Characterization of new thermo-responsive hydrogels for optical sensing applications

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ABSTRACT

We report the use of new hydrogels based on poly-N-isopropylacrilamide and MeOXA in order to measure temperature using optical transmittance. We have obtained thermo-responsive hydrogels based on the radical copolymerization of N-isopropylacrylamide (NIPAAm) and bis-macromonomers of 2-methyl-2-oxazoline (MeOXA). The hydrogels show conformational transitions at defined temperatures, which are a function of the molar ratio NIPAAm / MeOXA inside of the hydrogel. The temperatures of transition have been determined by means of ^{1}H NMR spectroscopy and by turbidity measurements using an optical setup with optical fibers and a diode laser. We show the first experimental results and we discuss some future applications such as an optical switch or a device for optical sensing.

Keywords: Thermo-responsive proprieties, smart hydrogels, optical sensing.

1. INTRODUCTION

Stimuli-responsive polymers are a type of promising materials with potential applications in the field of optoelectronics and biotechnology. These new materials have many fields of application, by example the medical diagnostic and environmental protection including the industrial applications. An example of these "smart materials" is the poly(N-isopropylacrylamide) (polyNIPAAm), which present thermo-responsive characteristics [1,2]. The polyNIPAAm polymer, because to the aqueous solutions shows a conformational transitions at lower critical solution temperature (LCST), where it happen a precipitation of the polymer in all water polymer [3].

In recent years, the hydrogels have attained most interest for their potential applications. Mutlu et al. described a thermally responsive polymer microvalve made without mechanical parts [4]. In other hand, Michie et al. demonstrated a distributed sensor using a swellable polymer system for pH measurements [5].

These hydrogels exhibit a remarkable hydration and dehydration under changes in aqueous solution in response to small changes of temperature. In optical sensors, the hydrogels present an interest very attractive for measurements of diverse physical and chemical parameters [1], examples of humidity sensors or pH sensors have been demonstrated [5]. At other hand, the plastic optical fibers (POF) present a series of advantages with respect to silica fibers. These fibers have grand diameter, high numeric aperture, they also are easy to use, excellent flexibility, and with the use of electronic devices as LED, photodiodes, all that constitute systems of low-cost [6].

In this paper, it is presented a preliminary characterization about the thermo-optical proprieties of the new hydrogels synthesized from NIPAAm and 2-methyl oxazolines, using spectroscopy and turbidity measurements in order to determinate their specific LCST. We also present the experimental implementation of an alarm system employing a extrinsic sensor of optical fiber for detecting and controlling inflammable liquids based on the thermo-responsive proprieties of polymer polyNIPAAm. The sensor employs a novel range of hydrogels as the active medium in the detection process to realize temperatures changes. The hydrogel is located at a glass capillary in liquid phase and at its

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ends, it is fixed two segments of POFs. At room temperature, the hydrogel is transparent to visible light, it transmits the light around 100%, but when the room temperature varies, it becomes opaque, then the transmitted light decreases depending of the molar ratio between the components of the hydrogel. This abrupt change on the light intensity transmittance induces an optical signal for acting such as an alarm. The connected optical fibers at its ends of the hydrogel do more easily to sense at distances in aggressive or dangerous environments.

2. SYNTHESIS OF THE HYDROGELS

2.1. Polymer preparation

The thermally responsive polymer material is poly (N-isopropylacrylamide). This material is formed by copolymerization of a mixture containing of N-isopropylacrylamide (NIPAAm) and azobisisobutyronitrile (AIBN initiator). This process produces polyNIPAAm copolymer. PolyNIPAAm is one of the best-known temperature sensitive polymers. It undergoes a rapid and reversible phase transition form extended hydrated chains (swollen state) below the lower critical solution temperature (LCST) of 32°C to collapsed hydrophobic coils (shrunk state) at a temperature above LCST.

The 2-oxazolines can be polymerized by ring-opening cationic polymerization, being this polymerization named lived type [3]. Both the polymethyl and polyethyloxazoline are hydrophilic and soluble in water. For taking advantage of the lived character of this polymerization of the oxazolines, it has been synthesized a bis-macromonomer of 2-methyl oxazoline, having vinyl group in the chain ends. After that this macro monomer has been copolymerized via free radicals with the co monomer NIPAAm for to obtain a hydrogel (see Fig.1).

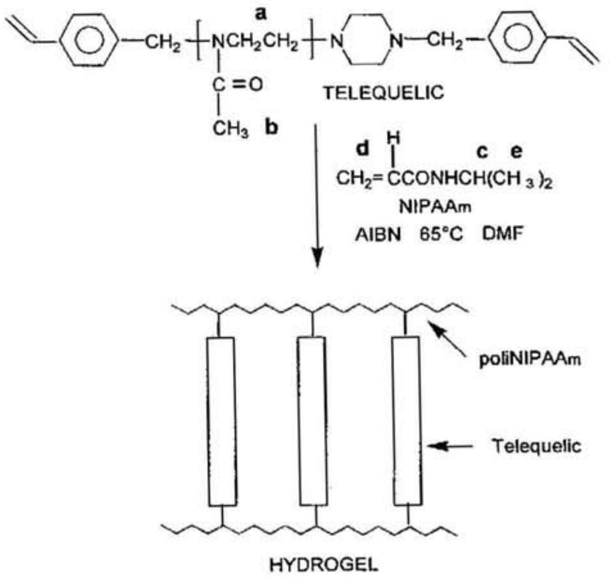

Fig. 1. Synthesis of the hydrogel NIPAAm and 2-methyl-2-oxazolines.

The yield of the synthesis of hydrogels was relatively high (more than 60%) and these materials had shown extremely high values of swelling in water (for example 40% for HG-II).

The hydrogels are cross-linking polymers in three-dimensional form of natural or synthetic nature. These hydrogels swell in contact with water forming a soft and elastic material, "swelling" a quantity of the water in its structure without dissolving. The solid polymers are especially adequate for forming gels thank to their structure of large chains. The flexibility of these chains permit that these can be deform with the aim of permit the entrance of the molecules of the dissolvent at its three-dimensional structure.

2. 2. Proprieties of the hydrogel (PNIPAAm)

The polyNIPAAm polymer, because to the aqueous solutions show a conformational transition at lower critical solution temperature (LCST) to 32°C, where it occurs a sudden precipitation of the polymer in all water polymer [2]. This process is reversible because when the temperature of system decreases, the poly(NIPAAm) dissolves again. The LCST value can to be controlled during the co-polymerization process adding hydrophilic or hydrophobic monomers respectively. The chemical structure of the poly(NIPAAm) polymer is shown in the Fig. 1.

The polyNIPAAm polymer in aqueous solution exhibits an LCST at 32°C. Physicochemical phenomena occurring in an aqueous solution of polyNIPAAm at the LCST have been the subject of studies carried out using a variety of experimental techniques. It has been demonstrated that the phase separation process of polyNIPAAm occurs in two steps. In the first step, an individual polymer chain collapses from an extended coil into a globule. In the second step, an aggregation of the individual globules occur leading to a macroscopic phase separation.

The optical proprieties of the poly(NIPAAm) polymer show a good transparency at room temperature, exhibiting a refraction index of 1.47 [7]. When the polymer gets the LCST value, this becomes opaque to the incident light intensity, acting as an authentic switch. This characteristic can be used for design an alarm sensor. When the poly(NIPAAm) is synthesized with 2-methyl-2-oxazoline (MeOXA), the thermo sensibility of the hydrogel can be varied between a range 32°C and 55°C [3].

3. PHYSICAL CHARACTERIZATION

3.1 NMR spectroscopy

Using NMR-MAS spectroscopy, it has been demonstrated that for each type of hydrogel, it happens a conformational transition at a defined temperature, depending of the molar ratio between MeOXA and NIPAAm. In the Fig. 2, we show the result for the hydrogel HG-II, where the LCST is equal to 36°C.

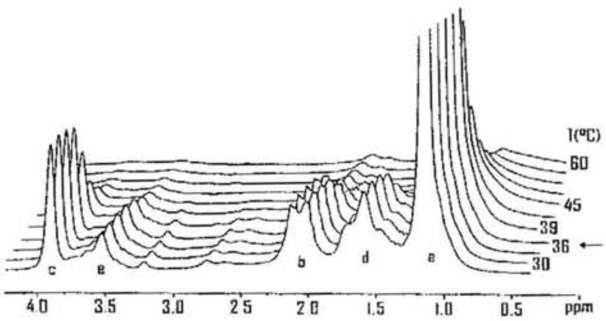

Fig. 2. Determination of the transition temperature of the HG-II hydrogel using the NMR-MAS.

3.2 Turbidity measurements

We have implemented an optical setup for turbidity measurements. The lower critical solution temperatures (LCSTs) for the polymer samples were determined by estimation of the cloud points from optical power (transmittance) detected at photodiode PIN, which is connected to PC for data recording. The polymer samples were located in a quartz cell on a holder. The temperature of this cell was controlled by a water-circulating bath and varied from 20 to 80°C at a rate of about 0.4 °C/min. The exact temperature of the sample fluid was tested using a thermocouple inside the cell with the hydrogel. As light source, we had used a laser beam (He-Ne) with wavelength 632.8 nm. In the Fig.3, it is shown the optical setup, where the beam is split in two arms, by a non-polarizing prism. Two photodetectors are located for intensity measurements. The first photodetector measures the reference intensity and the second one the intensity changes by optical transmittance though the hydrogel. This setup was implemented in order to avoid the fluctuations on the output intensity of our laser. The temperature measurements were carried out with a thermocouple and a temperature sensor Dostmann model P610.

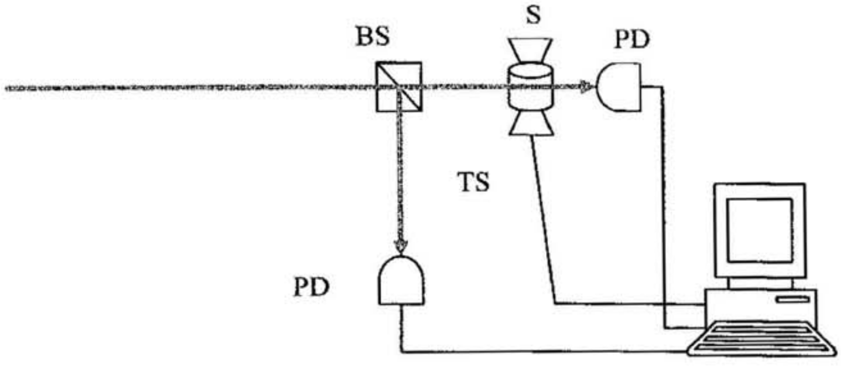

Fig. 3. Optical setup for turbidity measurements, PD: photodiodes, BS: beam splitter, S: sample holder inside water circulating bath, TS: thermocouple sensor.

From Fig. 4, it is shown the LCST for each one of the synthesized hydrogels using turbidity measurements. By example, the HG-IVA hydrogel exhibits its LCST value equal to 55.0°C, the HG-V at 58°C, the HG-VII at 46.5°C and the HG-VIII hydrogel at 34°C. All these hydrogels correspond to same series, and theirs variations depends of the differences between NIPAAm and MeOXA.

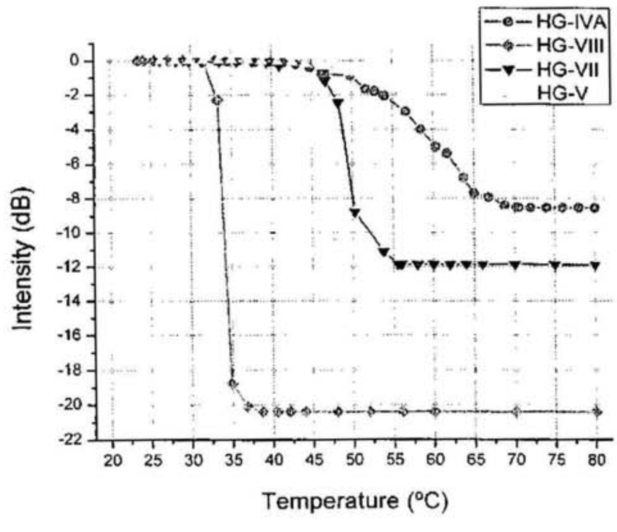

Fig. 4. Intensity attenuation of the hydrogels with different molar ratios between NIPAAm and MeOXA.

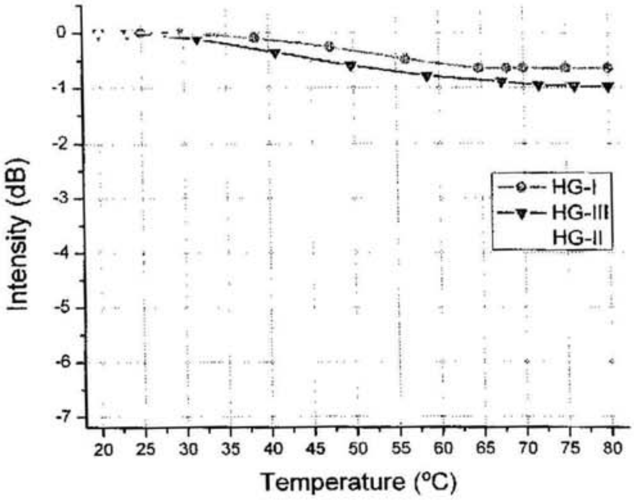

Fig. 5. Intensity attenuation of the hydrogels with different molar ratios between NIPAAm and MeOXA.

In Fig. 5, we present the results for three different hydrogels. The HG-II hydrogel has a percentage of 50% more of NIPAAm polymer, in contrast with the other hydrogels. This difference in the molar ratio between NIPAAm and MeOXA is evident when it is observed the attenuation of the transmitted signal for the hydrogel with more NIPAAm. For the HG-II hydrogel, its LCST value is equal to the obtained transition temperature using the NMR spectroscopy (see Fig.2).

4. OPTICAL SENSING APPLICATION

4.1 Design of a novel optical sensor

In this section, we present the construction and test of a generic form of sensor for optical sensing using the thermo-responsive proprieties of the hydrogel. We had implemented a novel optical sensor using plastic optical fibers. The sensor employs the polymeric material (hydrogel) as the active medium in the detection process to realize intensity changes.

The simplicity of the sensor construction enables it to be adapted readily to a number of chemical species without modification of the basic design. The active component in the sensor is the hydrogel itself, and these gels have been demonstrated to be sensitive to a number of parameters, including pH, photoirradiation and temperature. Selection of the appropriate gel system allows the sensor to be adapted to suit a specific measurement parameter.

The optical setup is shown in the Fig. 6. The fiber used is a PMMA-POF index step with diameter 2 mm including the jacket, where core index and cover index are n_{co}=1.492 and n_{cl}= 1.402 respectively. A source of light LD in wavelength 660 nm has been used. The transducer head for measuring temperature inside inflammable liquids is based on a closed capsule, where is the poly(NIPAAm) hydrogel with its ends connected to two optical fibers. The changes of transmitted intensity are detected by the PIN photodiode placed in the fiber ending. When the transducer head is inserted in a tank of inflammable liquids, from which it is necessary to sense the temperature for avoiding explosions, the photodiode registers variations in the transmittance.

In Fig. 7, it is shown how this sensor works as alarm system. It consists of a source, plastic optical fiber, the transducer head with the poly(NIPAAm) hydrogel, the detector and the optoelectronics unit. The source is a laser diode, the detector is a photodiode. These two components are driven by the optoelectronic unit, where the signal is processed for converting the light intensity changes in voltage and after to emit a sound or other type of alarm. Both the source and the detector are coupled with the plastic optical fiber. The transducer head is a small ampoule where it is located the polyNIPAAm hydrogel.

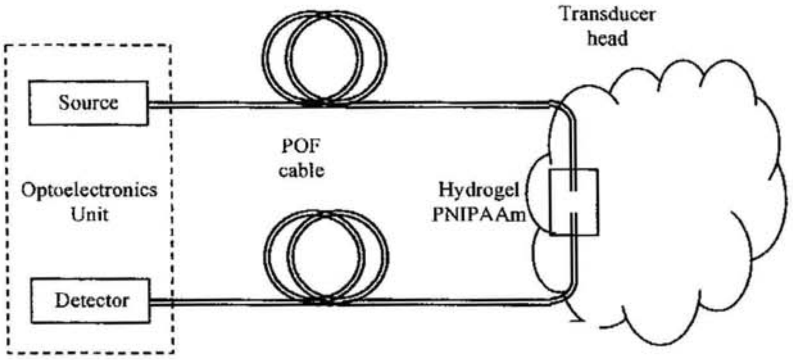

Fig. 6. Optical setup for measuring temperature under environmental.

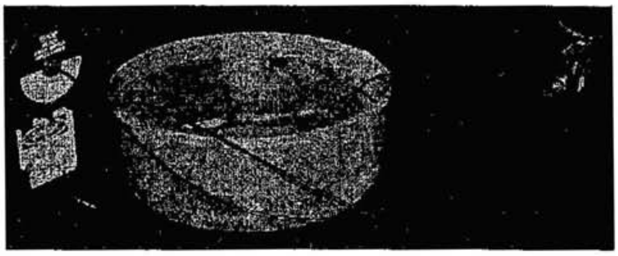

Fig. 7. A novel sensor based on the thermo-responsive hydrogel where the transducer head is submerged on water.

5. CONCLUSIONS

We have presented a preliminary characterization for new thermo-responsive hydrogels based on the poly(NIPAAm) and 2-methyl-2-oxazolines. We have demonstrated the availability of a novel generic form of sensor capable of performing measurements on a chemical species. This optical sensor has been shown to be an efficient means of detecting temperature as an alarm system based on two optical fibers for sensing inflammables liquids using the thermal sensibility of the polyNIPAAm polymer. We have experimentally determined the LCST value for different synthesized hydrogels. For each one, we have obtained their temperature threshold when a sudden precipitation occurs. These synthesized hydrogels with different molar ratio between the polyNIPAAm and the MeOXA permit to vary the thermal sensitivity exhibiting their stimuli-responsive characteristic at a specific LCST. This advantage opens the possibility for using them as an optical switch and for other applications. Moreover, the novel optical sensor presented in this work, based on the alarm system using POFs is very easy to handling, easy to connect to sources and light detectors and low-cost.

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REFERENCES

1. H.G. Schild. *Prog. Polym. Sci.* 1992, 17, 163-249.
2. T. Okano Ed.; *Biorelated Polymers and Gels*; Academic Press: San Diego, CA, 1998.
3. J.C. Rueda, S. Zschoche, H. Komber, D. Schmaljohann and B. Voit. *Macromolecules*, 38, 7330-7336 (2005).
4. S. Mutlu, C. Yu, F. Svec, C.H. Mastrangelo, J.M.J Frechet and Y.B.A. Gianchandani. "Thermally responsive Polymer Microvalve without mechanical parts photo-patterned in a parylene channel". *Proceedings Sensors* 2004.
5. W.C. Michie, B. Culshaw, I. McKenzie, M. Konstanktakis, N.B. Graham, C. Moran, F. Santos, E. Bergqvist and B. Carlstrom. « Distributed sensor for water and pH measurements using fiber optics and swellable polymeric systems". Opt. Lett.20, 103-105 (1995).
6. R.J.Bartlett, R.P.Chandy, P.Eldridge, D.F. Merchan, R. Morgan and P.J. Scully. "Plastic optical fibre sensor and devices". Trans. Inst. Measurement and Control 22, 431-457 (2000)
7. Handbook of Chemistry and Physics, CRC Press, 56 Edition 1975.