Sensors and Actuators B: Chemical

Tuning the dynamic range and sensitivity of optical oxygen-sensors by employing differently substituted polystyrene-derivatives

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ABSTRACT

Ten different polystyrene-derivatives were tested with respect to their potential use as matrix materials for optical oxygen sensors in combination with the platinum(II) meso-tetra(4-fluorophenyl) tetrabenzoporphyrin as indicator dye. Either halogen atoms or bulky residues were introduced as substituents on the phenyl ring. A fine-tuning of the sensor sensitivity was achieved, without compromising solubility of the indicator in the matrix by providing a chemical environment very similar to polystyrene (PS), a standard matrix in optical oxygen sensors. To put the results into perspective, the studied materials were compared to PS regarding sensitivity of the sensor, molecular weight and glass-transition temperature. The materials promise to be viable alternatives to PS with respect to the requirements posed in various sensor application fields. Some of the polymers (e.g. poly(2,6-dichlorostyrene)) promise to be of use in applications requiring measurements from 0 to 100% oxygen due to linearity across this range. Poly(4-tert-butylstyrene) and poly(2,6-fluorostyrene), on the other hand, yield sensors with increased sensitivity. Sensor stability was evaluated as a function of the matrix, a topic which has not received a lot of interest so far.

1. Introduction

Optical oxygen sensors based on phosphorescent dyes are state-of-the-art measurement devices in industry and academia alike [1]. High accuracy achieved over a large range of analyte concentrations and simple instrumentation are the major advantages of such sensors. Additionally contactless measurements are possible through any transparent media.

The basic components of an optical oxygen sensor are a luminescent indicator and a sensor matrix which serves as a solvent for the indicator [2]. Optical oxygen sensors rely on collisional quenching of the luminescence of the indicator by molecular oxygen. This results in a decrease of the luminescence intensity and the decay time. Luminescent transition metals complexes [3,4], especially metalloporphyrins [5–9], are frequently used as indicator dyes. Polymers or organically modified silica (ormosils) are mainly employed as matrix materials [10,11]. Usually, the indicator dye is entrapped in the matrix and the resulting sensor is deposited onto an optical fibre or a support.

Indicator and matrix affect sensor performance, most importantly dynamic range, sensitivity, selectivity and robustness. In detail the important parameters regarding the indicator are the decay time, influencing the dynamic range and sensitivity, the molar absorption coefficient and the quantum yield, both influencing brightness, and the spectral properties, determining requirements with respect to needed filters and light sources. Additionally its photophysical and chemical stability has an impact on the lifetime of the sensor.

The sensor matrix is of similar importance regarding the sensor performance. The matrix influences the dynamic range, sensitivity and even long-term stability of the sensor. The question of the potential usability of a matrix material can be addressed by considering several key parameters.

For optical oxygen sensors the matrix has to be permeable to oxygen, while being impermeable to other potential quenchers (mainly ions). This requirement is among the key considerations regarding the use of a polymer as an optical oxygen sensor matrix. Additional requirements for matrix materials include their availability – either commercial or simple large scale synthesis, chemical stability, solubility in organic solvents as well as its suitability as a chemical environment for the indicator dye.

As the permeability of the matrix influences the sensitivity and dynamic range several different matrix materials are generally used. Those materials include common polymers like polystyrene

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(PS), polymethylmethacrylate (PMMA) and cellulose derivatives [10,12,13], but also less common polymers [14,15], ormosils [16,17] and other materials [18]. These materials are generally chosen for their intrinsic permeability towards oxygen. Their varying permeabilities towards oxygen arises from varying degrees of void volume present in the materials.

Tuning the sensitivity by changing the polymer may pose too big an intervention for an established sensor system given that the matrix has to provide a suitable environment for the indicator. A possible solution may be the use of polymers with similar structure, but varying permeability and copolymers of such. Surprisingly, this possibility has rarely been considered so far and has not been studied in detail.

In this contribution, ten different styrene-derivatives and copolymers of two of the styrene-derivative monomers were produced and studied with respect to their potential use as oxygen sensor matrices. The oxygen permeability of the set of materials, as well as the possibility of fine tuning sensor sensitivity and its dynamic range via copolymerisation were evaluated. For a few selected materials, the photostability of the indicator in the matrix was evaluated and the effects of the matrix on this parameter were assessed.

2. Experimental

The indicators platinum(II) and palladium(II) meso-tetra(4-fluorophenyl)tetrabenzoporphyrins (PtTPTBPF$_4$ or PdTPTBPF$_4$) were synthetised in our lab [5], all solvents were purchased from Carl Roth (www.carlroth.de) and used as received.

2-Fluorostyrene, 2,4-difluorostyrene, 2-chlorostyrene and 2,6-dichlorostyrene were purchased from ABCR (www.abcr.de). 2,6-Difluorostyrene, 4-phenylstyrene and 2,2′-azobis(2-methylpropionitrile) (AIBN) were obtained from Sigma (www.sigmaaldrich.com).

Polystyrene (www.acros.com), poly(4-chlorostyrene), poly(α-methylstyrene) (both from Scientific polymer, www.scientificpolymer.com) and poly(4-tert-butylstyrene) (Sigma) were purchased, the other polymers were synthesised using the following procedure.

2.1. Synthesis

The monomers were filtered through a column packed with aluminium oxide, to remove the contained inhibitor (4-tert-butylcatechol). An appropriately sized Schlenk-flask was charged with one equivalent of monomer. The liquid was stirred at room temperature under heavy flow of argon for 20 min. 1 mol% of AIBN was added under argon. The flask was sealed and the solution was allowed to react at 75 °C for up to 4 h while stirring. Upon complete solidification due to polymerisation, the polymer was allowed to cool.

Then, the polymer was dissolved in dichloromethane to give a roughly 10 wt% solution. The solution was added dropwise to a five-fold volume of methanol, resulting in the precipitation of a white, powder-like precipitate. The suspension was filtered through a paper filter and redissolved in dichloromethane to give a solution containing about 10 wt% of polymer. This step of dissolving and precipitation was repeated three to five times. The polymer was dried in the oven at 60 °C to yield a white, powder-like solid.

2.2. Polymer characterisation

Weight and number average molecular weights (Mw and Mn), as well as the polydispersity index PDI = Mw/Mn, were determined by size exclusion chromatography (SEC) with the following setup: Merck Hitachi L6000 pump, separation columns from Polymer Standards Service (8 mm × 300 mm, STV 5 μm grade size; 106, 104 and 103 Å pore size), refractive index detector (model Optilab DSP Interferometric Refractometer) from Wyatt Technology. Polystyrene standards from Polymer Standard Service were used for calibration. All SEC runs were performed with tetrahydrofuran (THF) as the eluent.

Differential scanning calorimetry (DSC) measurements were made with a Perkin Elmer Pyris Diamond Differential Scanning Calorimeter equipped with a Perkin Elmer CCA7 cooling system using liquid nitrogen. A nitrogen flow of 20 mL min^{-1} and different heating rates varying between 10 and 40 °C/min were used. The described transitions were taken from the second heating run with a heating rate of 20 °C/min.

2.3. Preparation of sensor films

Sensor foils of defined thickness were prepared by knife coating cocktails of comparable viscosity onto poly(ethylene glycol terephthalate) support (Mylar®) from Goodfellow (www.goodfellow.com) using a 25 μm spaced Gardner coating knife. Cocktails typically contained 10 wt% of polymer in chloroform (HPLC-grade) and 1 wt% of PtTPTBPF$_4$ or PdTPTBPF$_4$ with respect to the amount of polymer employed. After casting, the sensor foils were carefully dried for 24 h at 60 °C to ensure complete removal of solvent before characterisation.

2.4. Calibration curves

Absorption spectra were measured at a Cary 50 UV-VIS spectrophotometer (www.lzs-concept.com). Luminescence phase shifts and consequently decay times were measured with a two-phase lock-in-amplifier (SR830, Stanford Research Inc., www.thinksrs.com). Excitation was performed with the light of a 435 nm LED which was sinusoidally modulated at a frequency of 5 kHz for PtTPTBPF$_4$ or 500 Hz for PdTPTBPF$_4$. A bifurcated fibre bundle was used to guide the excitation-light to the sensor film and to guide back the luminescence. A BG12 excitation glass filter and an RG9 emission filter (both from Schott, www.schott.com) were used. The luminescence was detected with a photo-multiplier tube (H5701-02, Hamamatsu, www.sales.hamamatsu.com). Temperature was controlled by a cryostat ThermoHaake DC50. Gas calibration mixtures were obtained using a gas mixing device (MKS, www.mksinst.com).

2.5. Photostability

Photostability was assessed by exposing sensor films to prolonged irradiation, by focusing the light emitted by a 458 nm high-power 10 W LED array (11.12 V, 0.699A, 7.8 W) (www.led-tech.de) through a lens purchased from Edmund optics (www.edmundoptics.de). Absorption spectra between 350 nm and 800 nm and luminescence lifetimes upon de-oxygenation were measured every 15 min.

2.6. Oxygen consumption

The sensor films were coated with 10% poly(vinyl alcohol) (PVOH), Mw = 86,000 (Scientific Polymer) in water to give a 7.5 μm thick blocking layer. The film was dried at 60 °C. Measurements were performed under continuous illumination using the two-phase lock-in-amplifier setup described above.

Table 1
Molecular weight, polydispersity index and glass-transition temperature of the polymers.

Polymer	Mw (g mol^{-1})	PDI	T_g (°C)
PS	250,000	n.d.	100 [19]
tButPS	50,000–100,000	n.d.	n.d.
aMePS	186,300	1.04	167–169 [19]
4PhPS	25,210	1.7	132.8
2FPS	38,540	2.0	91.9
4ClPS	69,700	2.8	122.2
2ClPS	82,480	2.8	129.2
2,6FPS	138,240	2.7	107.5
2,4FPS	38,150	1.8	88.3
2,6ClPS	106,320	1.9	157.0
2,6ClPS + 4ClPS (1 + 1)	379,500	2.8	138.6
2,6ClPS + 4ClPS (2 + 1)	381,800	4.4	136.6
2,6ClPS + 4ClPS (1 + 2)	759,000	3.5	123.1

3. Results and discussion

3.1. Polymer synthesis and characterisation

The effects on sensor parameters, caused by the introduction of various substituents in a PS based sensor matrix were studied for a set of PS-derivatives in combination with platinum(II) and palladium(II) benzoporphyrins as indicator dyes (Scheme 1). Some of the polymers used in this study were purchased, while others where easily prepared via radical polymerisation. In all cases the polymerisation was carried out in a solvent-free manner. The polymerizations were stopped after a solid had formed. The polymers were precipitated several times and washed in order to remove oligomers, the remaining initiator and other low molecular weight components. Molecular weight and PDI were determined for all polymers and are listed in Table 1. Although the obtained polymers show a partly rather broad size distribution, they are perfectly suitable as matrix material for optical oxygen sensors, as high molecular weights ensure good processability. All polymerizations worked well and could be reproduced with similar molecular weights.

Except for the fluorinated polymers the materials were generally characterised by glass-transition temperatures (T_g) higher than the corresponding value for PS. This may be beneficial considering steam sterilisation, generally performed at 120 °C. A T_g lower than the temperature applied during sterilisation can lead to migration processes and thus compromises sensor calibration and usability. The higher T_g values found for some of the substituted polystyrenes (Table 1) have a beneficial impact on this problem.

3.2. Sensor characteristics

As outlined in the introduction the sensitivity of an optical oxygen sensor is determined by both the indicator dye used and the polymer the dye is embedded in. While for some applications highly sensitive materials are needed, other applications demand sensors with linear calibration plots up to 100% oxygen. Potential fields of interest could be sensors in diving-technology or the study of photosynthesis with optical oxygen sensors. In both cases oxygen partial pressures (pO_2) can exceed 200 hPa. In this range ($pO_2 > 200$ hPa), conventional sensors employing PS as matrix show a low signal to noise ratio and are characterised by unfavourable dynamics.

The sensitivity of an optical oxygen sensor can be tuned by changing the sensor matrix, as its oxygen-permeability directly influences the sensitivity. When adapting a sensor system to requirements posed by a new application, this effect has often been made use of, by swapping one class of polymer for a totally different one. For example PAN (polyacrylonitrile) polymers are generally

used as virtually gas-impermeable materials [20] whereas Teflon AF or silicones are employed in applications demanding high permeability. Solubility of the indicator in the matrix is highly important, yet Teflon AF and silicones are very bad solvents and unsuitable environments for most oxygen indicators. Furthermore, swapping the matrix may cause changes in sensitivity by several orders of magnitude, and compromises the processability of the sensor material. Due to the drastic changes in sensitivity interchanging between very different matrices may not be considered as "fine-tuning".

By only slightly modifying the polymer with respect to their chemical nature the limitations regarding suitability as chemical environment for the indicator and the lack of possibilities for fine-tuning can be overcome and the sensitivity could be adjusted. In this study, we introduced halogen atoms or bulky substituents at different positions of the phenyl ring of polystyrene. In one case, the effect of a methyl group introduced on the polymer backbone was also investigated. By introducing those substituents we want to change the void volume inside the polymer. PtTPTBPF$_4$ and PdTPTBPF$_4$ were used as oxygen indicators in this study due to their high brightness and strong absorption in the blue and red part of the spectrum, luminescence emission can be detected in the near-infrared part of the spectrum [5]. All sensors were calibrated from 0 to 1000 hPa O$_2$ (Table 2 and Fig. 1). It is important to note that the chosen indicator is well soluble in all of the polymers investigated. Furthermore, all polymers can easily be dissolved in organic solvents such as dichloromethane, chloroform or toluene which facilitates preparation of sensor foils.

All prepared sensors showed a fairly fast response to a change in oxygen concentration. Generally, all roughly 2.5 μm thick sensors films had a response time (t_{90}) of less than 10 s, so changing the polymer had no significant effect on the response of the sensor. Regarding the measured decay times of the indicator in the different polymers some variations were observed. Except for 2,6ClPS all other halogenated polymers yielded an increase in the observed decay time (compared to the one measured in PS). Contrary to this trend the introduction of alkyl groups or an additional aromatic ring resulted in a slightly decreased τ_0. This indicates a reduction in the nonradiative deactivation of the indicator inside most of the halogenated polymers.

By plotting the intensity (or decay time) in the absence of the quencher (I_0 or τ_0) divided by the intensity (or decay time) in the presence of the quencher (I or τ) against the quencher concentration (pO_2) calibration plots were obtained following Stern–Volmer kinetics (Eq. (1)). In this calibration the sensor sensitivity is expressed by the Stern–Volmer constant, K_{SV}. Alternatively also the I_0/I or τ_0/τ values at certain oxygen partial pressures (normally air or pure oxygen) can be used as measure for the sensitivity.

$$\frac{I_0}{I} = \frac{\tau_0}{\tau} = 1 + K_{SV} \times pO_2 \tag{1}$$

Introducing halogen atoms on the phenyl ring had a significant impact on the sensitivity. The biggest change was observed in the case of 2,6ClPS, where the sensitivity was reduced by more than 50% (compared to K_{SV} in PS). Also the other chlorinated polymers showed lower permeability. Fluorinated polymers on the other hand, were more difficult to classify. Two of the polymers, 2FPS and 2,4FPS, lowered the sensitivity, while 2,6FPS had the opposite effect. It is interesting to note, that 2,6FPS is around three times more sensitive than 2,6ClPS. Introducing a methyl group on the backbone or extending the phenyl ring by adding an additional one had only a small impact on the permeability (lowered by roughly 10%). This is surprising as we hoped to increase the permeability by introducing those groups. The biggest effect was observed for tButPS. In this polymer the sensitivity increased dramatically, which is in agreement with the literature [21]. The difference in
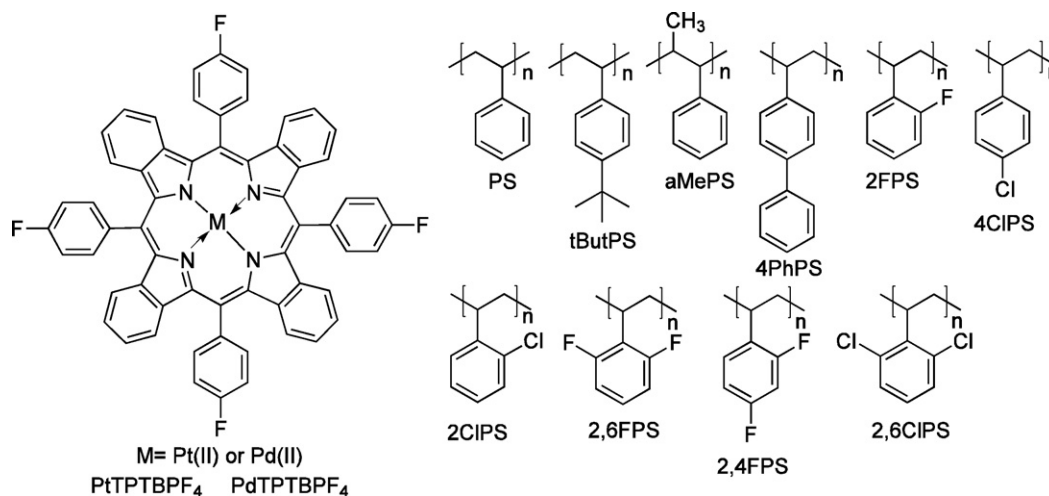
Scheme 1. Structures of the studied differently substituted polystyrene-derivatives and the incorporated indicators.

Table 2
Properties of the oxygen sensing materials based on PtTPTBPF$_4$ in various polymers.

Polymer	τ_0 (µs)	$\tau_0/\tau - 1$ at 210 hPa O$_2$	$\tau_0/\tau - 1$ at 1000 hPa O$_2$	$I_0/I - 1$ at 210 hPa O$_2$	$I_0/I - 1$ at 1000 hPa O$_2$	K_{SV} (hPa^{-1})[a]
PS	52.55	3.13	9.98	3.92	17.35	0.0174
tButPS	51.15	7.09	9.79	13.10	48.12	0.0477
aMePS	51.25	2.52	8.30	3.23	16.04	0.0157
4PhPS	49.26	2.88	9.95	3.37	15.28	0.0153
2FPS	54.48	1.87	6.44	2.16	9.57	0.0096
4ClPS	52.79	2.72	8.82	3.27	14.59	0.0147
2ClPS	53.60	1.69	6.30	1.96	9.42	0.0093
2,6FPS	54.54	4.30	11.30	5.68	24.80	0.0245
2,4FPS	57.78	2.36	7.66	2.82	12.25	0.0124
2,6ClPS	50.90	1.38	5.24	1.63	8.25	0.0080
2,6ClPS + 4ClPS (1 + 1)	53.20	2.38	8.08	2.97	14.14	0.0139
2,6ClPS + 4ClPS (2 + 1)	53.53	2.22	7.69	2.76	13.29	0.0131
2,6ClPS + 4ClPS (1 + 2)	54.31	2.92	9.56	3.63	16.87	0.0168

All measurements at 25 °C.

[a] Determined from I_0/I via linear fit (except tButPS all $R^2 > 0.998$).

sensitivity measured in the polymers corresponds to a change in permeability for oxygen, which is in turn related to the void volume in the polymer. The introduction of a tert-butyl group increases the spacing between the polymer strands and creates void volume. Other substituents lead to a denser packing inside the polymer and restrain oxygen permeability.

Interestingly, the Stern–Volmer plots obtained from the intensity signals were highly linear for nearly all of the sensors while the decay time-based Stern–Volmer plots (supplementary information) showed a high degree of non-linearity. Especially

tButPS gives a highly non-linear calibration plots (I_0/I and τ_0/τ) at high oxygen concentrations. This can be explained by the fact that quenching does not occur in a homogenous manner throughout the polymer. In agreement with the two-site model [16,22] (equation in supplementary information), two distinct domains, one quenchable, one less-quenchable, contribute to the overall behaviour of the sensor. Although the two-site model is physically meaningful only for the luminescence intensity plots, it often fits decay time data very well. At high quencher concentrations the luminescence of the quenchable fraction is extinguished, while the luminescence
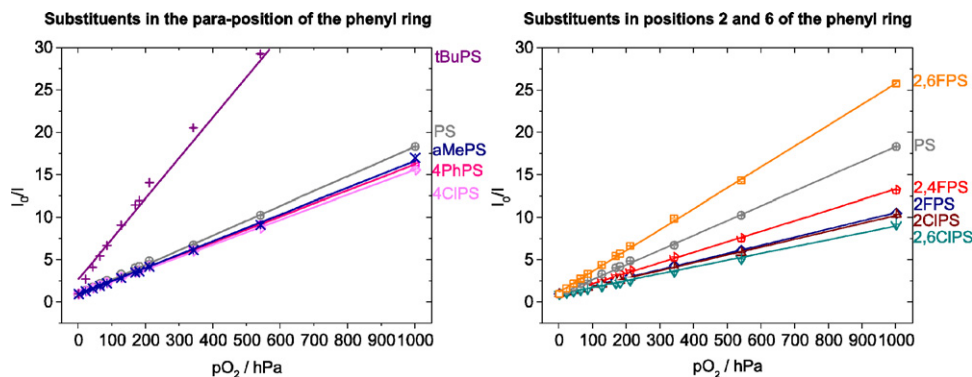

Fig. 1. Stern–Volmer plots of the investigated polymers incorporating PtTPTBPF$_4$ as oxygen indicator. Except for tBuPS all other materials gave highly linear calibration plots up to a pO$_2$ of 1000 hPa (all measurements at 25 °C).
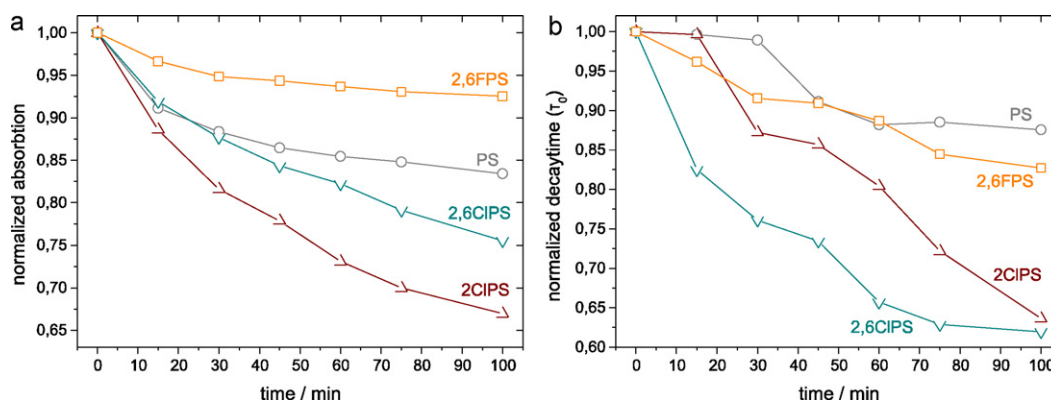
Fig. 2. Sensor photostability: (a) measured photobleaching of PdTPTBPF$_4$ at 445 nm; (b) change in decay time in for different polymers upon continuous illumination (all measurements at room temperature).

of the less-quenchable fraction is not affected. Even if only a small amount of indicator is in the less-quenchable fraction this leads to a non-linear calibration plot, especially for decay time-based Stern–Volmer plots where the decay time of the less-quenched fraction is similar to τ_0 (Figure S1 in supporting information). So tButPS is highly suitable for measuring low and even trace oxygen concentrations. On the other hand this material as well as 2,6FPS and even PS (especially decay time-based) are not well suitable for measuring high oxygen partial pressures. For applications involving oxygen partial pressures higher than 200 hPa sensors based on 2,6ClPS, 2ClPS or 2FPS are very promising. Sensors based on those polymers show desirable dynamics from 0 to 1000 hPa pO_2 in intensity- as well as decay time-based calibrations. The possibility of fine tuning the sensor sensitivity was assessed by studying products of the co-polymerisation of 2,6ClPS and 4ClPS, whose respective bulk-polymers are characterised by very different oxygen permeabilities. The prepared co-polymers showed different sensitivity than the respective bulk-polymers. However, no linear correlation between the monomer ratio and the sensitivity was observed. The respective calibration curves closely resemble the one obtained for 4ClPS and the influence of varying amounts of 2,6ClPS is rather weak (Figure S2 in supplementary information).

Although it was not possible to predict the sensitivity by employing co-polymerisation-products of different styrene derivatives, the possibility of tuning the sensor sensitivity over a broad range of oxygen concentrations by using a set of chemically very similar matrix materials is demonstrated. The sensor matrices presented herein constitute promising alternatives to polystyrene as a sensor matrix, especially in sensor applications, where lower or higher sensitivity is required.

3.3. Sensor stability

Singlet oxygen produced in the quenching process is a potential source of dye and polymer degradation, and compromises sensor stability. Sensor stability is commonly believed to be dependent on the indicator dye. Yet the impact of the matrix on the stability of a sensor should not be underestimated. Apart from acting as a chemical barrier, that protects the sensor from chemical degradation processes such as hydrolysis, the matrix also plays a role in reducing potential photo-degradatory reactions affecting the dye. It is thus essential for sensor stability. This influence is highly dependent on the chemical nature of the sensor matrix and is demonstrated in this work for a selected set of different, yet comparable, polystyrene-based polymers.

For this purpose sensors were prepared containing PdTPTBPF$_4$ as indicator. This indicator was chosen as it is nearly fully quenched

by oxygen at ambient conditions [5]. Consequently the production of singlet oxygen is increased and photo-degradation processes can be observed on a shorter timescale.

The stability of the indicator was assessed by monitoring the decrease in the absorption bands (Fig. 2a). Additionally the stability of the sensor was monitored via measuring the change in decay time (τ_0) in the absence of oxygen (Fig. 2b).

It is important to state that bleaching was only observed after continuous irradiation with a high power LED array. In typical sensor applications, where the sensor is only illuminated by short light pulses, bleaching is not so critical.

Compared to the standard PS based sensor only introducing fluoride increased the stability, while chloride had an opposite effect. Furthermore, the measured decay time changed in all polymers after light exposure. Such a change may be explained by the formation of quenchers in the sensor material – a realistic assumption, as the produced singlet oxygen is known to form peroxides or similar structures upon reacting with the matrix [23,24].

In order to validate this theory the photo induced oxygen consumption within the sensor material was measured using a new approach.

3.4. Oxygen consumption

The underlying quenching process in optical oxygen sensors is fully reversible and does not consume any oxygen [25]. However, the highly reactive singlet oxygen produced in the quenching process could be consumed during the reaction with the components of the sensing material (indicator or polymer). For researchers applying optical oxygen sensors such effects are highly important and need to be considered during the experiment. Especially at low oxygen concentrations in stagnant systems oxygen depletion could become an issue. Therefore we investigated oxygen consumption within the new polymers in the following manner. The sensors were covered with an oxygen impermeable poly(vinyl alcohol) (PVOH) layer and continuously illuminated while measuring the decay time. By introducing this blocking layer an exchange with the environment is no longer possible, the produced singlet oxygen reacts within the sensor material (Fig. 3a) and oxygen depletion can be measured. As shown in Fig. 3b the oxygen concentration within all the sensors decreased over time. This rate of reaction is relatively low and therefore such behaviour can only be observed under continuous illumination in the absence of diffusional exchange with surrounding. Our experimental results are in agreement with the measurements regarding sensor stability and lead to the conclusion that oxidation of the matrix occurs within optical oxygen sensors.
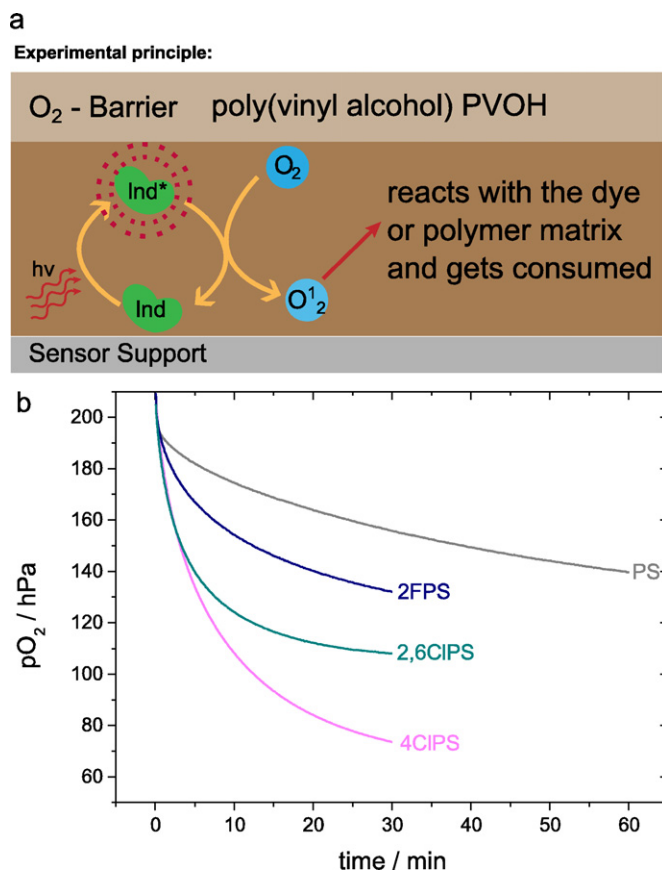
a

Experimental principle:

b

Fig. 3. Photo induced oxygen consumption in the sensor material: (a) experimental setup – an oxygen barrier is coated on top of the sensor membrane. The produced singlet oxygen reacts with the sensor components and gets consumed; (b) measured decrease in oxygen concentration inside the sensor upon continuous illumination indicating the consumption of oxygen (all measurements at room temperature).

Due to its high relevance for optical oxygen sensors, a detailed study on this phenomenon is planned.

4. Conclusion

In this study, we demonstrated that different polystyrene-derivatives can be obtained in a fairly simple polymerisation and be used as sensor matrices in optical oxygen sensors. The materials studied herein can be used to tune the sensitivity of the sensor without compromising the favourable characteristics of polystyrene as a sensor matrix, since a high degree of similarity in chemical nature is conserved. For applications demanding high sensitivity and low oxygen levels tButPS can be used. In applications involving high concentrations of oxygen 2,6ClPS and 2ClPS may prove to be of special interest, due to their favourable dynamics in higher concentration ranges. Furthermore, we also gained some insight into photoreactions inside sensor membranes. We observed that the sensor matrix takes part in photoreactions. This can lead to the formation of quenchers inside the sensor and can compromise the measurements due to oxygen consumption. More detailed investigation of oxygen consumption in sensing materials and the means of reducing these effects are on-going.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.snb.2012.09.057.

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