



Improved polyHEMA–DAQ films for the optical analysis of nitrite

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ABSTRACT

A series of crosslinked poly(2-hydroxyethyl methacrylate) films containing 1,2-diaminoanthraquinone (DAQ) have been synthesized and characterized spectroscopically by FT-IR and UV–vis. Their response towards nitrite anion in acidic medium has been evaluated by means of time-resolved UV–vis spectroscopy. This kinetic analysis has provided a tool for the dynamic characterization of nitrite-sensitive films which could have application in biomedical analysis (nitrite monitoring of biological fluids) and environmental science (control of nitrite levels in drinking water).

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1. Introduction

Sensing polymers have attracted the interest of researchers during the last years [1–5]. Many approaches have been followed in order to create new solid-state materials capable to quantify the presence of certain chemical species. One of such approaches is the entrapment of a sensitive optical probe into a polymeric matrix capable to fix it. Polyvinyl chloride (PVC) [6,7] and hydrogels [8] are paradigmatic examples of supports employed to host a great variety of chemical sensors. Most of the research in the field of supported sensing has been focused on the introduction of chemical modifications in the molecular sensor embedded into the inert polymer matrix, in order to improve its sensitivity and selectivity. Nevertheless, even minor structural modifications of the sensing molecule are often accompanied by dramatic changes in its behavior and this can significantly limit the use of this methodology. An alternative approach can be to accom-

plish a systematic variation of the properties of the matrix, in order to find the optimum situation in terms of the diffusion of the analyte and microenvironment of the sensing unit. This is particularly useful in the case of colorimetric and fluorescent sensors, where the signal can be modulated by some properties, such as the polarity of the environment [9–11].

Recently, we presented some preliminary results on a new kind of polymeric films sensitive to nitrite anion (NO_2^-) and to nitric oxide (NO) [12]. This type of films are based on poly-2-hydroxyethyl methacrylate (polyHEMA), a well known water permeable polymeric matrix, entrapping the colorimetric sensor for NO_2^- and NO 1,2-diaminoanthraquinone (DAQ) shown in Chart 1 [13–16]. Materials based on the polyHEMA matrix have attracted great interest during the last years due to their important applications found in tissue engineering, chromatographic separations, chemical sensing, environmental decontamination, etc. [17–27]. The prepared films are red coloured due to the absorbance at ca. 520 nm of DAQ, and such absorption is bleached upon the action of the aforementioned analytes. One of the most remarkable features of such materials is the absence of leaching of DAQ out of the films even after 6 months of storage. Two simple

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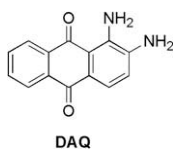


Chart 1. Chemical structure of 1,2-diaminoanthraquinone (DAQ) used as the sensing molecule.

formulations using 2-hydroxyethyl methacrylate (HEMA) as a hydrophilic monomer and ethyleneglycol dimethacrylate (EGDMA) as a crosslinker were initially described. The corresponding monomeric mixtures were thermally polymerized using a radical initiator (AIBN). The two formulations varied in the degree of crosslinking and concomitantly in the dynamic response to NO_2^-/NO : those with a 10% of crosslinker displayed a much faster response than those using 25% EGDMA.

In order to improve the dynamic response of the polyHEMA films we have explored new compositions of monomers and crosslinkers. Here we report on the synthesis of a family of 19 different new polyHEMA sensitive films and on the study of their dynamic response towards nitrite. The films were synthesized after a systematic variation of the initial reactive formulation (Chart 2): 2-hydroxyethyl methacrylate (**1**), 2-methoxyethyl methacrylate (**2**), ethyl methacrylate (**3**), 2-ethylhexyl methacrylate (**4**), acrylic

acid (**5**), ethyleneglycol dimethacrylate (**6**), diethyleneglycol dimethacrylate (**7**), triethyleneglycol dimethacrylate (**8**), 1,6-hexanediol dimethacrylate (**9**), polyethyleneglycol dimethacrylate (Mw 550) (**10**).

As it will be shown, the prediction of the properties of the final polymer is not always straightforward through a simple analysis of the individual elements of the reactive mixture, and the use of the appropriate experimental techniques such as time-resolved UV-vis spectroscopy is needed. By means of this study we have improved the response time of the films already reported by a factor of ca. 3 and identified the key monomers and crosslinkers for the future development of polyHEMA films, specially for biomedical applications, providing the relevance of NO and NO_2^- in medical studies [28,29]. Several solid-state devices for the analysis of NO and NO_2^- have been developed to date, employing poly(ethylene glycol), silicone rubber, poly(*p*-phenylene vinylene), poly(1,8-diaminonaphthalene) and others [30–33]. Up to our knowledge the use of polyHEMA matrices as supports for an optical probe has not been reported, but these results reveal that these films are very well suited for this kind of practical applications.

2. Experimental

2.1. Materials and methods

The monomers and crosslinkers used in this study were supplied by Aldrich and were used without further purification. AIBN and sodium nitrite were obtained from Fluka. Acetic acid was obtained from Scharlab. Water was Millipore Q quality.

UV-vis absorption spectra were recorded in a Hewlett-Packard 8453 apparatus. FT-IR spectra were acquired using a FT/IR-6200 type A Jasco spectrometer, with 4 cm^{-1} resolution and 50 scans accumulation. Thermal analysis measurements were carried out using a Perkin-Elmer DSC instrument (40–400 °C at a heating rate of 10 °C/min and 400–40 °C at a cooling rate of 10 °C/min, two scans). DSC experiments were carried out in a static air atmosphere.

2.2. Preparation of polymers

Step 1: The appropriate amount of polymerizable monomers and crosslinkers (as indicated in Table 1) were weighted and mixed in small vials (typically 1 g of final monomeric mixture). Providing the low amount of DAQ to be added to the mixture, the following strategy was followed: 60 mg DAQ were previously dissolved in 30 g of 2-hydroxyethyl methacrylate (**1**) since this is a common element for all the monomeric mixtures. Then the appropriate weight of such HEMA/DAQ solution was employed in such a way that the concentration of DAQ in the final mixture was of 0.0045 M.

Step 2: A 1% wt of AIBN was added to the monomeric mixture and it was stirred at r.t. until complete dissolution.

Step 3: The solution containing monomers, crosslinkers, AIBN and DAQ was introduced in the narrow space created between two microscopy slides separated by two thin

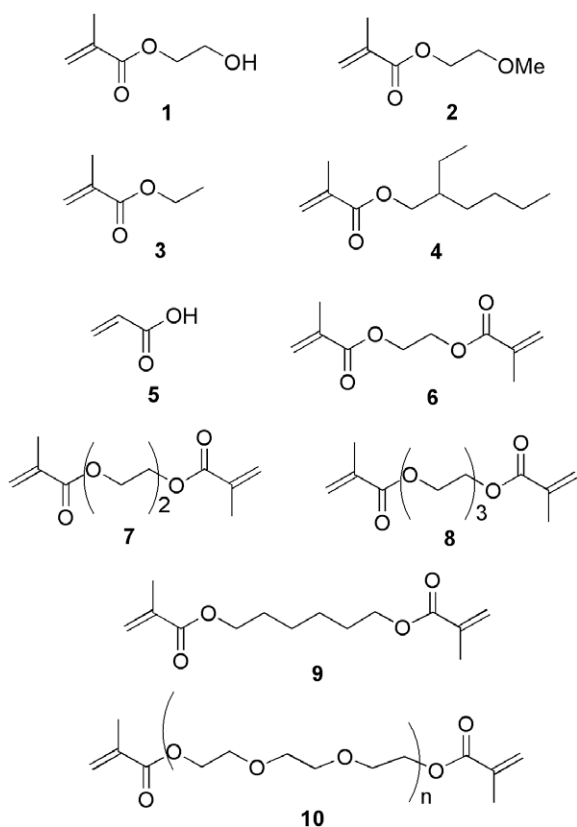


Chart 2. Chemical structure of monomers (**1–5**) and crosslinkers (**6–10**) used in this work for the preparation of polyHEMA films.

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