



Hydrogel films engineered in a mesoscopically ordered structure and responsive to ethanol vapors



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ABSTRACT

Responsive hydrogels filling the interstitial spaces of photonic crystals can form mesoscopically structured materials, which exhibit reversible shifts in the Bragg diffracted light as a response of environmental changes. These materials can be used to generate chemical or biochemical sensors. The present work reports on the synthesis and characterization of ethanol responsive hydrogels that can be used in the design of novel breathalyzers. The dynamic mechanical behavior of the macroscopic hydrogels and their swelling features in the presence of different liquids or vapors have been investigated to orientate the choice of the best responsive material and curing process. The swelling behavior of a selected hydrogel embedding the photonic crystal made of polystyrene nanoparticles as function of the concentration of ethanol vapor was studied through UV–Vis optical transmission spectroscopy and compared to the behavior of the macrogel analogue.

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1. Introduction

Stimuli responsive hydrogels have been extensively studied as active materials for a variety of chemical and biochemical sensors, for their ability to undergo reliable, robust and often reversible “phase transitions” in response to small local environmental modifications, which bring them away from their equilibrium states [1–6].

Different hydrogel systems, in terms of chemical composition, crosslinking degree and density can be designed to confer specific sensitivity to a stimulus or a combination of stimuli, such as temperature, electrical field, light, pH, solvent composition and specific ions, and to control the extent of material modification, generally in terms of its stiffness, shape, volume or mass [7–9].

Hydrogel-based sensors can be miniaturized and integrated into microfluidic systems and microsystems [10–13].

At the basis of the hydrogel responsiveness there are modifications of polymer–solvent interactions, as a result of changes of the environmental conditions, which may cause further solvent uptake and swelling or solvent outflow and deswelling. Therefore, mainly thermodynamic criteria and network mechanics govern hydrogels

responsiveness. Synchronized, cooperative motions of several polymer segments of the network are required for these systems to achieve a local or global free energy minimum in a new equilibrium position. As a result, the time-dependence of these responses may exceed the temporal switching dynamics required for sensing applications. Reducing the mass or the volume of the switching systems, and simultaneously increasing the interfacial area with the environment, yet preserving the robustness of the signal derived by the collective response of the material, should facilitate mass/heat transport and enable higher responsivity and/or faster response.

Stimuli-responsive hydrogel thin films, with a periodically ordered structure at the mesoscale, represent a promising platform for obtaining increased stimulus-sensitivity and reduced response-time optical sensors. As demonstrated by the pioneering work of Asher and coauthors [14], stimuli-responsive hydrogels filling the interstitial spaces of either silica or polymeric nanoparticles organized in a crystalline array can diffract the light at visible wavelengths determined by the lattice spacing, d , which gives rise to an intense color in the visible range. Hydrogel swelling or shrinking, in response to an external stimulus, changes the mean separation between the colloidal spheres and induces a diffracted light Bragg peak shift to either longer or shorter wavelengths. Removal of nanoparticles template leads to the formation of

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hydrogel inverse photonic crystals (HIPCs) with a periodic distribution of voids.

The hydrogel-infiltrated photonic crystal, depending on its chemical composition, can exhibit significant reversible visible light diffraction shifts in response to a variety of stimuli, such as temperature, pH, presence of specific molecules or biomolecules and mechanical forces [15,16,14,17,18]. The stimuli-responsiveness must be accompanied by an adequate elasticity and chemical stability of the hydrogel network. As a result the mesostructured film will be able to withstand repeated swelling/de-swelling cycles, when in use, as well as erosion due to prolonged exposure to the swelling medium. Moreover, it will survive to the action of acid etching or organic solvents extraction required by the colloidal crystal template removal process for the preparation of the inverse photonic crystal [19].

For the development of ethanol vapors sensors, ethanol-responsive hydrogels can be considered as active materials. Yet, it should be considered that ethanol can be only one of the components of a vapor-phase in equilibrium with an aqueous liquid mixture of different composition, generally being water the most abundant component. Therefore, regardless the number and variety of other components that can be present in the vapor phase, the presence of water imposes either the recourse to technological solutions for dehydration, with relative costs implications, or, more preferably, to properly designed materials which are able to respond to variations of ethanol concentration also in the presence of substantial amounts of water.

There are interesting studies which report Bragg diffraction shifts in a wide region of the visible spectral region when e.g., a crosslinked 2-hydroxyethyl methacrylate (HEMA) hydrogel is exposed either to pure liquid water or to concentrated ethanol/water liquid solutions [20].

However, at the best of our knowledge, there are no equivalent studies that report on the ability of hydrogel inverse opals to specifically respond to ethanol vapors after saturation with water. In particular, the hydrogel network should be designed so that it can uptake and retain water, when exposed to water vapor-rich atmospheres, and swell further when the atmosphere is progressively concentrated of ethanol vapors. For this purpose, 2-hydroxyethyl methacrylate (HEMA) was used as the main building block of the network for its known favorable Flory–Huggins mixing parameter with ethanol. Acrylic acid (AA) at two different ratios was also considered as co-monomer for its affinity toward water and its contribution to hydrogel network mechanical properties, due to the establishment of further crosslinking through strong secondary interactions. Finally, poly(ethylene glycol) dimethacrylate (PEG₂₀₀-DMA) was used as crosslinking agent. The polymerization process combined a “cold” UV-photocrosslinking step and a thermal post-cure. FTIR spectroscopy and dynamic mechanical thermal analysis were carried out on the macrogel analogues (macrogels), i.e., wall-to-wall hydrogels polymerized from the same monomer mixture and with the same cure and post-cure cycles as for the mesoscopically ordered hydrogel films. That was performed in order to seek for confirmation of the success of polymerization and to withdraw useful information on the complex shear moduli of the hydrogels synthesized, respectively. Preliminary swelling studies were carried out exposing macrogels to liquid water, ethanol, methanol and acetone and to any of these organic solvents after equilibration with water. The most promising of the two formulations, selected from the preliminary screening, was used to infiltrate a polystyrene (PS) colloidal crystal generated onto pre-etched silica microscope slides through self-assembly from aqueous dispersions of the nanoparticles [21]. The periodically ordered hydrogel film was then evaluated as active component of an ethanol vapor optical sensor by means of UV–Vis transmission measurements at the variance of ethanol vapor concentration. Differences in the swell-

ing behavior of the periodically ordered PS/hydrogel thin film and the corresponding macrogel will be discussed.

2. Experimental

2.1. Preparation of HEMA/AA hydrogels

Hydrogels are composed by 2-hydroxyethyl methacrylate (HEMA), acrylic acid (AA) and poly(ethylene glycol)₂₀₀ dimethacrylate (PEG₂₀₀DMA), all from Sigma Aldrich. HEMA was distilled under vacuum prior to the use, while all the other monomers were used as received. Azobis-isobutyronitrile (AIBN) was used as initiator at 0.15% wt/vol. Two formulations were investigated, with two different amounts of AA, as reported in Table 1. The monomer and solvent (water) mixture was cured within silicon molds of 12 mm diameter closed with a quartz cover slip to prevent excessive water loss during photo-polymerization. UV-irradiation was carried out for 2 h with a UV irradiator from Helios Italquarz “Polymer 125 UV”, equipped with a high-pressure Hg lamp “Zp-type” (2 mW/cm²). The temperature inside the chamber was maintained at 25 ± 1 °C. After photocuring, a thermal post-curing treatment in an oven at 60 °C for further 2 h was carried out. Hydrogel circular disks (12 mm diameter and 2 mm thickness) were then subjected to prolonged extraction (72 h) with water at room temperature to remove unreacted monomers.

2.2. Solubility tests and FTIR analysis of poly(HEMA-co-AA) hydrogels

Gel fractions in water, defined as $GF = W_g/W_0$, where W_0 is the total amount of solids in the sample before extraction and W_g is the weight of the water-insoluble network, were measured by Soxhlet extraction. Reported data are the average of minimum three independent measurements. Variability on the datum is within the unity.

Structural confirmation of the HEMA–AA copolymerization and crosslinking upon photo-irradiation and thermal-post curing was sought via FTIR analysis carried out on the water insoluble fractions. In particular, FTIR spectra were recorded in the range 4000–400 cm⁻¹ using a Perkin–Elmer 1720 Fourier Transform Spectrophotometer with a resolution of 1 cm⁻¹, each spectrum recorded after 100 scan. Solid samples were dispersed in KBr and pressed into disks.

2.3. Dynamic mechanical thermal analysis

Dynamic mechanical properties of the hydrogels were investigated by Dynamic Mechanical Thermal Analysis, using a Rheometrics DMTA V instrument. DMTA analysis was performed on hydrogel pellets in their equilibrium swelling conditions in water at 25 °C. Tests were performed in compression, both as function of the strain, at the fixed frequency of 1 Hz, and as function of the frequency in the 0.1–10 Hz range, at a fixed strain of 0.5% (within the LVR). Temperature was maintained at the constant temperature of 25 ± 1 °C. Storage modulus (E') and loss modulus (E'') versus either strain or frequency were recorded. Highly reproducible mechanical spectra were obtained.

Table 1
Composition of the monomers in the feed.

System	I (mol)	II (mol)
HEMA	0.35	0.27
PEG ₂₀₀ DMA	0.0013	0.0013
AA	0.009	0.09
Water	0.634	0.634

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