Amphiphilic diblock copolymer based multi-agent photonic sensing scheme

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ABSTRACT

Efficient functionalization of polymer optical fibers' (POF) surface by a novel block copolymer material towards the development of low cost multi-agent sensors is presented. The employed poly(styrene sulfonate-b-tert-butylstyrene) diblock copolymer (SPS-b-PtBS) possesses two blocks of distinctively different polarity and charge, the hydrophilic SPS which is sensitive to polar substances and the hydrophobic PtBS which is sensitive to organic solvents. The coexistence of two different blocks allows for the detection of a wide variety of agents, ranging from ammonia, and organic solvents, to biomolecules like lysozyme, at room temperature as opposed to alternative usually more complicated techniques, all with the sole use of one sensing medium. Copolymers' high glass transition temperature enables the formation of stable and environmentally robust overlayers. The sensing performance of the material is evaluated experimentally on the customizable platform of polymer optical fibers, demonstrating fast response, high operational reversibility and also reusability in successively different testing agents.

KEYWORDS: Block copolymer; polymeric materials, sensors, biosensors; photonics

INTRODUCTION

The increased demand for accurate and reliable sensing devices of various analytes in both household and industrial environments has led to the exploitation of photonic sensors[1], which are advantageous compared to conventional types of sensors regarding electrical passiveness, multiplexing capabilities and immunity to electromagnetic interference. In particular the well known platform of Polymer Optical Fibers (POF) are becoming again a quite favorable solution with excellent characteristics of adaptability and customization towards sensors development as they combine many characteristics such as low cost, light weight, low transceivers' circuitry complexity[1,2] allowing thus devices' rapid prototyping. Currently there

is a clear trend and industrially driven need for the development and employment of low cost and energy autonomous sensors, and in this context we are proposing this sensing platform and special implementation. Furthermore recent advances in polymer chemistry have promoted the synthesis of novel polymers such as block copolymer materials, with tailor-made, although diverse and combined, physicochemical properties, that exhibit potentially unique sensing characteristics[3] ,with enhanced functionality and associated with high added value. The concurrent presence of two or more distinct blocks covalently connected and having diverse chemical affinity, e.g. hydrophilic and hydrophobic in the same macromolecule, allows in principle for multi-sensing capabilities

against a plethora of analytes with a single probe.

In the present approach and study here, a charged amphiphilic diblock copolymer material, namely poly(styrene sulfonate-b-tert-butylstyrene) (SPS-b-PtBS) is used for the detection of both polar and non polar analytes, such as benzene, toluene, humidity, ammonia and lysozyme, providing reliable results by using a sensor of low cost and complexity, since it is capable of concurrent multi-agent sensing with a single probe. We show that the presence of a hydrophilic charged block and a hydrophobic block of high glass transition temperature T_g are providing the diverse sensing characteristics of the particular block copolymer material.

The use of hydrophobic polymers as active sensing materials for nonpolar substances and particular hydrocarbons has been reported in the past[4] whereas hydrophilic polymeric materials are used for polar compounds, e.g. for the detection of humidity.[5-7] In the case of ammonia sensing at a ppm detection limit has been reached by using metal oxide sensors, although a lack in selectivity to a particular gas is reported,[8] and an elevated temperature process of about 400°C is needed, which is prohibitive for demanding and dangerous industrial environments. The industrial use is further restricted due to long response times,[9] or very expensive setups.[10] Additionally, optical approaches have been exploited for ammonia sensing based on diffraction methods,[11,12] or optical fibers, as for example colorimetric changes of bromocresol purple[13], polyaniline[14] or a swelling resin.[15] Moreover, block polymers have been employed for sensing applications. Recently, a real-time humidity sensor was developed by using a poly(styrenesulfonate-methylbutylene) (PSS-b-PMB) block copolymer with tailored hygroscopic properties where the deposition of the sensing material conducted in thin films and the detection method was based on changes of the reflected color signal.[16] In another study, poly(NIPMAM-co-CPMA) block copolymer was developed consisting of thermo-

and pH-responsive fluorescent signaling parts units[17] where the response of the block copolymer was purely demonstrated spectroscopic by depositing the material in a 1-cm quartz cell.[17] In contrast the present work here proposes the employment of the sensitive copolymers as overlayers of polymer optical fibers' segments, achieving thus a much simpler implementation procedure, as well as a simple sensor's response interrogation scheme.

Due to increased research and technological interest of biosensing we are considering also here the sensing capabilities of material-based functionalization of polymer fibers[18] towards low cost biodetection schemes for proteins and enzymes. Preliminary results are presented on lysozyme detection which is an enzyme that acts as catalyst for the hydrolysis of glycosidic bonds, particularly those associated with the peptidoglycan networks that form the outer walls of bacteria. Due to its wide use as a food preservative[19] there has been an extensive study on lysozyme's physical and chemical properties, and in context, the electrostatic characteristics of lysozyme has been extensively investigated.[20-23] A number of different and quite diverse approaches for lysozyme detection have been developed, such as aptasensors where based on electrochemical interactions, a high degree of selectivity in the coexistence of other proteins has been achieved,[24] electrochemical impedance spectroscopy based on antilysozyme aptamer as molecular recognition element,[25] monitoring of Atomic Force Microscopy -AFM cantilevers' deflection and bending under electrostatic interactions,[26] Bulk Acoustic Wave (BAW) viscosity sensor,[27] and surface plasmon resonance (SPR) detection schemes have been also widely utilized for lysozyme sensing.[28, 29]

Although some of the aforementioned techniques achieve a high degree of sensitivity, their implementation and use are rather laborious, expensive and require complex interrogation setups leading to time consuming processes that in many cases are inapplicable

In contrast the proposed POF based detection scheme offers an efficient detection scheme potentially useful in certain applications.

The outline of the paper is as follows: first, the material design, sensor fabrication and experimental setup are presented, followed by the performance investigation of the sensor towards nonpolar analytes detection. Next, the response to analytes containing polar groups is reported and a special section is dedicated to biosensing capabilities of the proposed sensor for lysozyme detection. Afterwards a number of optimization issues are discussed and demonstrated. The paper is concluded with the work highlights and the material synthesis and characterization section.

EXPERIMENTAL

SENSOR'S FABRICATION

Block copolymer material design, synthesis and characterization

In order to develop a multifunctional polymeric material able to interact with both polar and nonpolar analytes, as well as charged biomacromolecules like enzymes and proteins, an amphiphilic block copolymer structure of the type poly(styrene sulfonate-b-tert-butylstyrene) (SPS-b-PtBS) was selected to be synthesized. The highly polar sulfonate groups of the SPS-b-PtBS copolymer are expected to interact strongly with polar and particularly with widely used analytes such as water and ammonia. The sulfonate groups can be also deprotonated easily due to their strong acidic character at the whole usual pH range. Furthermore permanent negative charges can be created on the copolymer by neutralization of the sulfonate groups with NaOH in aqueous media. This allows for interactions with positively charged species in solution (like lysozyme). The PtBS block is highly nonpolar and is expected to enhance interaction with nonpolar analytes. The high transition temperature T_g of the diblock (above 120°C) ensures mechanical robustness of the formed polymeric overlayers

on the POF surface. The chosen asymmetric composition, keeping the PtBS block as the majority component, together with its high T_g, ensures insolubility of the copolymer overlayers in aqueous environment, utilized in the case of protein detection. The use of anionic polymerization for the synthesis of the precursor poly (styrene-b-tert-butylstyrene) (PS-b-PtBS) copolymer ensured maximal control on the molecular weight, composition and molecular weight distribution of the two blocks. The sulfonation reaction utilized for the functionalization reaction of the PS block, in order to introduce the sulfonate groups has been shown to be a very efficient functionalization reaction for this type of block copolymer leading to the synthesis of well-defined amphiphilic block copolymers.[30-33]

Detailed molecular characterization of the precursor PS-b-PtBS and the final material, by SEC, NMR, ATR-FTIR, elemental analysis and titration experiments, proved that the block copolymer utilized had the expected molecular characteristics in respect of molecular weight, functional chemical groups, degree of functionalization and composition of the components. The molecular characteristics of the SPS-b-PtBS copolymer were found to be: Mw = 197,000 g/mol, Mw/Mn = 1.03, 89% mole PS sulfonation, 34wt% SPS. The chemical structure of the amphiphilic block copolymer used in the current work is shown in Fig. 1.
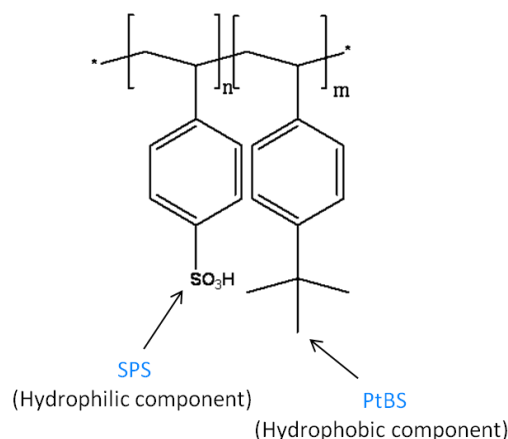

FIGURE 1 Schematic of the diblock copolymer.

Fiber Optic Sensing Scheme

The POF used was an ESKA GH-4001P, Mitsubishi-Rayon Co., with an overall fiber diameter of 1 mm, and a core diameter of 980 μm. The core of the POF is poly(methyl-methacrylate) (PMMA, n_{core}=1.49), while the cladding is fluorinated polymer n_{clad}=1.40. The sensitization of the fiber was achieved by forming a U-Bend fiber sensing tip through 180° bending using a simple heat induced softening followed by careful bending. This way a high number of protected and isolated guided modes in the fiber core are coupled to radiation and cladding modes with a high overlap area in the outer-cladding sensing area. This fiber functionalization induces due to bend losses an additional 5dB power loss which in our sensing applications is totally acceptable. The deposition of the sensitive copolymer material (n_{pol}=1.57) was performed with the dip coating technique from the dispersion solution of the copolymer in methanol. The sensitive material forms an overcladding layer around the bent fiber tip leading to an increase of the evanescent field active area. The U-bent fiber tip exhibits at that area a strong overlap with the functional polymeric material and responds to the concentration of different measurands by the local change of light absorption and also by the local refractive index change due to the adsorption of the agents' molecules. This combined action of those mechanisms results in changes in radiated light power upon measurands presence and thus in corresponding measured light power changes at the output end of the fiber. The power meter for recording the fibers' output light in the current work is a Newport model 2832-C Dual Channel equipped with detectors model 818-UV. The light source used is an LED operating at 650 nm with maximum output power of 1 mW. The Scanning Electron Microscopy images were taken with a ZEISS EVO MA 10 and Nova Nanosem 230.

The process for gas sensing is essentially the following: the agent is initially injected in liquid form, as solution droplets, on a peltier device placed in the testing chamber of 4.3 liters, ensuring the rapid evaporation of the liquid. The lid is hermetically sealed providing a sensing environment without interaction of the testing environment with the ambient atmosphere. A pump adjusted on the chamber wall is placed for the rapid evacuation of the chamber allowing thus the calculation of the sensors' time response and the relaxation and reversibility period. The experimental setup used is shown schematically in Fig. 2.
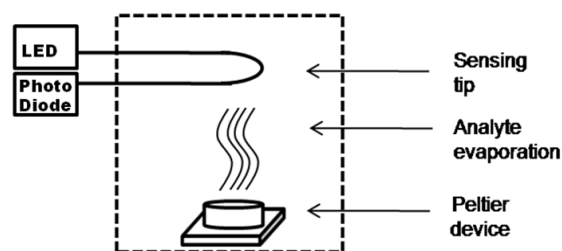

FIGURE 2 Experimental setup for characterizing POF gas sensors.

SENSOR'S CHARACTERIZATION AND PERFORMANCE

As discussed earlier the diblock copolymer material, due to its dual character, is expected to be capable of sensing cyclic aromatic nonpolar compounds (i.e. due to the presence of the PtBS block), as well as polar compounds (i.e. due to the presence of SPS block). The experiments were categorized according to the polymeric block responsible for the sensing ability of the material (i.e. PtBS block sensing toluene and benzene and SPS block sensing water, ammonia and lysozyme).

Performance of PtBS hydrophobic block

The existence of PtBS group in the copolymer chain makes the material sensitive to nonpolar analytes. In the current work, the material coated on a POF was tested towards toluene and benzene presence.

Response to toluene

Toluene, due to its nonpolar nature and its good solubilization ability for the PtBS block is an analyte that potentially could be detected by using the specific amphiphilic block copolymer. The characterization experiments validated this prediction and the performance of the sensor upon toluene presence is shown in Fig. 3a. In addition, the performance of the sensor over time is shown in Fig. 3b. The high T_g of the PtBS block (ca. 120°C) and the low mobility of the PtBS blocks at ambient temperature result in the sensor's relaxation time ranging from several minutes up to hours depending on toluene's volume adsorbed on the block copolymer overlayer volume. Thus, the analyte's desorption rate is expected to be low. The aforementioned consideration is further consolidated by the fact that once the sensor was left overnight (i.e. relaxation time of several hours) in clean room ambient atmosphere, the signal was fully restored to the initial reference value, indicating the long relaxation time needed for full reversibility of the sensor.

Response to benzene

Based on material's characteristics, the sensor was expected to operate successfully for benzene detection and monitoring (benzene is also a good solvent for the PtBS block). The sensor showed a clear, though small, but fast response (in the order of seconds) in the presence of benzene. The results are shown in Fig. 3a. Furthermore, the sensor showed full reversibility upon benzene exposure, with the signal returning to the initial reference level after the required relaxation (Fig. 3c). The lowest detection limit was found to be about 700ppm. It was noticed that benzene's relaxation time differed from toluene's probably due to the dissimilar molecular volume which allows for a faster diffusion of benzene within the PtBS block phase.
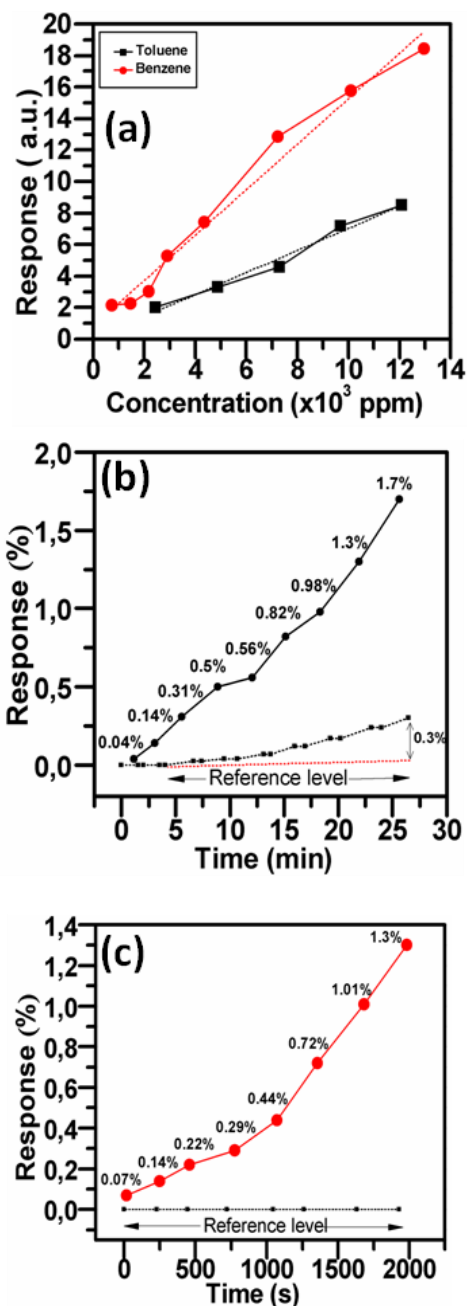

FIGURE 3 (a) Sensor response in the presence of toluene (black) and benzene (red). Response over time for (b) toluene and (c) benzene where the reference level indicates the degree of reversibility of the sensor after successive measures of constant step concentration increase, by equal mass droplets injection.

Performance of SPS hydrophilic group

The sensor, due to the presence of the SPS hydrophilic group in its chain is sensitive to analytes that contain polar groups such as water (humidity) and ammonia. The performance of the sensor to those analytes' presence is analyzed below. In addition, due to its electrostatic charge, the sensor in tested as potential candidate for biosensing and especially its performance upon lysozyme presence.

Response to relative humidity

As previously mentioned, the material due to SPS block (i.e. hydrophilic and thus sensitive to polar analytes) is expected to show remarkable response to relative humidity fluctuations upon performing successive duty cycles covering the whole humidity range in ambient atmosphere. Water droplets were injected in the chamber on a peltier device through a hole on the lid. The droplets upon evaporation created the humid atmosphere in the testing chamber. A commercial capacitive-type humidity meter placed in the transparent chamber was monitoring constantly the RH in real time. The system was then left to reach plateau (thermodynamic equilibrium) and an optical measurement was taken. The chamber was then evacuated by pumping. The experiment was repeated for successive increasing water concentrations leading to higher RH levels. After each duty cycle, upon relaxation, the signal was returning to the initial reference level, indicating the full reversibility of the sensing process. The time needed for thermodynamic equilibrium was found to be about 60 seconds, with that time slightly extended for increased RH levels, as it is shown in figure 4a. The sensing range is about 30% - 75% RH with the sensor response, which is defined as:

$$Response = \frac{I_{signal} - I_{reference}}{I_{reference}} \times 100\% ,\qquad (1)$$

ranging from 0-16%, as shown in Fig. 4a.

Response to ammonia

Ammonia, being a polar molecule, is expected to affect the polar/acidic SPS block, and thus should be successfully sensed by the particular sensor architecture. Several aqueous solutions, 25%, 10% and 1% w/w were used to exploit the sensor's behavior to ammonia and the sensing separation threshold between ammonia and water.

All experiments performed demonstrated a clear response to ammonia as shown in Fig. 4b. The low threshold for ammonia solution of 1% detection was found about 50 ppm. The response time was in the order of seconds and the relaxation time was in the range of minutes (Fig. 4c). Upon relaxation a full restoration of the signal up to the reference level was noticed indicating that all adsorption/desorption phenomena are fully reversible. From a physicochemical point, the analyte's adsorption is a parameter which depends mainly on the chemical composition of the active material (e.g. hydrophobicity, surface charge). Thus, reversibility indicates that physical adsorption of the analyte to the sensor surface takes place. During that process, the sensitive material is not chemically modified and the analyte molecules adsorbed are attached to sensor surface through intermolecular Van der Waals forces. As a result, ammonia molecules are adsorbed from the sensitive film surface, but during relaxation ammonia molecules are rapidly released again in the environment. It should be stressed here that the response (shown in percentage in Fig. 4b) follows analyte's concentration. The sensor response to polar group containing analytes was found to be much higher. In addition, it was noticed that in the case of toluene sensing the relaxation time needed is higher (Fig. 3b), as compared to that of ammonia (Fig. 4c). This should be correlated to the nature and the physicochemical characteristics of the active block copolymer component (polarity, T_g etc) in each case, as well as the physicochemical characteristics of the analyte (e.g. toluene is a larger molecule

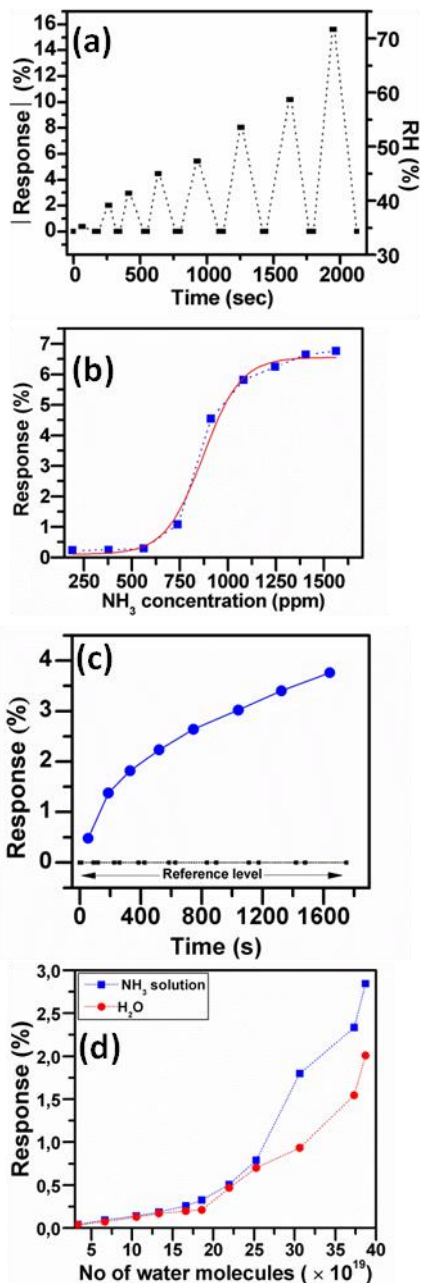and has a higher boiling point compared to ammonia).

FIGURE 4 (a) Sensor response vs time for increasing RH. The process is reversible. (b) Sensor's response in ammonia presence. (c) Sensor's response over time, for a number of different ammonia concentrations showing the reversibility of the sensing process. (d) Experimental graph showing the sensor response to water (red dotted line) and

ammonia (blue dotted line) above the threshold value.

Cross sensitivity to humidity and ammonia

Regarding industrial and realistic scenarios, in many cases ammonia needs to be detected in rather humid environments (e.g. industrial warehouses). Thus, the cross response of the sensor to humidity and ammonia and the sensing separation between the two differential contributions is a challenge.

In order to cope with that task, two sets of experiments had to be performed, with the first part relating to the sensor testing upon humidity presence. The exact number of water molecules was calculated with accuracy in order to obtain the reference values. The experiment was then repeated with aqueous ammonia solution. The exact number of water molecules in ammonia solution was again calculated taking into account the quantity and concentration of the solution, the geometrical dimensions, the pressure, and the temperature of the chamber. Thus, the same number of water molecules was obtained in two different cases. Any difference in sensor response can then be attributed solely to the excess presence of ammonia molecules in the second case. After performing multiple tests, it was found that above a threshold of about 180 ppm of NH_3, ammonia's response is clearly separated from water's contribution signal (Fig. 4d).

Multi-agent sensing and sensor's reusability aspects

In certain experiments each sensor tip was dedicated for a certain agent, i.e. humidity, ammonia, toluene etc. However, in order to investigate the potential versatility and reusability of the sensor, several experiments were performed where the same tip was used for a series of testing on different agents. It should be stressed that the sensor's tip showed high degree accuracy on measuring several and different agents in consecutive tests without any saturation or poisoning, given of course

reasonable time for relaxation after each testing. These observations demonstrate the great potential of the proposed scheme for multi-agent sensing using the same device and thus with dramatic reduction in cost for industrial applications.

Biosensing capabilities - Lysozyme detection

Upon lysozyme presence, due to its positive charge at physiological pH,[23] strong electrostatic attractive forces are exerted between lysozyme particles and block copolymer material. This results in the formation of an excessive protein layer which in turn causes alterations in the refractive index at the outer material interface. Due to the electrostatic nature of the interaction, only the material surface in contact with the protein aqueous solution is affected, while the material's bulk volume is expected to remain rather unaffected. The experiment was performed in two cases: lysozyme in distilled water and in buffer solution. It should be mentioned here that the buffer solution strongly simulates the biological liquids, since it exhibits the same level of salinity and pH. In both cases, the unjacketed region of the bent fiber tip was first immersed in distilled water / buffer solution to measure the reference value. Then, it was immersed in the lysozyme solution in water or buffer, respectively. The sensor was tested in successive diluted lysozyme solutions with different concentrations in order to determine the lower sensing threshold. The experiment for each case was repeated ten times taking the mean value in order to increase the validity of the results. The successive measurements demonstrated excellent repeatability with a consistent response. The response of the sensor upon lysozyme presence in both buffer and aqueous solutions (Fig. 5) was found to be monotonic. From the resulted graphs it can be deduced that in the case of buffer solution the response was more than 10% whereas in the aqueous solution it was about 3%. Additionally, due to the inherent electrostatic nature of the detection mechanism the response was verified

to be almost instantaneous, in the order of a fraction of second.

In order to enhance the sensor's response, a chemical treatment on the sensor with NaOH aqueous solution was introduced and performed. The treatment with NaOH results in an acid/base reaction to produce salt groups on the copolymer material. The fiber tip was immersed in NaOH solution 0.1M for a period of 10 seconds and then it was dried with the aid of nitrogen flow. The treated tip was washed with distilled water and then it was again immersed in the diluted solution. A remarkable enhancement in the measured response was observed. The response's enhancement was almost tenfold for the buffer solutions and eightfold for the water solution, reflecting the dramatic effect that sodium hydroxide treatment has on the effective charge of the block copolymer surface and consequently on the ability to interact with the oppositely charged lysozyme.
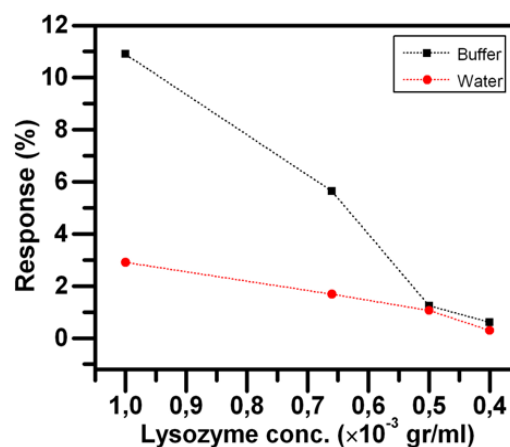

FIGURE 5 Sensor response to lysozyme in buffer (black) and water (red) solution.

OPTIMIZATION ASPECTS OF THE SENSING SCHEME

Parameters such as layer thickness and modification of the fiber tip are considered important factors in the sensor performance.[34] Thus, in an attempt to optimize the sensor performance, several tests were performed in order to evaluate the effect of each factor.

Effect of layer thickness to sensor response

The multiple dipping of the sensor tip to the polymer material increases the thickness of the layer that has been deposited around the fiber sensing tip. Since the solvent used in the current work was not the optimum solvent for the block copolymer, a rather inhomogeneous layer is formed after dipping. More details on this subject are given in supporting material (supporting file 1). The investigation of the effect of the layer thickness to the sensor response is of crucial importance for the optimization of the sensor performance. Particularly, by depositing layers of different thickness of the sensitive material allows control of the dynamics of molecular chains.

Changes in the mobility of the chains of the deposited sensing material directly relate to the adsorption and diffusion phenomena. In this context, tips with 1, 2 and 4 layers were tested on exactly the same conditions of low ammonia concentration, as shown in Fig. 6a. The sensor's response was found to be optimized for the single layer in the case of low NH_3 concentrations (in the order of hundreds ppm). For low NH_3 concentrations shown in Fig. 6a the ammonia solution was 1% and the concentration was adjusted by evaporating different number of solution's drops (of 5 micro-litre) in the test chamber. In addition, similar tests with one and four layers were performed for the case of toluene (Fig. 6b) and benzene (Fig. 6c). In all cases, monolayered sensor tips, i.e. after performing one dipping cycle, were found to perform better.
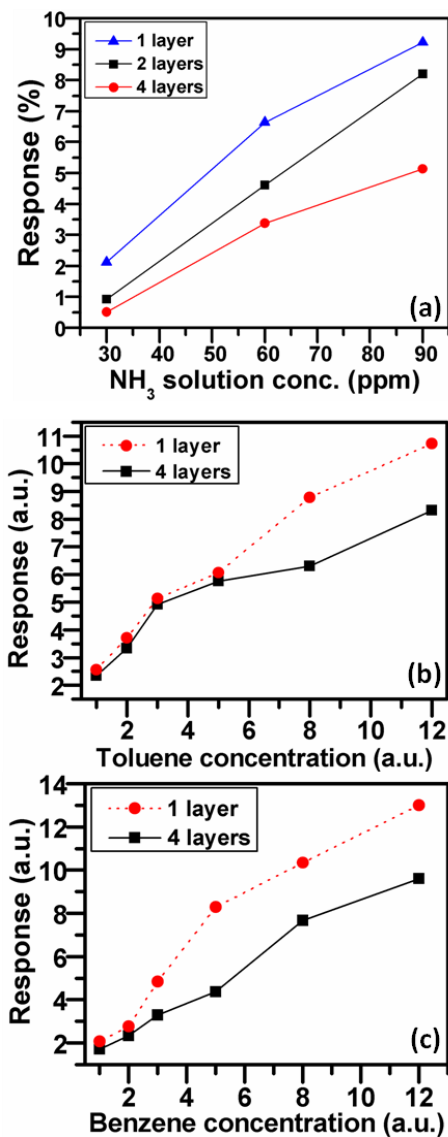

FIGURE 6 Effect of number of layers on sensor response to (a) ammonia, (b) toluene and (c) benzene.

The test was then repeated for high NH_3 concentrations (in the order of thousands ppm), using 25% ammonia solution, with a single and a fourfold layered sensor. The increasing concentration of ammonia was building up again by injecting consecutive drops of the solution on the peltier element in the test chamber. The increased concentration of ammonia penetrates to deeper regions of the material which was not initially active. Therefore, an increased volume of sensitive material interacts with ammonia molecules

resulting to an increased response. The results are shown in Fig. 7a and Fig. 7b, where the fourfold layered sensor was found to perform better.
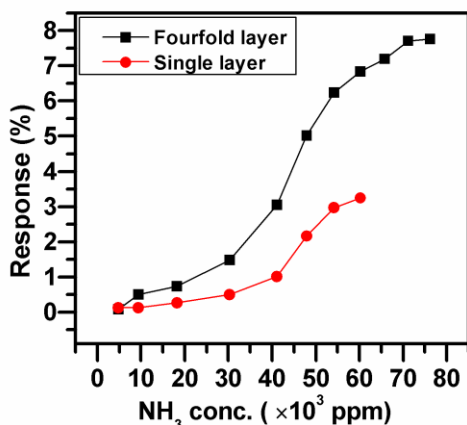

FIGURE 7 Sensor response at high NH_3 concentrations for (a) single and (b) fourfold layer.

In both cases the same trend is followed, giving an almost sigmoid curve. The single layer sensor reached a plateau at about $55 \cdot 10^3$ ppm NH_3, indicating the saturation region and upper limiting point of operation. The fourfold layer sensor was able of sensing as high as $70\text{-}75 \cdot 10^3$ ppm NH_3 without any saturation and with also a substantial response enhancement. Due to the limited testing chamber space, for that ammonia concentration, condensation at the side walls was apparent and no further measurements could be obtained. The ammonia concentration range in the case of the fourfold layer sensor is thus expected to be above $75 \cdot 10^3$ ppm NH_3. Furthermore, the response range is 0-8 %, whereas the range in the case of the single layer sensor is only 0-3.5%. Thus, for high ammonia concentrations, a scenario that finds a lot of applications in industrial environments, a rather thick layer is preferable in sensor's development.

Effect of fiber's polishing to sensor sensitivity

A common way for enhancing the sensitivity of POFs to external measurands is by increasing the radiation distribution field at the interacting region. Further to the formation of the sensitive U-Bend fiber tip this could be implemented by selectively removing a certain thickness of the cladding and/or core material exposing thus more drastically the fiber modes to the external environment. Using special fine polishing papers a number of U-bend fiber tips were further polished increasing thus the overall loss by almost an additional 3dB. The effect of this additional treatment in conjunction with layer thickness is shown in Fig. 8a, where the single layered fiber tip was proved to be more sensitive upon ammonia presence as compared to a double layered fiber tip. Furthermore, as shown in Fig. 8b, upon polishing, the sensor performance is increased remarkably for fiber tips of the same layer thickness. Thus, a side polished fiber tip is preferable for optimized sensing applications. An alternative and equivalent in terms of performance would be the diameter tapering of the fibers along a certain length, however the results discussed above demonstrate efficiently the potential for considerable improvement.
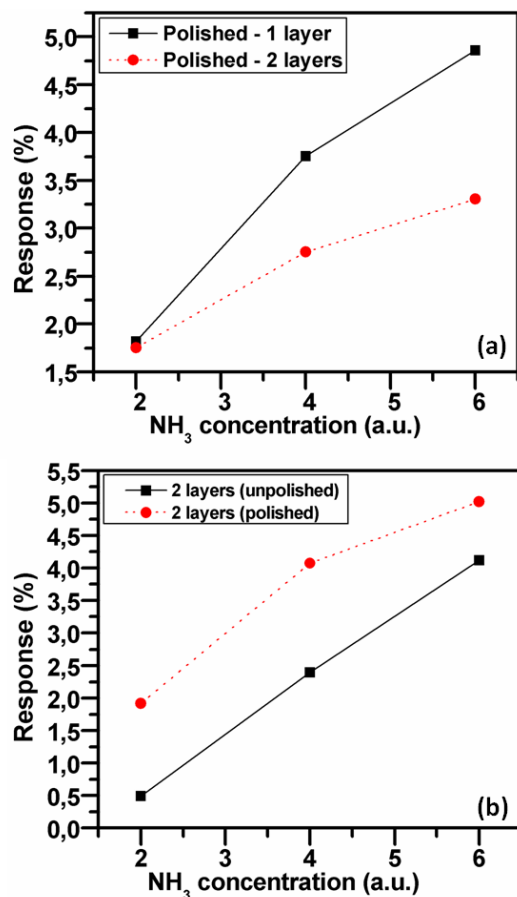
FIGURE 8 (a) Sensor response for one and two layers on fiber tips, after polishing. (b) The side polishing of the POFs increases the response for fiber tips of the same overlayer thickness.

CONCLUSIONS

A Polymer Optical Fiber based sensor employing a novel amphiphilic block copolymer as the active sensing material has been demonstrated. The block copolymer material incorporates two distinct in terms of physicochemical properties, yet chemically connected, blocks in its molecule offering advantages stemming from its dual character. The blocks, one being hydrophilic and sensitive to polar substances and the other hydrophobic and sensitive to non polar aromatic compounds, are responsible for a wide range of chemical analytes including even biomolecules and proteins. By suitably adjusting the blocks ratio in the macromolecule a sensitivity preference could be engineered. The proposed sensor architecture, operating at normal room temperatures, is a low cost and low complexity optical device that exhibits robustness, flexibility and reliability in flammable or intense electromagnetic field environments. Polar containing compounds such as humidity and ammonia are successfully sensed showing good sensor response and excellent repeatability over time. In addition, the sensor shows promising results in the case of cyclic aromatic compounds, as for instance toluene and benzene. Furthermore it was demonstrated a scheme for rapid detection of lysozyme at moderate concentrations based on electrostatic interaction mechanism. The effect of material layer thickness and fiber polishing on sensor response was investigated in order to obtain useful information for the optimization of the platform. It should be stressed that the results demonstrated the excellent repeatability and reusability of a single sensor head to successively different analytes' without any material degradation and performance deterioration suggesting thus the potential for development of inexpensive and reusable sensors.

The successful demonstrated deposition of the sensitive block co-polymer on the polymer optical fibers allowed the implementation of an efficient refractive index based sensing scheme with operational characteristics and associated costs that make possible their integration in energy-autonomous sensing nodes for deployment in emerging applications like broad area wireless sensor networks.[35] Further exploitation of other material platforms and advanced photonic architectures[1,36] with inherently higher sensitivity such as Bragg gratings[37] and ring or disk resonators[38] in silica on silicon are currently investigated and is expected to lead to dramatic sensitivity enhancement and increased functionality by the employment of such diblock copolymer materials.

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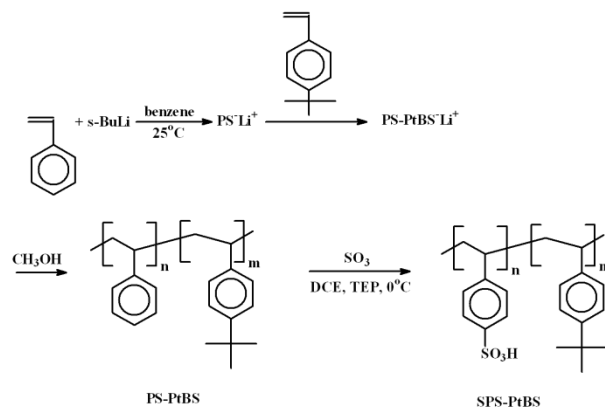
Scheme S1 Synthesis of the SPS-b-PtBS block copolymer.

SUPPORTING INFORMATION

Preparation of diblock copolymer

Poly(styrene sulfonate-b-tert-butylstyrene) diblock copolymer sample (SPS-b-PtBS, code name SD-2) was prepared via sulfonation of a poly(styrene-b-tert-butylstyrene) diblock copolymer precursor. The synthesis of the latter was performed by anionic polymerization high vacuum techniques by sequential addition of monomers.[31] In order to achieve sulfonation, Valint and Bock method was used.[32] This involves the reaction of SO_3 with the phenyl rings of the copolymers and leads to selective sulfonation of the phenyl rings of the polystyrene blocks, primarily at the para position. PtBS block sulfonation is minimal due to the steric hindrance of the tert-butyl group of the PtBS segments.[33] Both precursor and final block copolymer were characterized in terms of composition, chemical substitution, molecular weight and molecular weight distribution, by size exclusion chromatography (Waters system composed of a Waters 1515 isocratic pump, a set of three μ-Styragel mixed bed columns, with a porosity range of 102 to 106 Å, a Waters 2414 refractive index detector, operating at 40°C, and controlled through Breeze software), 1H-NMR spectroscopy (Bruker AC 300 instrument in $CDCl_3$ at 25°C), ATR-FTIR spectroscopy (Bruker Equinox 55 Fourier transform instrument, equipped with an attenuated total reflectance diamond accessory from SENS-IR, spectral range 500-5000 cm^{-1} with 100 scans at 4 cm^{-1} resolution), acidimetric titration and elemental analysis.

Solution preparation and dipping process

The solution was prepared by mixing 0.1 gr copolymer with 10 ml methanol and stirring overnight in order to produce a solution of 1%. The sensitive material was deposited on the fiber tip by performing dipping cycles of about 5 seconds followed by about 10 second drying periods for each cycle.
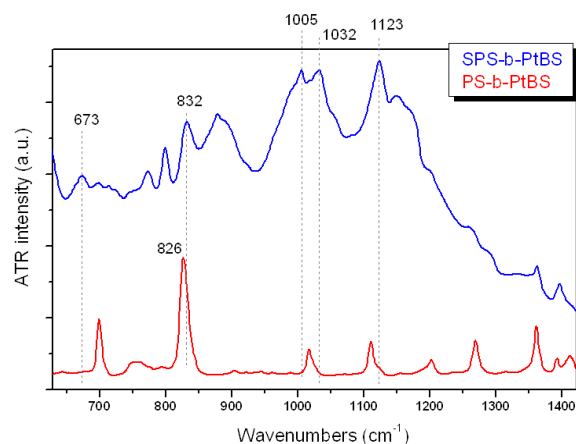

Figure S1 ATR-FTIR spectrum of PS-b-PtBS precursor (red) and the final SPS-b-PtBS block copolymer (blue).
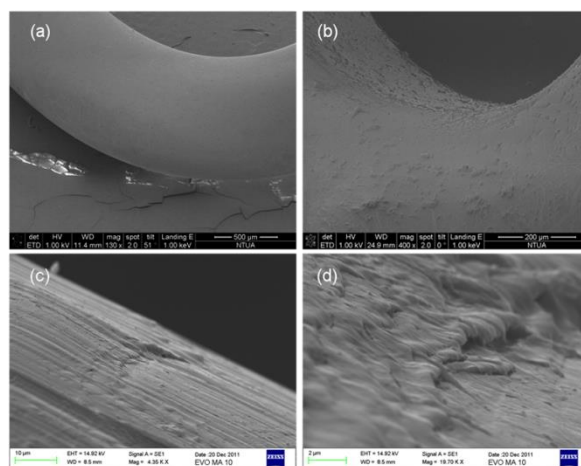

Figure S2 Scanning Electron Microscope (SEM) images of (a) original POF surface. (b) Bent

region of deposited material (c) POF layer morphology (d) close up of a deposited POF region. Block copolymer material is visible on POF surface.

The layers of sensitive material were successfully and permanently deposited on the POF surface (cladding layer), as shown in Scanning Electron Microscope (SEM) images presented in Figure S2. However the deposition was not entirely homogeneous due to the fact that methanol is not the ideal solvent for the block copolymer material. Thus, the copolymer is actually dispersed in the solution in the form of micro-nanoparticles and not in molecular form. This could result to a difficulty to produce uniform layers and disturbs accurate layer thickness measurements. However, it was intentionally selected the use of methanol as a solvent in order to make feasible the overlayer deposition on the PMMA POFs' surface, being chemically resistant to methanol, without deteriorating the fiber- copolymer interface properties. Use of more efficient and suitable solvents like tetrahydrofuran (THF), for the diblock copolymer could lead to chemical attack and etching of fibers' surface modifying

its uniformity as can be seen in Figure S3 and inducing additional scattering loss centers. Despite the restrictive selection of solvents and the use of methanol the overlayers on POFs' surface were very well controllable, and furthermore were stable and robust with excellent adhesion, allowing well defined and repeatable sensors performance.
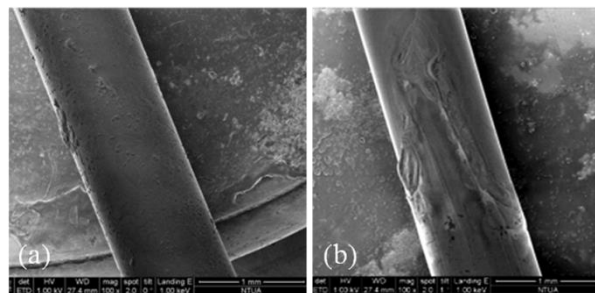

Figure S3 Scanning Electron Microscope (SEM) images of POF deposited surface with the copolymer SPS-b-PtBS diluted (a) in methanol and (b) THF solvent, showing the deterioration of fluorinated polymer cladding.

GRAPHICAL ABSTRACT

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Amphiphilic diblock copolymer based multi-agent photonic sensing scheme

An amphiphilic diblock copolymer is applied as the active sensitive material to a Polymer Optical Fiber, forming a multi-agent sensing head. The copolymer consisting of an hydrophobic and hydrophilic block exhibits sensitivity to cyclic aromatic compounds and polar substances allowing the implementation of a robust, inexpensive and reusable sensor for toluene, benzene, humidity, ammonia and lysozyme. Modification of the blocks ratio in the macromolecule could result to further sensitivity customization and enhancement for specific measurands.