



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

Klaus Koren^{a,*}, Lukas Hutter^{a,1}, Barbara Enko^b, Andreas Pein^c, Sergey M. Borisov^a, Ingo Klimant^a

^a Institute of Analytical Chemistry and Food Chemistry, Graz University of Technology, Stremayrgasse 9, 8010 Graz, Austria

^b Institute of Physical and Theoretical Chemistry, Graz University of Technology, Stremayrgasse 9, 8010 Graz, Austria

^c Institute for Chemistry and Technology of Materials, Graz University of Technology, Stremayrgasse 9, 8010 Graz, Austria

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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.

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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

* Corresponding author. Fax: +43 31687332502.

E-mail address: kkoren@ist.ac.at (K. Koren).

¹ These authors contributed equally to this work.

(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 (PtTPTBPF₄ or PdTPTBPF₄) were synthesised 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 (M_w and M_n), as well as the polydispersity index $PDI = M_w/M_n$, 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 PtTPTBPF₄ or PdTPTBPF₄ 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 PtTPTBPF₄ or 500 Hz for PdTPTBPF₄. 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, 0.699 A, 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), M_w = 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.

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