A Soluble and Reusable Colorimetric Sensor Based on the Covalent Attachment of a Triarylpentenedione to Poly(ethylene glycol)

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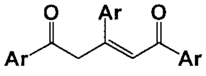
Keywords: Sensors / Polymers / Heterocycles / Cyclization / Colorimetry

3-(4-Aminophenyl)-1,5-diphenylpent-2-ene-1,5-dione (PDO) is a colorimetric sensor of Lewis acid cations that has been covalently attached to a poly(ethylene glycol) (PEG) scaffold. The resulting PDO-PEG is soluble in water and other organic solvents and acts as a colorimetric sensor of Lewis acid cations by undergoing cyclization into the triarylpyrylium form. In water, PDO-PEG also undergoes the colorimetric change in the presence of Brönsted acids, which may limit its usefulness. This modified PEG is recoverable by precipitation from cold ethanol and reusable after reopening of the triarylpyrylium heterocycle to the active pentenedione form. The testing-recovery-reuse cycle has been performed five times without noticeable differences in the response. In contrast to PDO-PEG, PDO on its own is insoluble in water and remains completely soluble in ethanol. This solubility behavior of PDO makes the molecule unsuitable for use as a reusable and recoverable sensor.

Introduction

Colorimetric sensors undergo visual changes during the sensing phenomena and they do not require any instrumental technique to reveal the presence of analyte.[1–5] One type of chromogenic sensor that has recently received some attention has a chemical structure derived from 1,3,5-triarylpent-2-ene-1,5-dione (PDO).[6–9]



PDO

Derivatives of this parent PDO having a covalently attached selective complexing unit have been reported for the sensing of metal ions as well as some inorganic anions and *cis* configured dicarboxylic acids.[8–11] Although there are many other colorimetric sensors that are soluble in water,[12] a possible limitation of this family of sensors based on PDO is their poor solubility in aqueous medium, which means that either organic co-solvents or pure organic solvents must be used to achieve sufficient solubility. Another aspect, related to the solubility, worthy of being explored for sensors based on the PDO structure is the possibility to recover and reuse the molecule.

In a recent paper we have reported the covalent attachment of a PDO derivative to silica particles or its inclusion in microporous zeolites.[13] The problem of this methodology, however, is the long response time required to observe the color change, which arises due to the mass-transfer phenomena between the solid and the liquid phases. In order to reduce the response time, one alternative that could circumvent this problem would be the covalent binding of the sensor molecule to a soluble polymer, thus rendering analyte sensing a homogeneous rather than a heterogeneous process. The polymeric backbone could serve to both increase the solubility of the sensing molecule in the desired medium and to permit the recovery of the sensor after use. In fact, the strategy consisting of attaching an organic molecule covalently to a polymeric scaffold is gaining importance in homogeneous catalysis to recover soluble catalysts.[14–19] Polymers,[20–22] sol-gels,[23–25] and hydrogels[26] have often been used in combination with a sensor to better adapt it to water and other media where the analyte is present. Herein we report the preparation of a 4-(*p*-aminophenyl)-2,6-diphenylpent-2-ene-1,5-dione covalently attached to a water-soluble poly(ethylene glycol) and compare its performance with that of a water-insoluble, low-molecular-weight polystyrene recently prepared by us.[13] The use of soluble poly(ethylene glycol) as a scaffold for catalysts or reagents is a topic of much current interest. Their solubility properties allow the reactions to be performed in homogeneous solution in some solvents and quantitatively recover the polymer by precipitation with diethyl ether after use.

We show here that attachment of a PDO sensor to poly(ethylene glycol) polymers allows the recovery and reuse of the polymeric sensors which, in some solvents, behave like the equivalent sensor not bound to the polymer. Unattached, molecular PDO is not soluble in water, and remains

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DOI: 10.1002/ejoc.200500004

completely soluble in ethanol. However, our study of the sensing response reveals that when attached to poly(ethylene glycol), the PDO-based sensor is not appropriate for use in an acidic aqueous medium due to the chemical instability of the sensing dione to Brönsted acids.

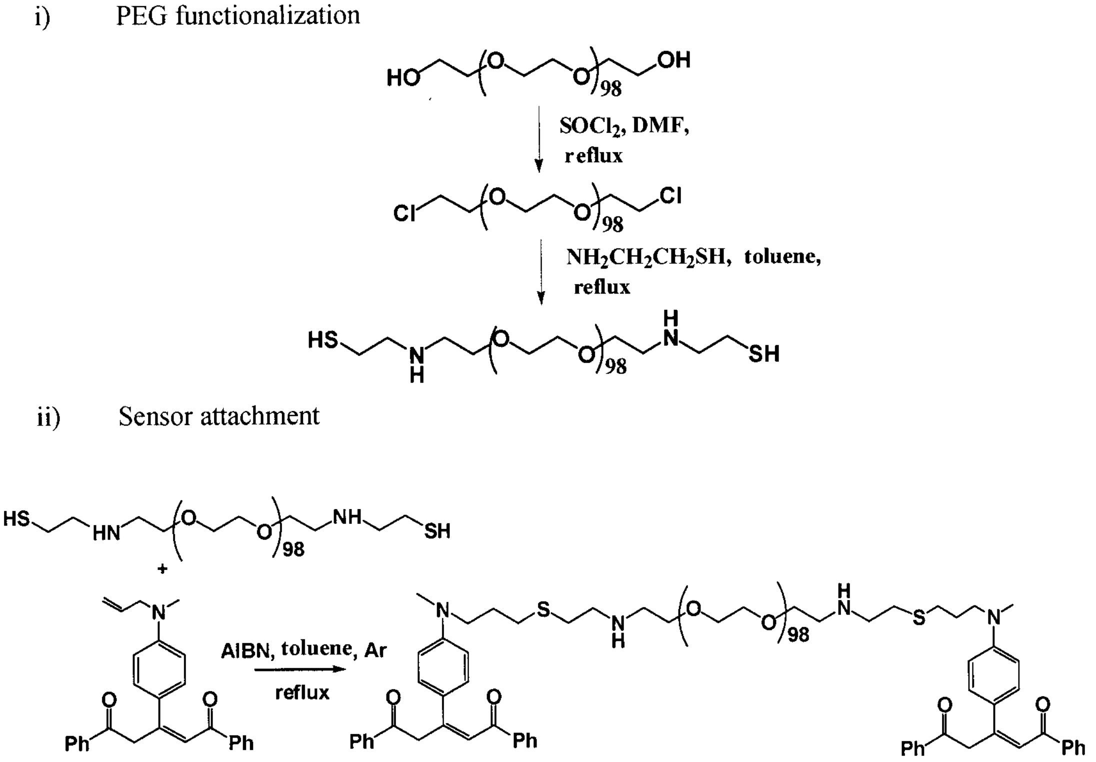
Results and Discussion

Preparation and Characterization of the PDO Sensor Attached to Poly(ethylene glycol)

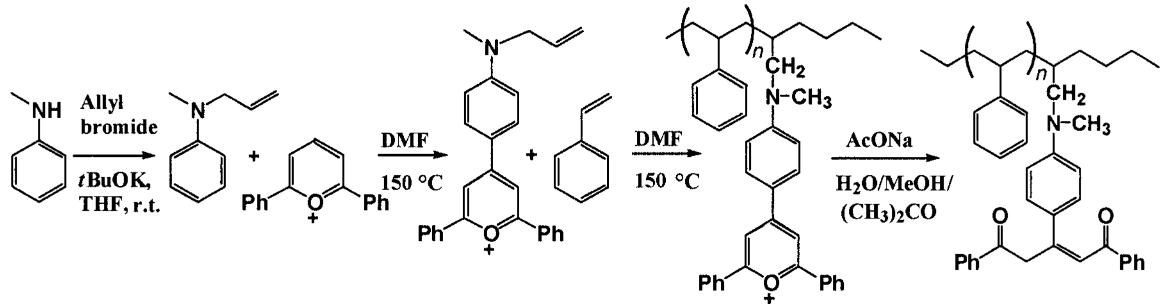
The key step in the preparation of modified poly(ethylene glycol) (PEG) containing terminal sensing diones is a radical chain addition of a mercapto group to a terminal carbon-carbon double bond connected to an appropriately functionalized PDO derivative. This radical-mediated addition of mercapto groups to vinylic functions has previously been used by many groups for the efficient covalent attachment of metallic complexes to modified solid surfaces under mild conditions.[27–31] To obtain the mercapto-functionalized PEG with the desired solubility properties, commercially available PEG (mol. wt. 5000 D) was reacted with thionyl chloride to convert the primary hydroxyl groups into the corresponding chlorides, which were subsequently substituted by treating then with 2-mercaptoethylamine. This modified PEG containing terminal mercapto groups was subsequently treated under an inert atmosphere with 4-[4-(allylamino)phenyl]pent-2-ene-1,5-dione perchlorate with AIBN as radical initiator to give 4-[4-(allylamino)phenyl]-pent-2-ene-1,5-dione by aromatic electrophilic substitution of 2,6-diphenylpyrylium with *N*-allylaniline in DMF followed by heterocyclic ring opening with a base. The actual synthetic steps, reaction conditions, and the required reagents are summarized in Scheme 1.

Alternatively, the precursor of the sensor molecule 4-[4-(allylamino)phenyl]-2,6-diphenylpyrylium was co-polymerized with an excess of styrene to form a co-polymer in which pyrylium ions are connected to a polystyrene (PS) backbone, as previously reported by us.[13] By controlling the pyrylium/styrene molar ratio, as well as the polymerization conditions, a co-polymer with adequate solubility in ethanol, dichloromethane, and other organic solvents, but insoluble in water, was obtained. The actual sensing form, namely the open pentenedione form, was again obtained by hydrolytic ring opening in a mixture of ethanol and water in the presence of sodium acetate as base to give PDO-PS. Scheme 2 depicts the synthetic route followed to obtain PDO-PS. As expected, PDO-PS is insoluble in water but soluble in ethanol or dichloromethane.

The PDO-PEG and PDO-PS polymers were purified by dialysis in water (PDO-PEG) or methanol (PDO-PS) in order to ensure the absence of residual pentenedione or pyrylium dye not covalently bonded to the polymer backbone that could interfere later in the sensing tests. Thin-layer chromatography showed that the dialyzed polymers were free from PDO precursors The presence of PDO in the water-soluble PDO-PEG polymer was confirmed by the presence of a singlet at $\delta = 4.79$ ppm in its ^{1}H NMR spectrum in solution, as well as signals in the aromatic region. These NMR signals, particularly the one at $\delta = 4.79$ ppm attributable to the methylene protons in position 4 of the



Scheme 1.



Scheme 2.

pentenedione moiety, are also observed in all PDO derivatives. Figure 1 shows an expansion of the ^1H NMR spectrum of PDO-PEG.

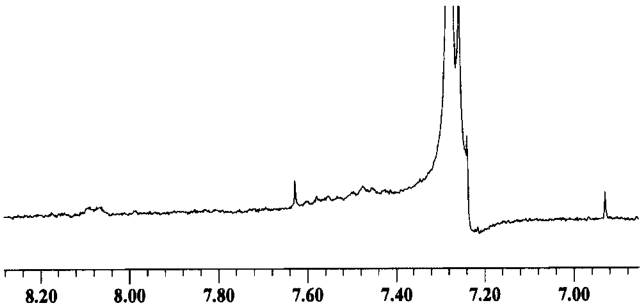


Figure 1. Expansions of part of the ^1H NMR spectrum of PDO-PEG.

The presence of PDO in the dialyzed polymers was also determined by transmission UV/Vis spectroscopy. PDO and the corresponding closed pyrylium form (TP) have characteristic bands in the UV/Vis spectrum at 420 nm and 520 nm, respectively. These absorption bands are responsible for the change in color during the sensing experiments. Figure 2 shows the transmission UV/Vis spectra for aqueous solutions of PDO-PEG and TP-PEG; the differences between the two spectra are clear. Due to the low amount of organic dye attached to the polymer chain, the characteristic absorption bands for the open PDO and heterocyclic forms appear on top of a baseline that grows in absorbance towards shorter wavelengths due the background of the polymer scaffold.

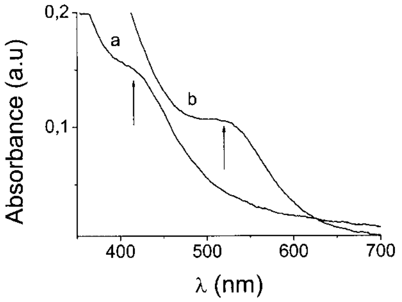


Figure 2. Transmission UV/Vis spectra of dichloromethane solutions of PDO-PEG (spectrum a) and TP-PEG (spectrum b). The arrows show the λ_{max} characteristic of PDO and TP precursors that are responsible for the color changes.

The PDO loading in the polymer was quantified by the variation in the combustion chemical analyses before and after PEG functionalization and before and after covalent attachment of the sensor. This technique gives a percentage of PEG functionalization of about 40% of the maximum theoretical value. This estimation was confirmed more simply by ^1H NMR spectroscopy using a commercial PEG having terminal methyl groups (PEG-OMe). Known amounts of PEG-OMe and PDO-PEG were dissolved in $CDCl_3$ and the peak integral used to quantify the amount of PDO present relative to the methyl groups of PEG-OMe.

PDO-PEG as a Soluble, Reusable Sensor

The purpose of this work was to develop a recoverable colorimetric sensor based on PDO that could be used in water and other solvents. It is appropriate to comment that previous reports on the use of chemosensors based on the pentenedione–pyrylium interconversion have not used pure water as solvent, but mostly a mixture of water and organic solvents or pure organic solvents.[10,11] Unfortunately, it soon became evident that in spite of the solubility of PDO-PEG in water and that the changes in the color are visually observable as expected, this system does not exhibit the selectivity previously shown in the literature for related derivatives containing selective complexing units attached to PDO.[10] Thus, aqueous solutions of PDO-PEG (5 $mg\,mL^{-1}$) change the color from yellow to red in the presence of strong Lewis acid cations such as Fe^{3+}, Cu^{2+}, and Pb^{2+} in concentrations between 10^{-2} and 10^{-4} M. Other metal cations that do not exhibit sufficiently strong Lewis acidity do not produce a response in the PDO-PEG sensor. This is the case of alkali metal ions and alkaline-earth cations. As reported in an earlier work on PDO attached to silica particles,[13] PDO responds also to Brönsted acids. For this reason, most of the experiments in aqueous media were conducted in HEPES buffered solution at pH 5. The range of pH values at which PDO-PEG is stable (pH > 3) is, however, not a major limitation for physiologically relevant cations, considering the pH of physiological fluids. As an example, to illustrate the visual changes produced upon sensing, Figure 3 shows the color change of PDO-PEG in water when Fe^{3+} was added to a solution of the sensor.

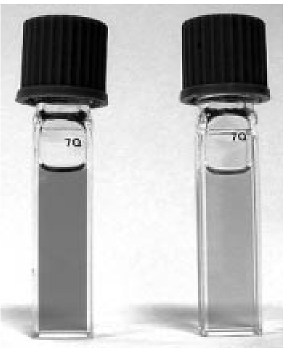
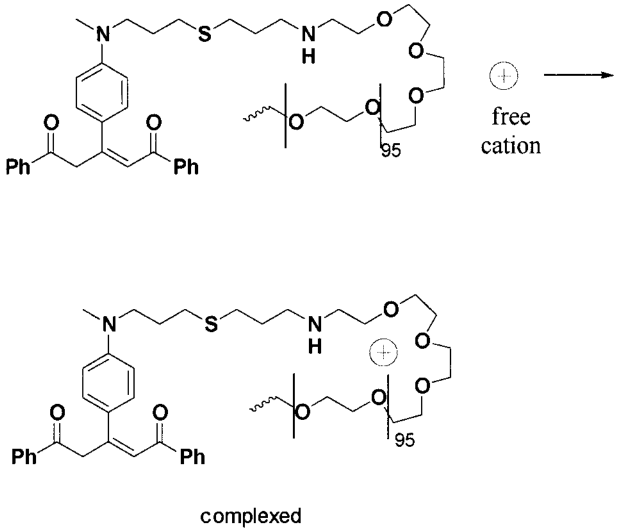


Figure 3. Photograph of two cells containing aqueous solutions of PDO-PEG (0.5 mg mL^{-1}) in the presence (left) or absence (right) of $Fe(NO_3)_3$ at a final concentration of 2×10^{-4} M.



Scheme 3.

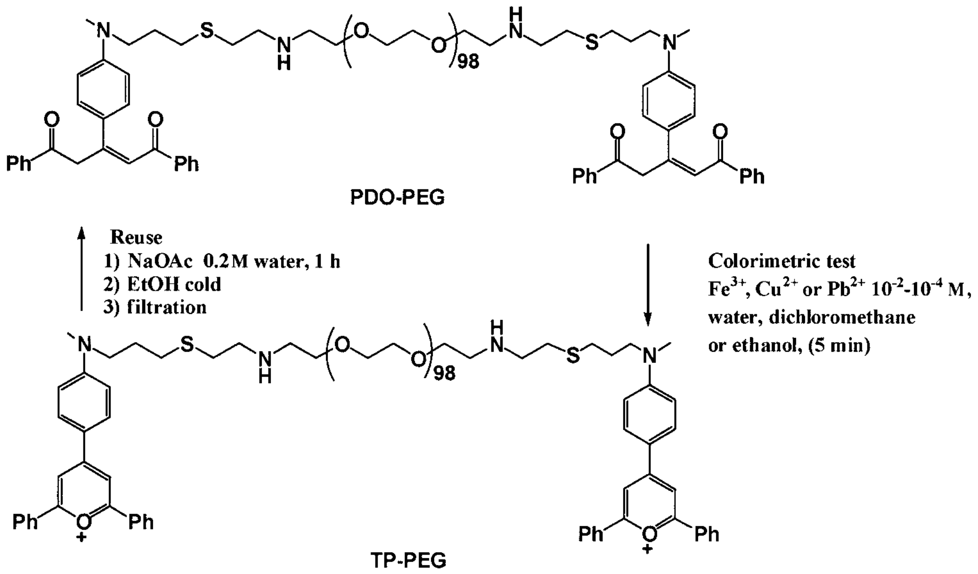
The use of dichloromethane as solvent instead of water, or the presence of other Lewis acid cation analytes, produces identical color changes provided that appropriate soluble metal salts are used. Importantly, PDO-PEG in water also changes color at acidic pH, thus indicating that Brönsted acids are also able to produce the colorimetric response. This behavior is, in fact, not completely unexpected considering that the color changes are related to a cyclization from the open PDO to the closed pyrylium form and vice versa. Since it is known that formation of pyrylium heterocycles from unsaturated pentenediones can be promoted by Brönsted or Lewis acids we anticipated that pure Brönsted acids such as HNO_3 and HCl could also promote the response of the sensor, as turned out to be the case.

One fact that was, however, unexpected was the extremely slow response of the PDO-PEG sensor in aqueous solution and other organic solvents. At the concentration used, the response requires tens of minutes at room temperature, and is considerably slower than simple derivatives in organic solvents. Under the typical conditions used (Figure 3) Fe^{3+}exhibits a clear response in 20 min, which is a somewhat faster response than those of Cu^{2+} and Pb^{2+}. This response time also depends on the solvent, and is notably slower in dichloromethane and water. We believe that this is due to the complexing ability of the PEG backbone, which could interact with the cations via the aminophenyl group (Scheme 3). This type of complexation between PEG and metal ions is well documented in the literature[32,33] and is the basis of the high catalytic activity of PEGs in the presence of cesium carbonate in organic solvents due to the sequestration of cesium and enhancement of the basicity of free carbonate.[34,35]

The sensor response evidently requires an interaction between the Lewis or Brönsted acid and the *para* amino group of the aryl ring at the 3-position of the pentenedione system, which provokes the cyclization to the pyrylium ring. A slow response was also found with dichloromethane as solvent, and it was not shortened by increasing the concentration of PDO-PEG. In fact, a high PDO-PEG concentration can be unfavorable from the sensitivity point of view, since the visual color change from red to yellow is less clearly observed for highly concentrated solutions. To shorten the response time we studied the influence of adding NaCl as we expected that addition of Na^+ would have a positive influence by replacing analyte at the spurious complexing sites in the polymer backbone (see Scheme 3). However, addition of a 10^{-2} M solution of NaCl has only a marginal effect on the response time, although some shortening of the time from addition of the analyte until the color change was noticed.

In contrast to water or dichloromethane, an appropriate solvent in which the response time was only a few minutes is ethanol. In this solvent at room temperature the solubility of the PDO-PEG is low but still sufficient to test the presence of analytes in a few minutes at a PDO-PEG concentration of 0.05 mg mL^{-1}. In contrast to PDO-PEG, and in agreement with what is known for polymer solubility, PDO-PS is insoluble in water but is extremely soluble in ethanol, dichloromethane, acetonitrile, and many other organic solvents. In support of the influence of the PEG chain slowing down the response time of PDO-PEG, PDO-PS responds to the presence of analytes in organic solvents in a few minutes and in all cases considerably faster than PDO-PEG. This reduced response time for PDO-PS as compared to PDO-PEG lends support to the influence of the nature of the polymer chain on the sensing process.

The main purpose of our work was to show the reusability of soluble polymers containing PDO sensing units. With the aim of showing this reusability, we devised a procedure consisting of the recovery of the sensing polymer by precipitating it from cold ethanol. Solutions of 1 mg of TP-PEG in 1 mL of ethanol were almost quantitatively recovered by concentrating the solution to 0.2 mL and filtering the precipitated solid. In contrast, unbound TP^+ remains in solution under the same conditions. The red TP-PEG solid was then dissolved in a 10^{-2} M aqueous solution of sodium acetate and the solution stirred at room temperature for 1 h. This treatment under basic conditions produced the ring opening of the pyrylium back to the open PDO sensing form (Scheme 4). This aqueous solution of yellow PDO-



Scheme 4.

PEG was concentrated under reduced pressure before reprecipitating in cold ethanol. The recovered PDO-PEG was reused for a consecutive run. This cycle (sensing/recovery/heterocycle reopening/reuse) was repeated five times without significant variation in the visual response of the analyte. Scheme 4 summarizes the procedure for the reuse of the recoverable PDO-PEG sensor.

Figure 4 shows the UV/Vis spectra recorded for solutions during some of the cycles to illustrate the interconversion between the open and closed forms of the PDO-PEG sensor upon consecutive reuse.

Conclusions

In summary, we have reported here that a recoverable and reusable soluble colorimetric sensor can be devised by the covalent attachment of a pentenedione colorimetric sensor to a polymeric poly(ethylene glycol) scaffold. The system can be recovered and reused after basic treatment and can be used for five cycles without loss of activity. Among the major drawbacks of the system are the limited selectivity and the slow response under some circumstances. The selectivity can be improved by adding appropriate complexing units to the structure, although the complexing ability of PEG also plays a role in the sensing. The presence of complexing units on the N atom of the PDO moiety can also influence positively the response time in some solvents. On the other hand, the influence of Brönsted acids limits the use of the PDO-TP sensing system in aqueous solution to neutral and basic pHs.

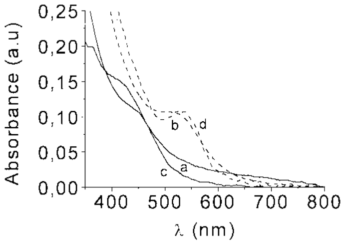


Figure 4. UV/Vis spectra of an aqueous solution of PDO-PEG (plot a) that was used as Fe^{3+} sensor and, therefore, transformed into TP-PEG (spectrum b, which was reused five times according to the cycle shown in Scheme 4 either in the PDO-PEG form (plot c) or after sensing with Fe^{3+} and transformation into TP-PEG (plot d).

Experimental Section

Synthesis of Chloride-Functionalized Poly(Ethylene Glycol): Commercial poly(ethylene glycol) (PEG, mol. wt. 5000 D; 1.00 g, 0.17 mmol) was dissolved in a mixture of $SOCl_2$ (6 mL) and dimethyl formamide (1 mL). The reaction mixture was stirred for 24 h at 60 °C, then cooled to room temperature and the solvent partially evaporated under reduced pressure. Residual thionyl chloride was decomposed by cautious addition of a 10^{-2} M aqueous solution of K_2CO_3. The reaction mixture was then concentrated and extracted with dichloromethane. The organic layer was dried with anhydrous Na_2SO_4 and the solvent was removed under vacuum to give chloride-functionalized PEG.

Synthesis of Mercapto-Functionalized Poly(Ethylene Glycol): Chloride-functionalized PEG (300 mg) was dissolved in toluene (10 mL) and 2-aminoethanethiol hydrochloride (300 mg) was added. The mixture was stirred at reflux temperature for 24 h then cooled to room temperature and concentrated under reduced pressure. Dichloromethane was added to the resulting crude and the 2-aminoethanethiol hydrochloride precipitate was removed by filtration. The organic layer was evaporated to give mercapto-functionalized PEG. Chemical analysis indicated that the modified polymer contains 1.05% sulfur.

Synthesis of *N*-Allyl-*N*-methylaniline:[13] *N*-Methylaniline (535.5 mg, 5 mmol) was dissolved in dry THF (10 mL) and K*t*OBu (561.4 mg, 5 mmol) was added. The mixture was stirred at 0 °C under N_2 for 1 h and then allyl bromide (604.9 mg, 5 mmol) was added. The suspension was left to warm to room temperature and magnetically stirred for 24 h. Then, the reaction was washed with a 1 M solution of HCl and extracted with CH_2Cl_2. The organic layer was washed with NaOH, dried with anhydrous Na_2SO_4, and concentrated under vacuum. *N*-Allyl-*N*-methylaniline (35%) was obtained as a yellow oil after preparative column chromatography with a mixture of hexane and diethyl ether (10:1) as eluent. ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 2.98 (s, 3 H, CH_3), 3.94 (d, *J* = 4.8 Hz, 2 H, CH_2N), 5.14–5.22 (m, 2 H, $CHCH_2$), 5.77–5.90 (m, 1 H, $CHCH_2$), 7.22–7.28 (m, 5 H, ArH) ppm. ^{13}C NMR (300 MHz, $CDCl_3$, 25 °C): δ = 36.6, 55.9, 113.0, 116.7, 117.0, 129.7, 134.4, 150.1 ppm.

Synthesis of 4-[4-(Allylmethylamino)phenyl]-2,6-diphenylpyrylium Perchlorate: *N*-allyl-*N*-methylaniline (160.3 mg, 1.1 mmol) was dissolved in DMF (3 mL) and then 2,6-diphenylpyrylium perchlorate (724.4 mg, 2.2 mmol), synthesized as described previously,[36,37] was added. The mixture was stirred at reflux temperature for 3 h, then cooled to room temperature and stirred for an additional 20 h. The solvent was removed under reduced pressure and the resulting brownish-red triarylpyrylium oil used for the next step without purification.

Synthesis of 4-[4-(Allylmethylamino)phenyl]-1,5-diphenylpent-2-ene-1,5-dione: Sodium acetate (183.3 mg, 2.23 mmol) was dissolved in a mixture of water (0.6 mL), methanol (1.9 mL), and acetone (3.8 mL), triarylpyrylium perchlorate was added, and the mixture stirred for 15 h at room temperature and then left for 10 h without stirring. After this time the solvent was evaporated under reduced pressure and the residue was purified by flash chromatography with diethyl ether as eluent to give pentenedione (PDO; 55%) as a yellow oil. ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 3.01 (s, 3 H, CH_3), 3.92 (d, *J* = 4.5 Hz, 2 H, CH_2N), 4.91 (s, 2 H, CH_2COPh), 5.08–5.24 (m, 2 H, $CHCH_2$), 5.63–5.96 (m, 1 H, $CHCH_2$), 7.14–7.98 (m, 14 H, ArH) ppm. ^{13}C NMR (300 MHz, $CDCl_3$, 25 °C): δ = 36.6, 55.9, 112.4, 116.8, 126.7, 127.0, 128.1, 128.6, 128.9, 129.2, 129.4, 129.6, 133.5, 135.7 ppm. HPLC-MS (electrospray): *m/z* = 396.2 $[M + H]^+$. $C_{27}H_{25}NO_2$: calcd. C 82.00, H 6.37, N 3.54; found C 81.26, H 6.46, N 3.14.

Covalent Binding of PDO to Mercapto-Functionalized PEG: Mercapto-functionalized PEG (300 mg) was dissolved in toluene (5 mL) then a solution of PDO (40 mg) in toluene (5 mL) and a catalytic amount of AIBN were added sequentially. The mixture was stirred at reflux temperature for 20 h under an inert atmosphere. Then, the solution was cooled and the solvent evaporated under vacuum. The resulting crude was purified by dialysis in methanol to give the PDO-PEG polymer as a yellow solid. The ^1H NMR spectrum of dialyzed PDO-PEG free from PDO (as evidenced by thin-layer chromatography) shows weak signals between δ = 7.9–7.1 ppm corresponding to the aromatic protons of PDO and a signal at δ = 4.79 ppm attributable to -CH_2-CO-Ph. Due to the relatively low PDO loading, the ^{13}C NMR spectrum of PDO-PEG does not show any characteristic signal of the covalently attached colorimetric sensor. Evidence for the binding between the PEG backbone and PDO was also obtained by combustion chemical analysis, IR spectroscopy, and UV/Vis spectroscopy. Elemental analysis of PDO-PEG shows the presence of nitrogen (0.78%) and sulfur (0.89%), values which, when compared with the initial value of the PEG scaffold, indicate that there are 26 mmol of PDO per 100 g of PEG. This corresponds to a PEG functionalization of about 80% of the maximum capacity. An expansion of the carbonyl region of the IR spectrum of PDO-PEG shows two bands at 1680 and 1648 cm^{-1}, indicating the presence of PDO. In the UV/Vis spectrum the characteristic PDO band at 430 nm was found in the solution spectra of PDO-PEG polymers. ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 1.90, 3.60–3.80, 3.70–3.80 (t, ArN-CH_2), 4.97 (s, PhCO-CH_2), 7.20 (s, PhCOCH=C), 7.40–7.60 (ArH), 8.20–8.30 (ArH ortho to CO) ppm.

For use as a sensor, a few milligrams of PDO-PEG (typically 5 mg) was dissolved in the appropriate solvent (3–5 mL) and then a volume of a solution containing a known concentration of the analyte in the same solvent was added with a syringe, thus allowing the determination of the final concentration. For re-use, the solution was concentrated to 0.3 mL and the TP-PEG precipitated with cold ethanol. The solid was collected and dissolved in 2 mL of a 0.5 M aqueous solution of Na_2CO_3 at room temperature until the color changed to yellow. The resulting PDO-PEG was recovered after concentrating the solvent to 0.3 mL and precipitating the sensor with cold ethanol.

Acknowledgments

Financial support by the Spanish Ministerio de Ciencia y Tecnología (MAT2003-1226) is gratefully acknowledged. EP thanks the Universidad Politécnica de Valencia for a post-graduate scholarship. C. A. is the recipient of a fellowship from the Ana y Jose Royo Foundation.

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Received: January 5, 2005