



Short communication

Solid sensory polymer kit for the easy and rapid determination of the concentration of water in organic solvents and ambient humidity



Miriam Trigo-López, Asunción Muñoz, Saturnino Ibeas, Félix C. García, Felipe Serna, José M. García*

Departamento de Química, Facultad de Ciencias Universidad de Burgos, Plaza de Misael Banuelos s/n, E-09001 Burgos, Spain

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ABSTRACT

We have prepared a solid sensory polymer kit to detect and quantify the water in organic solvents, as well as the ambient humidity; these determinations are cheap, easy and rapid with our new material. The limit of detection of water is $7 \times 10^{-4}\%$ in acetone, $4 \times 10^{-3}\%$ in THF, and $3 \times 10^{-4}\%$ in toluene. Additionally, the relative humidity in air can be measured between 20% and 100%.

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1. Introduction

The determination and quantification of the water present in organic fluids is currently an important topic. For example, in synthetic chemistry, dehydration procedures are often performed on water-sensitive reagents to ensure experimental reproducibility. Additionally, the determination of moisture in lubricants is routinely carried out because the presence of water affects the lubricants' efficiency and causes detrimental reactions that can degrade machinery efficiency and performance, such as corrosion. The determination of water content is also important within other industries, such as the sugar, food and petroleum industries. The standard process for the determination of water contamination is the Karl Fischer method, which requires a highly skilled operator to obtain reliable results. It does not provide reliable results at very low concentrations of water, cannot be used with samples containing redox active substances and its color change is not straightforward to quantify. Moreover, the Karl Fischer reagent is expensive and has a very short shelf life; The Standard Test Method for Water in Petroleum Products and Bituminous Materials by Distillation, ASTM D 95-05, is another widely used method for the quantification of water. The distillation process used in this

method is very slow and is only effective for water concentrations above 0.5–1%. Other water quantification methods include infrared spectroscopy (IR) and ultraviolet spectroscopy (UV) [1]. Infrared spectroscopy is not accurate because it is based on the correlation of the intensity of the oxygen-hydrogen stretch of water, which occurs at approximately 3400 cm^{-1} , and the water concentration; other diagnostic resonances indicative of a reaction between any substance with the contaminating water may be used in place of the resonance at 3400 cm^{-1} . The method utilizing ultraviolet spectroscopy requires the addition of a solvatochromic substance and the calculation of a complex calibration curve, the molar extinction coefficient of the additive and other tedious empirical calculations. Moreover, undesirable secondary reactions may occur between the solvent and the solvatochromic substance. D.T. Benedyk introduced a method that used a pigment to quantitatively determine of the presence of water in different solvents and fluids; however, in concentrations between 0.001% and 0.1%, the quantification of water was not possible [2]. Other techniques have been described, such as a ^{19}F NMR-based method, which is very tedious, or a photo-induced electron transfer method, in which the sensitivity depends on the polarity of the solvent [3].

The measurement of humidity determines the amount of water vapor present in a gas, which can be a mixture, such as air, or pure. Most humidity sensors are relative humidity sensors and can be classified into ceramic, semiconductor, and polymer humidity sensors [4,5].

* Corresponding author. Tel.: +34 947 258025; fax: +34 947 258 831.

E-mail addresses: jmiguel@ubu.es, grupodepolimeros@gmail.com (J.M. García).

Ceramic materials, such as Al_2O_3 , TiO_2 , SiO_2 , LiCl-doped MnWO_4 and spinel compounds, detect water based on the decrease in the conductivity and the increase in the dielectric constant when the humidity increases; this mechanism was reported approximately 200 year ago. In wide-gap semiconductor materials, such as SnO_2 , In_2O_3 , ZnO , or perovskite compounds, water is adsorbed on the surface, which results in an increase in the conductivity of n-type materials and a decrease in the conductivity of p-type materials. This effect might be caused by the donation of electrons from the chemically adsorbed water molecules to the ceramic material or the replacement of the previously adsorbed and ionized oxygen by water molecules, which would trigger the release of the electrons from the ionized oxygen.

Polymeric sensors are thin films with micropores in which a change in a physical property can be attributed to water absorption. There are two categories of polymeric sensors: resistive- and capacitive-types. The former responds to moisture variations by changing its conductivity, while the latter responds to water vapor by varying its electric constant. A recent work by Ohira et al. describes the potential application of these materials to the trace moisture measurement in gases and organic solvents [6].

To facilitate the detection of substances, the development of molecules acting as chromogenic or fluorogenic sensors is currently a topic of scientific and technological interest [7,8]. The design, synthesis and optimization of new sensors led to new analyte detection technologies that are inexpensive, highly sensitive and easy to handle, which enables the use of the sensors by non-specialized individuals. Within this context, water is an incredibly important target molecule, but there are few examples of successful water samples because strong and selective water: host interactions are both elusive and difficult to establish [9,10].

Sensors for water [11–13] and humidity [14–16] can be prepared via the physical immobilization of discrete sensory molecules onto different surfaces or materials; this interesting approach generates manageable sensors with improved selectivity and sensitivity toward water. Moreover, the design, preparation and eventual polymerization of functional monomers generates dense hydrophilic membranes that may function as sensory materials and advance the development of this field [17,18]. In this regard, the preparation of solid films with sensory motifs, which are chemically anchored to polymer structure to avoid migration, that can be handled easily in both dry or swelled states would open new avenues within this field.

2. Results and discussion

We prepared fluorescent methacrylic monomers containing fluorenone and 1,2,3-triazole moieties for the fluorogenic water sensing motif (2) and copolymerized them with a hydrophilic monomer (1) (Fig. 1). The monomer (2) was prepared in a straightforward manner following four high-yielding and easy synthetic steps (Supplementary Data – SD, Section SD.1 and Scheme SD1). A crosslinker (3) was used to obtain solid materials with good mechanical properties. Structural monomer 2-hydroxyethyl acrylate, as well as the ethylene glycol dimethacrylate crosslinker, were fully miscible and could be mixed in any molar ratio. Preparation of the dense membrane began with a solution of the photochemical initiator, the crosslinker and 2-hydroxyethyl acrylate (solution total volume = 600 μL); the functional monomer (2) was added to this solution. The homogeneous polymerization mixture was subsequently treated with bubbling nitrogen to eliminate any dissolved oxygen and immediately injected into silanized glass molds; the polymerization was conducted smoothly under a UV light lamp. The silanization of the glass mold facilitated the unmolding of the plasticized material. The structure of the copolymer network of the

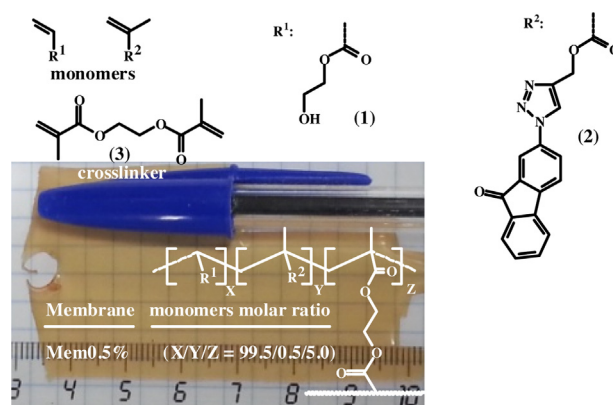


Fig. 1. Chemical structures of the monomers and the copolymer. The copolymer structure and code are shown over a digital picture of the sensory film. For the detailed experimental synthetic procedure, see the Supplementary data.

membrane and the sensing material are depicted in Fig. 1, in addition to a digital picture of the membrane that demonstrates its good optical properties. The content of (2) was quite low (0.5%, mole), and the other comonomers, (1) and (3), are widely used in industry and are therefore commercially available and inexpensive, which means that these materials can be used to make an inexpensive material that might have practical applications.

The membrane's hydrophilic or hydrophobic character was correlated with the water-swelling percentage (WSP); it was related to the weight percentage of water uptaken by the films after soaking until equilibrium was reached in pure water at rt. The prepared membrane has a water-swelling percentage (WSP) of 84%. WSPs higher than 40% and lower than 100% are optimal for sensory materials designed for applications in aqueous environments because low water uptake means a low diffusion rate of water and of other water solvated target molecules, and higher water uptake can impair the mechanical performance of the swelled materials [17].

The membrane demonstrated reasonably good thermal resistance under both nitrogen and air atmospheres when observed via thermogravimetric analysis. A 5% weight loss was observed at 288 °C and 298 °C under nitrogen and dry synthetic air atmospheres, respectively.

All of the membranes, both dry (Young's modulus of 4 MPa and a tensile strength of 3 MPa) and solvent-swelled materials, were highly tractable and transparent and had good mechanical properties. Membranes with dimensions of 80 × 50 × 0.1 mm were easy to handle and could be cut into appropriate sensing strips with dimension of approximately 20 × 5 × 0.1 mm using a home cutter or scissors.

When the monomer was dissolved in a dry solvent, the dry membrane swelled in a dry solvent or the dry membrane exposed to a gas phase, an intense fluorescence band was observed at approximately 515 nm when excited at 410 nm. In the SD, Fig. SD7 depicts the fluorescence activity of monomer (2) in different solvents. After the addition of water (miliQ), the fluorescence at 515 nm displayed by the monomer or membrane was quenched. This behavior was also observed when the membrane was in contact with increasingly humid environments. In addition, the membrane could be dried and re-used at least 10 times (for testing purposes we have reused the membrane 10 times without any apparent loss of performance).

To test the fluorimetric sensing ability of the monomer and the membrane, increasing amounts of water were added to a fluorimeter cell already containing a solution of the monomer in dry acetone (Fig. 2) or the film swelled in dry acetone (Fig. 3), resulting in a gradual diminishment in the intensity of the 510 nm band with increased water content. The membrane was previously dried for

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