spin-casting techniques. The resultant polymeric films can recognize HSO_4^- ions among a series of common anions in aqueous solution with high selectivity and sensitivity. The promising new film probe for HSO_4^- has distinct characteristics such as a rapid response, enough stability in an aqueous media and practicality.

Introduction

The detection and sensing of environmentally and biologically important anions have attracted much attention over the last few decades.[1] Among various anions, hydrogen sulfate (HSO_4^-) may be of particular interest because it plays pivotal roles in a wide range of chemical and biological processes.[2] This amphiphilic anion tends to dissociate at high pH values to generate toxic sulfate ions, which cause irritation of the skin and eyes and even respiratory paralysis.[3] Accordingly, a lot of fluorescent and chromogenic chemosensors, most of them belonging to small organic molecules, have been developed for monitoring HSO_4^- ions.[3,4] While these existing sensors have proven to be considerably effective in the solution state, they cannot be applied to the continuous online detection owing to the intrinsic limitations of small molecules in device fabrication.

In contrast with small molecule-based chemosensors, polymeric counterparts would offer particular advantages such as signal amplification, an enhanced binding efficiency and selectivity to specific analytes due to possible cooperative effects of multiple recognition sites.[5] More importantly, rationally designed polymer sensory materials can be prepared as films and thus to facilitate the construction of commercially viable devices.[5] Recently, Tian and his co-workers described a
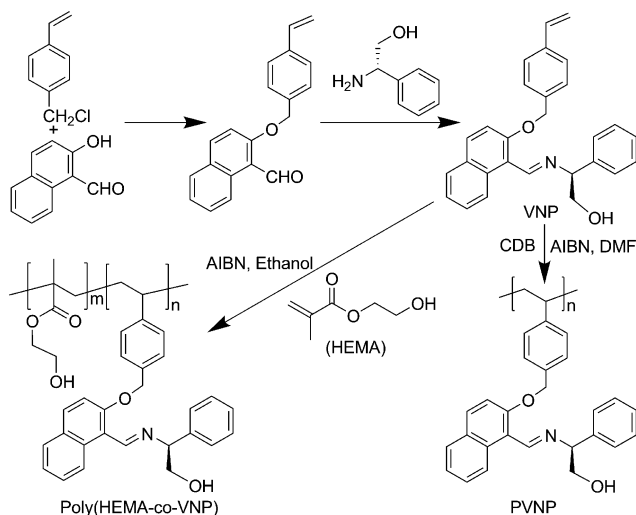
novel hydrophilic copolymer-based film sensor with turn-on fluorescence, high selectivity and a rapid response to pyrophosphate anions, showing an ideal hydrophilic film strategy for low-cost chemosensors or chips which can be used in online monitoring and high-throughput bioprocessing.[6] With the same strategy, they also developed a long wavelength fluorescent copolymer, which could be potentially applied as a microbioreactor pH indicator.[7] In the design of these polymeric sensors, 2-hydroxyethylmethacrylate (HEMA) was thought as an appropriate copolymerization monomer, wherein the polymer PHEMA endowed the main polymeric matrix with excellent hydrophilicity and film-forming properties.

We previously reported a polymeric sensor PVNP that shows a turn-on fluorescence response for HSO_4^- in THF solution, which is prepared by the RAFT polymerization of a simple Schiff base derivative of (*S*)-phenylglycine 2-{[2-(4-vinylbenzyloxy) naphthalen-1-yl]methyleneamino}-(*S*)-2-phenylethanol (VNP, Scheme 1).[8] Moreover, the polymer bearing a chiral pendent group displayed distinctive changes in the circular dichroism (CD) spectra upon HSO_4^- binding, thereby providing a new signalling channel for the recognition event. However, despite its high selectivity and sensitivity toward HSO_4^-, PVNP as a chemosensor can only function in an organic solution. Also, the corresponding film sensor is unavailable due to the poor film-forming ability of the polymer matrices.

In view of the above-mentioned facts, we designed and synthesized a hydrophilic copolymer, poly(HEMA-*co*-VNP), as the sensor for hydrogen sulfate (Scheme 1). An investigation into the sensing properties of these copolymers revealed that in

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Scheme 1 The synthesis of the VNP monomer, the PVNP homopolymer and the poly(HEMA-co-VNP) copolymer.

both the solution and thin film state they all exhibit an enhanced and red-shifted fluorescence emission with a high sensitivity for HSO_4^- ions over other common anions such as $H_2PO_4^-$, HPO_4^{2-}, PO_4^{3-}, $CH_3CO_2^-$ and NO_3^-. To the best of our knowledge, until now no similar reports on polymer-based fluorescent sensors, particularly polymeric film probes, have been made for the selective detection of bisulfate ions in aqueous media.

Experimental section

Measurements

^{1}H- and ^{13}C-NMR spectra were taken on a Bruker Avance AMX-400 and AMX-500 NMR instrument, respectively. Elemental analysis was performed on a ThermoFinnigan Flash EA 1112 analyzer. A Bruker Vector 22 Fourier Transform Infrared spectrometer was used to record the IR spectra in KBr pellets. The molecular weights of the polymers were evaluated with a PL-GPC 220 apparatus equipped with a set of PL gel columns (MIXED-B 300 × 7.5 mm) and a differential refractometer detector using DMF as the elution solvent. The GPC chromatogram was calibrated against standard poly-methylmethacrylate (PMMA). The copolymer composition was determined from the formal working curve in the absorption spectra. UV-vis and circular dichroism (CD) spectra were recorded at 25 °C using a quartz cell of 1 cm on a MOS-450 (Biologic Co., France). Steady-state fluorescence spectra were recorded on a PerkinElmer LS-55 fluorescence spectrometer in the right-angle geometry (90° collecting optics). Epifluorescence images were recorded by fluorescent microscopy (Nikon ECLIPES TI-U). Front-face fluorescence was used to detect the fluorescence of the polymeric films (see: Fig. S6, ESI†).

Materials

α,α′-Azobisisobutyronitrile (AIBN, Shanghai Chemical Reagent Co.) was purified by recrystallization from methanol.

Tetrahydrofuran (THF) was purified by distillation in the presence of a benzophenone–Na complex. Dichloromethane (DCM) was dried over CaH_2 and distilled in an atmosphere of dry nitrogen. N,N-Dimethy formamide (DMF) was distilled under vacuum before use. Dimethy sulfoxide (DMSO) was treated with CaH_2 at room temperature for 12 h and then distilled before use. All of the tetrabutylammonium (TBA) salts (F^-, Cl^-, Br^-, HSO_4^-, $CH_3CO_2^-$, $H_2PO_4^-$) and 2-hydroxy-1-naphthaldehyde were purchased from Aladdin Shanghai Reagent Co. Sodium salts of various anions (SO_4^{2-}, HCO_3^-, S^{2-}, NO_3^-, NO_2^-, HSO_4^-, CO_3^{2-}) and ammonium salts of anions ($H_2PO_4^-$, HPO_4^{2-}, PO_4^{3-}, $CH_3CO_2^-$, HCO_2^-, $C_2O_4^{2-}$, $C_6H_5CO_2^-$) were purchased from Shanghai Sinopharm Chemical Reagent Co., Ltd. 4-Vinylbenzyl chloride and (S)-(+)-2-phenylglycinol were purchased from Sigma-Aldrich Co. and Shanghai Qiude Biochemical Engineering Co., respectively. The functional monomer 2-{[2-(4-vinylbenzyl-oxy)naphthalen-1-yl]methyleneamino}-(S)-2-phenylethanol (VNP) and its homopolymer PVNP were prepared according to the reported method.[8]

Synthesis

Poly(HEMA-co-VNP). A typical copolymerization procedure is described as follows. 2-Hydroxyethyl methacrylate (HEMA, 780 mg, 6.0 mmol), VNP (49 mg, 0.12 mmol), and the initiator AIBN (7 mg, 0.043 mmol) were dissolved in ethanol (4 mL). The mixture was stirred at room temperature for 5 minutes and then subjected to three freeze–thaw cycles. After heating for 24 h at 70 °C, the resultant mixture was poured into a large amount of n-hexane to precipitate the crude product. Further purification was conducted by dissolving the polymer in ethanol and then precipitating it from n-hexane. This process was repeated four times and the desired copolymer was dried under vacuum to give a white solid (0.65 g) in an 81% yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ = 0.76–0.93 (m, –CH$_3$), 1.61–1.99 (br, –CCH$_2$), 3.56 (s, –CH$_2$–CH$_2$–OH), 3.88 (s, –CH$_2$–CH$_2$–OH), 4.78 (s, –CH$_2$–CH$_2$–OH), 7.22–7.70 (m, weak aromatic H), 7.93 (m, weak aromatic H), 8.24 (br, weak aromatic H), 9.12 (br, weak aromatic H), 9.34 (br, –CH=N). The weight-average molecular weight of the resulting copolymer was 12.9 × 10^4 with a M_w/M_n of 3.22 (**P1** in Table 1).

The fabrication of the polymer films

In order to obtain high-quality thin films, the quartz plates were carefully cleaned with distilled water and ethanol sequentially in an ultrasonic bath and dried in air before use. The typical operation process of the polymer films is described as follows: a methanol solution of **P1** (10 mg mL^{-1}) was prepared and the tiny particles were filtered out with filter membranes to guarantee the film smoothness. The thin films were obtained by spin-casting the polymer solution on the clean quartz plates (8 mm × 25 mm × 1 mm) at a spin rate of 800–4000 rpm. Finally, the films were placed in a vacuum box at room temperature to remove residual solvents.

Table 1 The results of the copolymerization of VNP with HEMA[a]

Sample code	VNP/HEMA (feed ratio)[b]	Copolymers			
		Yield (%)	$M_w{}^c$ (10^4)	$M_w/M_n{}^c$	VNP[d] (mol%)
P1	3/97	81	12.90	3.22	0.98
P2	5/95	77	11.70	2.22	2.3
P3	8/92	87	10.02	2.97	4.7
P4	10/90	61	6.45	2.17	7.5
P5	20/80	66	6.13	3.12	12.0
P6[e]	100/0	28	1.95	1.35	100

[a] See: experimental section. [b] Molar ratio. [c] Taken from GPC and calibrated against standard PMMA using DMF as the eluting solvent. [d] Determined by UV-vis absorption analysis. [e] **P6** is the homopolymer of VNP (PVNP), which was prepared by RAFT polymerization in DMF according to ref. 8; CDB was used as the chain transfer agent and AIBN as the initiator (70 °C, 48 h).

Results and discussion

### The design and synthesis of poly(HEMA-co-VNP)

It is generally known that the sensing performance of a polymeric film is primarily dependent upon the permeability of the envisaged analyte into the polymer matrix, the affinity of the polymer binding sites toward the analyte and the flexibility of the polymer main chains.[6,7,9] In our target copolymers, PHEMA was chosen as the main polymeric matrix for its high hydrophilicity to improve the permeability of the anions. This hydrophilic polymer-based sensor would be especially suitable for the detection of aqueous samples in both the solution and film state. Moreover, such a polymeric film probe is expected to find potential applications in bioprocess monitoring systems due to the excellent biocompatibility of PHEMA.[10]

Poly(HEMA-co-VNP) was straightforwardly synthesized by the radical copolymerization of easily available HEMA and VNP in ethanol at 70 °C for 24 h (Scheme 1). As shown in Table 1, the content of the VNP unit in the resulted copolymer is in proportion to the VNP/HEMA feed ratios, while its molecular weight decreases dramatically with the increasing VNP feed content. All of the copolymers are completely soluble in DMSO and DMF, but nearly insoluble in THF, water, toluene and *n*-hexane at ambient temperature. The copolymer samples (**P1** and **P2**) containing less than 3 mol% of VNP units dissolved well in ethanol and methanol, which is in contrast to the poor solubility of the homopolymer PVNP in the alcohols. In all of the experiments, the GPC analyses of the obtained copolymers give unimodal traces. The GPC graphs and ^{1}H NMR spectra of the copolymers can be found in the ESI (Fig. S1†).

The anion-sensing ability of poly(HEMA-co-VNP) in solution

The anion recognition ability of poly(HEMA-co-VNP) was first examined in a DMSO–THF (1 : 4, v/v) solution by UV-vis, fluorescence and CD spectroscopies as a reference to the corresponding film sensor. The main reason for choosing such a solvent mixture is to compare easily the spectral properties of the copolymer with those of PVNP obtained previously in THF.[8] Similar to PVNP, the copolymer showed two absorption bands

centred at 319 nm (band I) and 345 nm (band II) in the range of 275–450 nm, respectively (Fig. S2†). Upon the addition of TBAHSO₄ (30 equivalents with respect to the VNP units of the copolymer) to the solution, band II increased and was accompanied with a new broad shoulder around 390 nm, whereas the absorption at 319 nm decreased and became a small peak attached to band II. Fig. 1a displays the fluorescence responses of the copolymer **P1** toward various anions with excitation at 345 nm *i.e.*, the absorption band maximum of the copolymer for the purpose of avoiding specific solvent effects.[11] It can be seen
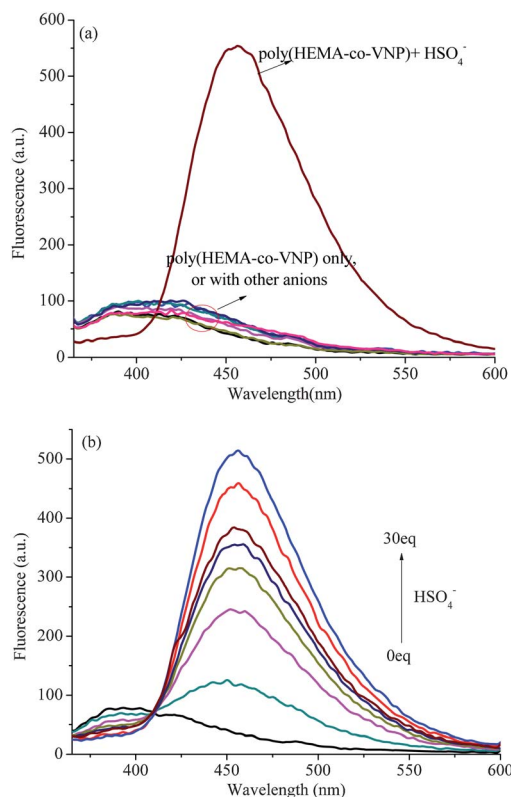
Fig. 1 (a) The fluorescence responses of **P1** (1.6 mg mL⁻¹) in DMSO–THF (1 : 4, v/v) toward various anions (F⁻, H₂PO₄⁻, AcO⁻, Cl⁻, Br⁻, I⁻, HSO₄⁻, as TBA⁺ salts, ~30 eq.); (b) the changes in the fluorescence spectra of **P1** (1.6 mg mL⁻¹) upon successive addition of HSO₄⁻ (0–30 equiv.) in DMSO–THF (1 : 4, v/v). λ_{ex} = 345 nm.

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that the addition of HSO_4^- (30 eq.) quenched the original fluorescence of the copolymer at around 385 nm. In the meantime, it also gave rise to a new enhanced emission band at 457 nm. In contrast, none of the other anions produced noticeable changes in the emission spectra. Similarly, only the addition of HSO_4^- to the copolymer solution causes a significant change in the CD spectra.[12]

Upon the fluorescence titration of the copolymer with HSO_4^- (0–30 eq.), a gradual decrease in the 385 nm emission and the emergence of a red-shifted emission band centred at 457 nm were observed with a sharp isoemission point at 410 nm (Fig. 1b). This fluorescence increment associated with a bathochromic shift from 385 to 457 nm is probably based on an ICT (intramolecular charge transfer) mechanism.[13] That is, the host–guest complexation changes the electronic distribution of the imine moiety (–C=N–) in the pendent groups and then efficiently enhances the ICT from the electron donor (naphthalene moiety) to the acceptor (–C=N– group) upon excitation by light. On the basis of the above observations and our previous studies,[8] a possible binding interaction between HSO_4^- and the polymeric sensor has been proposed, in which the combination of the imine moiety and the adjacent hydroxymethyl group would play a role as an anion binding motif through multiple hydrogen bonds (Scheme 2). It should be pointed out that a large fluorescent emission enhancement was observed at a longer wavelength (~526 nm) for PVNP upon binding with HSO_4^-,[8] which is most likely attributed to the emission of the intramolecular excimer generated from neighbouring side groups.

Considering the possibility of polymeric sensory systems presenting signal amplification,[5a,8,9] it was interesting to assess the influence of the copolymer composition on the binding affinity of poly(HEMA-co-VNP) for bisulfate ions. However, for a polymeric sensor it is usually difficult to obtain the binding constant to describe its recognition ability like the small molecule receptors.[14] Thus, we employed the fluorescence enhancement ratio (FE = I_{457}/I_{385}) instead of the binding constant to characterize the sensing capacity of the copolymers with different VNP contents. As seen in Fig. 2, an FE in the range of 12–16 was observed for these copolymers upon the addition of HSO_4^-, and even at a VNP loading of 0.98 mol% the value reached 15. The larger magnitude of emission increment
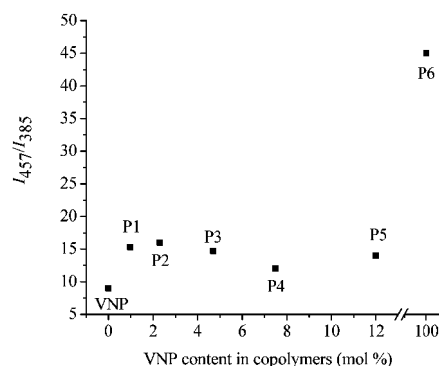

Fig. 2 A plot of I_{457}/I_{385} of the poly(HEMA-co-VNP)s as a function of the copolymer composition upon the addition of 30 eq. of HSO_4^- in the DMSO–THF mixture (1 : 4, v/v). FE = I_{526}/I_{382} for **P6**.

compared with its monomer (FE = 9) indicates that the copolymer sensors amplified the recognition event to a greater extent, albeit the signal amplification effect is much less than that of the homopolymer **P6** (I_{526}/I_{382} = 45). Based on the S/B criteria the detection limit was estimated to be 5×10^{-6} M for the copolymer **P1** in the DMSO–THF (1 : 4, v/v) mixture, which is higher than that of PVNP but comparable to those of most small molecule-based HSO_4^--sensors.[4]

The preparation of the polymeric films and their properties as anion sensors

As noted above, the copolymer **P1** exhibits a considerable fluorescence enhancement to HSO_4^- ions in solution although its VNP content is as low as 0.98 mol%. Expectably, such a low VNP loading does not distinctly affect the copolymer hydrophilicity and good film-forming properties. In fact, **P1** can be easily spin-coated to obtain high-quality thin films. Therefore, we took a **P1** film fabricated on the quartz slides as a representative sample for further study.

Fig. 3 shows the UV-vis spectra of **P1** in solution in DMSO–THF (v/v = 1 : 4) and as a thin film (0.8 g m^{-2}) in water. It can be seen that the absorption bands of **P1** in both the solution and film states are similar. The absorption of the film in water
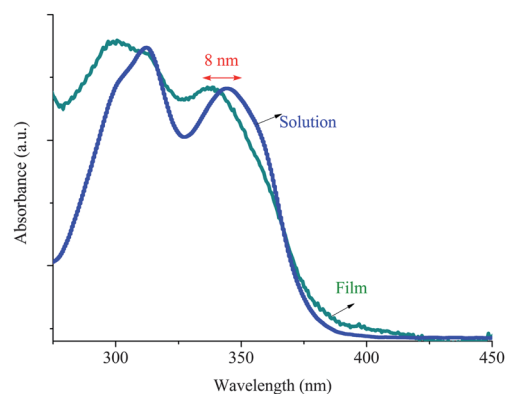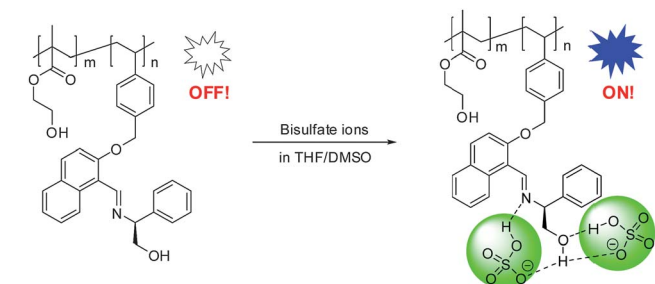

Scheme 2 The possible binding mode between poly(HEMA-co-VNP) and HSO_4^-.

Fig. 3 The normalized UV-vis spectra of **P1** in solution (DMSO–THF v/v = 1 : 4, c = 1.6 mg mL^{-1}) and the **P1** film (0.8 g m^{-2}) in water.

shows a small blue shift of about 8 nm compared to the polymer solution. Because the main matrix PHEMA in the copolymer has no absorption in the region over 300 nm, the absorption band centred at 336 or 354 nm is totally ascribed to the fluorophore of the VNP repeating units.

The sensing capacity of the **P1** films to various anions was studied by epifluorescence microscopy. Among a series of tested anions including spherical halides (F^-, Cl^-, Br^-, I^-) and bulky anions (SO_4^{2-}, HCO_3^-, S^{2-}, NO_3^-, NO_2^-, CO_3^{2-}, $H_2PO_4^-$, HPO_4^{2-}, PO_4^{3-}, $CH_3CO_2^-$, HCO_2^-, $C_2O_4^{2-}$, $C_6H_5CO_2^-$ and NO_3^-), only HSO_4^- produced a noticeable "turn-on" fluorescence upon interaction with the films (Fig. S5†). Fig. 4 shows the epifluorescence images of the polymeric films (0.8 g m^{-2}) after being exposed to an aqueous solution of NaHSO$_4$ for ~1 min. The sharp and fast change from a dim colour to a bright blue indicates that the polymeric film as a sensor is highly sensitive and selective to HSO_4^- ions. The rapid fluorescence responses may be attributed to the high permeability of the ions into the polymer matrix and the strong host–guest interaction.[15] According to the reported method,[16] the detection limit of the film probe is *ca.* 5×10^{-5} M toward the aqueous HSO_4^- sample in the form of sodium salt. The value is greater by an order of magnitude than that in the case of the solution system. It is worth mentioning that the high selectivity for HSO_4^- over NO_3^- may be of particular interest, because such hydrophilic polymeric materials might find a use in nuclear waste remediation requiring the selective removal of hydrogen sulfate from nitrate-rich waste mixtures.[17]

It is also noteworthy that the polymeric film as a sensor offers obvious advantages over the corresponding solution. Firstly, the film sensor is applicable for the detection of HSO_4^- ions irrespective of whether the analyte is in an organic or aqueous media (Fig. S5†). In contrast, the solution sensing system cannot be used for aqueous or semi-aqueous samples because the copolymer is water-insoluble. Secondly, the film

sensor will give nearly the same fluorescence response to HSO_4^- with different counter-ions, such as sodium, potassium and ammonium. That is, these counter-ions do not lead to any noticeable disturbance in the HSO_4^- detection. Furthermore, applying the polymeric film probe allows the easy detection of HSO_4^- with the naked eye under a common UV lamp. As shown in Fig. 5, the patterned fluorescence image of the letters "XH" is formatted by using a writing brush with NaHSO$_4$ on a quartz plate under a UV lamp at 365 nm. Nevertheless, the polymeric films displayed no evident CD signal, which may be due to the fact that the efficient VNP content is not sufficient for yielding a detectable chiroptical effect.
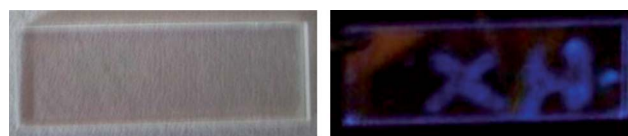
The fluorescence response of the polymeric films toward aqueous HSO_4^- solutions with various concentrations was investigated (Fig. 6). In these experiments, the film was attached to a settled bracket to make sure that the fluorescence is measured at the same point before and after exposure to the tested solution (Fig. S6†). The fluorescence intensity was recorded as the average value of three parallel measurements. In addition, the film thickness was fixed at 0.8 g per square meter. It shows that the film reached the steady fluorescence maximum in less than 3 minutes, indicating the high sensitivity to this ion with a fast response.

It can be seen from Fig. 6 that the polymer film also exhibited a remarkable "turn-on" fluorescence response at about 450 nm upon HSO_4^- binding, which is similar to that observed in the case of the solution state. For example, after immersing in a 2×10^{-4} M HSO_4^- solution for ~3 min, the fluorescence of the film increased about 8-fold. The Job plot of the film probe (Fig. 7) shows a linear relationship between the fluorescence increment and the HSO_4^- concentration in the range of 0–1.6×10^{-4} M, which meets further application in practice.

On the other hand, the stability of a film probe is of great interest for its practical utility. For determining the repeatability of the assay results, the film was washed with 5 mL distilled water three times before every test. The results showed that the measurement data have good reproducibility, and the fluorescence loss is less than 5% even after three "testing–washing–testing" cycles in the detection of HSO_4^- (2×10^{-4} M). This observation also suggests that the hydrolysis of the Schiff base does not seem to be the main sensing mechanism for the present HSO_4^--film probe, albeit such a hydrolytic mechanism was recently proposed by Upadhyay *et al.*[18] However, the HSO_4^--induced hydrolysis of the imine units may indeed exist to a certain extent, because a remarkable fluorescence loss of over 50% was observed for the polymer films that were subjected to ten "testing–washing–testing" cycles.
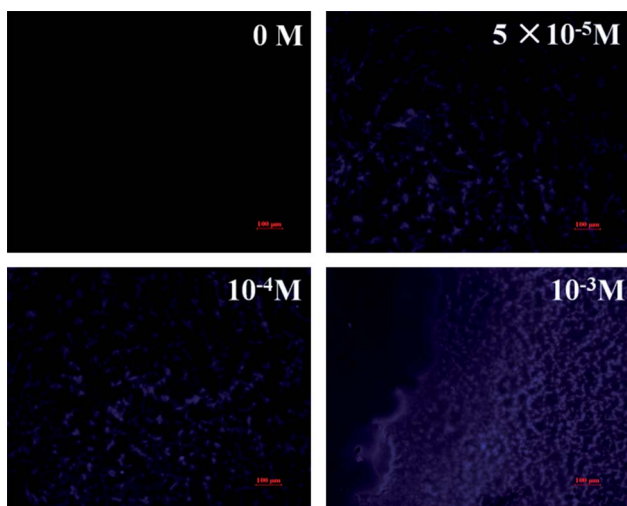

Fig. 4 Fluorescence images of the poly(HEMA-*co*-VNP) **P1** films (0.8 g m^{-2}) immersed in an aqueous solution of NaHSO$_4$ for ~1 min: 5×10^{-5}, 1×10^{-4}, and 1×10^{-3} M with UV irradiation.

Fig. 5 The photos of the polymeric film (**P1**) on a quartz plate (left) in visible light and (right) the formation of the patterned fluorescence image of the letters "XH" with an NaHSO$_4$ solution (1×10^{-4} M) under a UV lamp at 365 nm.
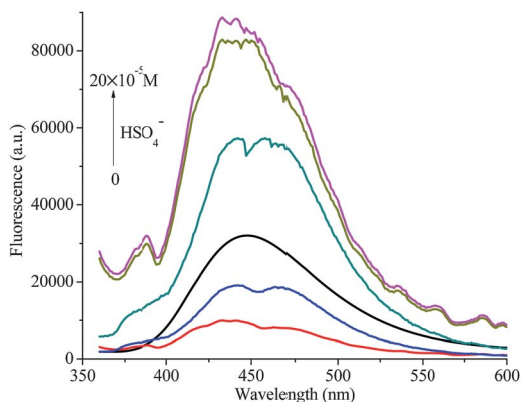
Fig. 6 The fluorescence response of the **P1** film (0.8 g m^{-2}) immersed in an aqueous solution of HSO_4^- for ~3 min: from 0 to 2×10^{-4} M.
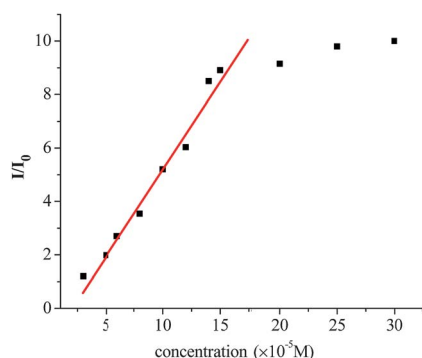
Fig. 7 The Job plot of the **P1** film probe at $\lambda_{em} = 450$ nm. Note: I/I_0 represents the ratio of fluorescence intensity after and before exposure to an aqueous $NaHSO_4$ solution. The measurement procedure for the fluorescence of the polymeric films is described in the ESI.†

Conclusions

With the objective of constructing fluorescent chemosensors for HSO_4^- anions that are capable of operating in an aqueous media, we synthesized a series of novel copolymers, poly-(HEMA-co-VNP), which incorporate the functional unit VNP into the hydrophilic poly(HEMA) matrix. These copolymers, in the solution or thin film state, are useful as highly selective and sensitive fluorescent sensors for the recognition of HSO_4^-. The polymeric film appears to be particularly attractive owing to the applicability for aqueous samples and the practicality in visual sensing of HSO_4^- ions, as well as providing a feasible way to construct a continuous online detecting system. Also, the polymer materials might have potential uses in nuclear waste remediation requiring the selective removal of hydrogen sulfate ions from nitrate-rich waste mixtures.

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