

# Pyrylium-containing polymers as sensory materials for the colorimetric sensing of cyanide in water

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A sensory polymeric material for the colorimetric sensing of cyanide in water has been developed based on the reactivity of this anion with the pyrylium cation.

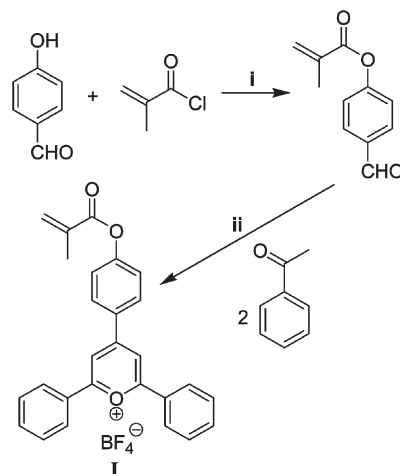
The development of new molecular chemosensors capable of sensing target guests *via* changes in optical signals is a field of interest. Despite the relatively large number of studies on cation sensing, anions have only been targeted in the last decade mainly due to new advances in receptor chemistry and the development of new sensing principles.<sup>1</sup> However, there are still particular problems connected with the development of new selective colorimetric probes for the chromogenic sensing of certain guests. This is especially the case for sensitive reusable colorimetric sensory materials capable of acting as probes in water for target anions.

Cyanide is a highly toxic anion that inhibits mitochondrial cytochrome-oxidase and hence blocks electron transport, resulting in decreased oxidative metabolism and oxygen utilization,<sup>2</sup> and its determination plays an important role in environmental control. Several methods for cyanide determination in aqueous environments have been reported, but, among them, very few are based on the use of chromofluorogenic chemosensors. Recent examples involve the use of Ru(II)-containing pyrrolylquinoxalines,<sup>3</sup> Zn(II) complexes of porphyrin derivatives,<sup>4</sup> boronic acid groups<sup>5</sup> and Re(I) polypyridyl complexes.<sup>6</sup> However some of these systems display colour changes in non-aqueous media or are not highly selective. It has also recently been reported that the nucleophilic attack of the cyanide anion on squaraine derivatives can be a useful method for the colorimetric determination of this environmentally important anion.<sup>7</sup> Using a somewhat similar design principle we report here the use, for the first time, of pyrylium derivatives as chromogenic reporters for the colorimetric detection of CN<sup>-</sup>. As an additional effect to enhance its applicability, we have covalently anchored the colorimetric probe into a polymer. The connection between certain types of chromogenic receptors for anions and polymers can be of interest. In fact, the development of new, robust, sensitive sensory materials remains as an emerging frontier and to date there are only few examples of chromogenic and fluorogenic polymer-based anion chemosensors.<sup>8</sup> Moreover, polymeric films can be easily prepared and are ideal candidates for the development of sensory materials for *in situ* sensing and rapid “naked eye” screening applications.<sup>9</sup> Additionally, water insoluble sensing molecules anchored into suitable polymers with good mechanical properties can be used as sensory materials practically in any solvent or atmosphere. We

have combined here the capabilities of polymers as materials and suitable chromogenic organic groups in order to develop new chromogenic devices with enhanced sensing properties.

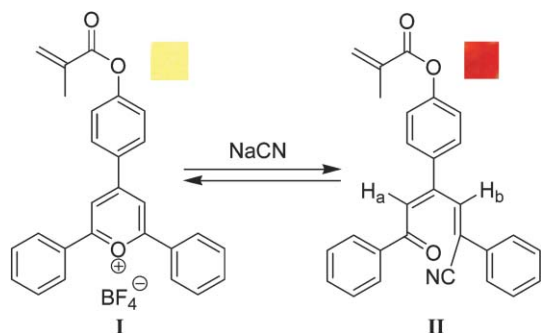
The electrophilic character of the pyrylium ring has been recently employed in the development of chromogenic probes for charged and neutral molecules.<sup>10</sup> With this in mind, we envisioned that the reaction between cyanide and a pyrylium derivative to give the corresponding cyano-enone<sup>11</sup> could also be used as an output signal in the development of novel sensory materials.

In order to incorporate the pyrylium chromophore into a polymeric matrix, the monomer **I** was synthesized by a two step reaction. In the first step, the reaction of methacryloyl chloride with 4-hydroxybenzaldehyde gave 4-formylphenyl methacrylate. The reaction of one equivalent of this compound with two equivalents of acetophenone and two equivalents of boron trifluoride diethyl etherate in 1,2-dichloroethane gave **I** as a yellow powder that was crystallized from acetic acid to yield yellow needles (see Scheme 1). Preliminary studies revealed that CN<sup>-</sup> addition to acetonitrile solutions of **I** resulted in a remarkable colour change from yellowish to red due to the formation of the corresponding cyano-enone derivative **II** *via* nucleophilic attack of the cyanide anion on the C1 carbon next to the oxygen atom in the pyrylium ring (see Scheme 2). This reactivity was confirmed by NMR studies. Thus, **I** shows characteristic pyrylium signals with equivalent Ha and Hb protons at 8.6 ppm. Upon reaction with tetrabutylammonium cyanide these two protons became non-equivalent, with observed resonances at 6.9 and 7.6 ppm for Ha



**Scheme 1** Synthesis of **I**. i: CH<sub>2</sub>Cl<sub>2</sub>, TEA, 0 °C; ii: BF<sub>3</sub>·OEt<sub>2</sub>, CH<sub>2</sub>ClCH<sub>2</sub>Cl, rt.

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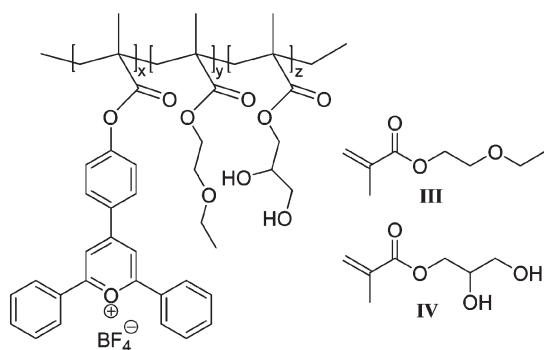


**Scheme 2** Reactivity of the monomer **I** with cyanide. A photograph showing the colour of the polymer upon reaction with cyanide is also included.

and H<sub>b</sub>, respectively. Mass spectra studies also indicated the formation of derivative **II** (base peak at 407 *m/z*). These data are consistent with the formation of the cyano-enone.<sup>12</sup>

A series of methacrylic copolymer films containing the pyrylium probe were prepared by radical copolymerization of the monomer **I**, 2-ethoxyethyl methacrylate **III**, 2,3-dihydroxypropyl methacrylate<sup>13</sup> **IV**, small quantities of ethylene glycol dimethacrylate as cross-linking agent and 2,2'-azobis(isobutyronitrile) (AIBN) as radical thermal initiator.<sup>14</sup> Nine different polymer films were prepared by varying two parameters: a) the concentration of **I** (see Scheme 3 and Table 1) and b) the ratio of hydrophilic (**IV**) to hydrophobic (**III**) monomers in order to optimize the characteristics of the films. At this point, it must be taken into account that more hydrophilic films (larger quantity of **IV**) would lead to a higher diffusion rate<sup>15</sup> of the water/cyanide into the membrane where the sensing probe is homogeneously distributed. This would result in faster response times, but also in a loss of mechanical stability of the polymer film. Therefore, a set of films with different hydrophilic/hydrophobic character, mechanical strength and content of the pyrylium probe were prepared in order to select that showing a better performance.

The different polymers prepared containing the pyrylium derivative are colorless or pale yellow (absorbance maxima centered at 425 nm) and highly fluorescent (emission band centered at 474 nm upon excitation at 394 nm). Prior to the studies with cyanide, the films were soaked in plain buffer (NaOH 10<sup>-3</sup> mol dm<sup>-3</sup>, pH 11) for 30 minutes to condition the polymer. During this time a partial development of a band at *ca.* 530 nm is



**Scheme 3** Structure of the sensing films and monomers **III** and **IV** used in their synthesis.

**Table 1** Composition of the polymeric films

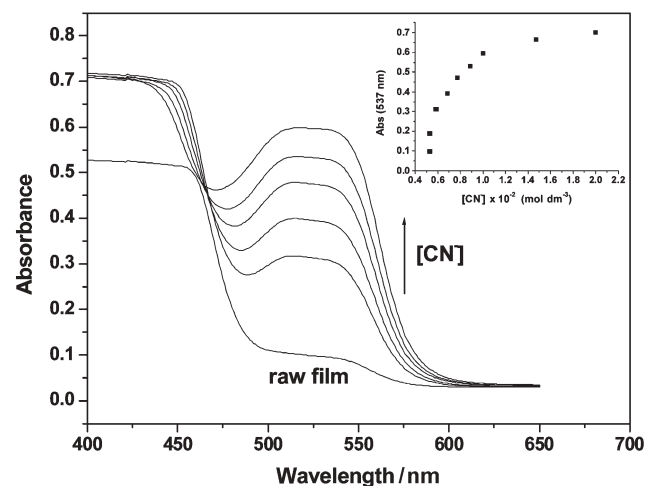
Film	<b>I</b> ( <i>x</i> ) <sup>a</sup>	<b>III</b> ( <i>y</i> ) <sup>a</sup>	<b>IV</b> ( <i>z</i> ) <sup>a</sup>
1	0.5	100	0
2	1.0	100	0
3	2.0	100	0
4	0.5	75	25
5	1.0	75	25
6	2.0	75	25
7	0.5	50	50
8	1.0	50	50
9	2.0	50	50

<sup>a</sup> Molar composition ratio of the monomers used for the preparation of the films.

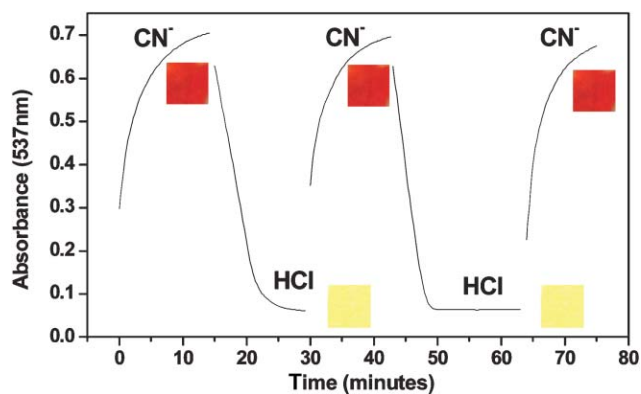
observed, probably due to an attack of the OH<sup>-</sup> anion on the pyrylium ring.<sup>16</sup> To test the anion sensing ability of the conditioned polymers, different anions were added to plain buffer solutions at pH 11. The addition of cyanide into the cell containing the pyrylium-doped films resulted in a change in the absorption spectra with a gradual enhancement of the 537 nm band with the cyanide concentration. In contrast, in the presence of the Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, H<sub>2</sub>PO<sub>4</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup> and SCN<sup>-</sup> anions, the films remained silent.<sup>17</sup> The response to cyanide can be seen in Fig. 1, which shows the titration of the films with aqueous CN<sup>-</sup>. The inset shows the corresponding binding isotherm. The best results in terms of response time and colour variation were obtained with the most hydrophilic film **9**, which contains a larger percentage of **IV** and also the higher content of the sensing probe **I**. Film **9** also showed a suitable mechanical stability.

In preliminary studies a detection limit of 4.0 × 10<sup>-3</sup> mol dm<sup>-3</sup> has been determined with the polymeric material **9** at pH 11.0.

One particular feature of the cyanide reactivity with pyrylium rings is that the process is reversible and it has been reported that in the presence of acidic solutions the pyrylium derivative could be retrieved. Therefore the attractive possibility of attaining reusable colorimetric probes was tested *via* recuperation of the sensing polymer by reaction of the cyano-enone derivative with acidic solutions to obtain the former pyrylium cation. Red films saturated with cyanide were soaked in 0.01M hydrochloric acid solutions



**Fig. 1** UV-Vis spectra of polymer **9** upon exposure to increasing amounts of cyanide in water at pH 11. The inset shows the respective binding isotherm by measurement of the 537 nm band.



**Fig. 2** Absorbance of the 537 nm band upon exposure to cyanide at pH 11 and to acidic HCl aqueous solutions (0.01 M). A photograph showing the colour of the polymer after each process is also included.

and recovery of the original colour of the pyrylium-containing films was observed (see Fig. 2). This acid treatment also reverted the ring opening caused by the plain buffer conditioning. This cyclic process was repeated at least 10 times without significant degradation of the sensing ability of the sensory polymer.

In summary we have shown here a new colorimetric probe for cyanide sensing in water based on the reactivity of the cyanide anion with pyrylium cation anchored into a polymer. The reaction used is reversible and the sensory polymer can be easily recovered by washing the film with aqueous acidic solutions. The combination of suitable chromogenic systems and polymeric materials could lead to new sensory systems for the development of reusable colorimetric easy-to-use *in situ* naked-eye chemosensors for target species of interest in water.

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- 14 The films were prepared by radical polymerization of a mixture of **I**, **III** and **IV** using 1,2-ethanedioldimethacrylate and AIBN (2.0 wt%) as initiator. The nominal cross-linking ratio, *i.e.*, the ratio of the number of moles of monomers to the cross-linking agent, was  $\sim 100:1$ , and the film thickness was  $\sim 110 \mu\text{m}$ . The addition of a cross-linking agent is necessary in order to obtain membranes with adequate mechanical properties. The reaction was carried out in a silanized glass mold of  $100 \mu\text{m}$  thickness in an oxygen-free atmosphere at  $65^\circ\text{C}$  for 5 h.
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- 16 Layers stored in buffer sodium hydroxide ( $10^{-3} \text{ mol dm}^{-3}$ ) for 24 hours showed a similar response upon cyanide addition to those only soaked for 30 minutes.
- 17 Under the experimental conditions employed in the cyanide detection, sulfide anion also gives a response, most likely due to a nucleophilic attack on the pyrylium ring. See: D. Jiménez, R. Martínez-Máñez, F. Sancenón, J. V. Ros-Lis, A. Benito and J. Soto, *J. Am. Chem. Soc.*, 2003, **125**, 9000.