

Poly(methylmethacrylate) as immobilization matrix for Ru(II)-complex, a potential optical oxygen sensor

J. ZAHARIEVA*, M. MILANOVA, D. TODOROVSKY

Faculty of Chemistry, University of Sofia, 1, J. Bourchier Blvd., Sofia 1164, Bulgaria

Microcomposites are produced consisting of optically active Ru (II)-tris(4,7-diphenyl-1,10-phenanthroline)dichloride (Rudpp) immobilized in poly(methylmethacrylate) prepared by polymerization of the monomer or by using chloroform solution of the polymer. The morphology of films and membranes (up to 1.5 mm in thickness) is studied in dependence of the matrix production method and conditions of specimens' preparation. Partial destruction of the complex is observed during the polymerization of the monomer causing decrease of the fluorescence intensity. The embedding of the fluorophore has no significant effect on its excitation and emission spectra. The response of composites to O₂ in gas phase or dissolved in water follows Stern-Volmer dependence with very good linearity but with relatively low quenching constant. The two weeks soaking of the samples in distilled water leads to a moderate decrease of the fluorescence intensity.

(Received March 9, 2011; accepted June 9, 2011)

Keywords: Optical oxygen sensors, Poly(methylmethacrylate), Ru(II) complex

1. Introduction

The optical oxygen sensors are promising alternative of the commonly used electrochemical devices avoiding some of the main disadvantages of the latter: consumption of oxygen, limited operation life due to instability of the electrode surface, necessity for a reference electrode. Optical oxygen sensing is usually based on collision quenching by molecular oxygen of a fluorophore embedded in a support matrix. Ru (II)-tris(4, 7-diphenyl-1, 10-phenanthroline)dichloride (Rudpp) is, so far, the most often used chromophore due to the sensitivity of its red emission intensity (when irradiated with blue light) to the O₂ – content. The immobilization matrix has to satisfy two contradictory requirements – to ensure strong enough entrapping of the dye and, in the same time, to guarantee the possibility of the smaller analyte species to diffuse into the matrix and to interact with the fluorophore. So, the matrix properties are of crucial importance for sensor sensibility, detection limit, calibration stability, areas of application and exploitation life.

The applicability of various inorganic (see for instance [1]) and organic polymers has been explored as immobilization matrices for optically active complexes including ethyl cellulose [2], fluoropolymers [3], ion-exchange polymers [4], poly(styrene) [5 - 9], poly(vinyl chloride) [10, 11], silicone rubber [10, 12 - 14]. Organic polymers have also been used as substrate for deposition of sol-gel produced films [15].

Poly(methylmethacrylate) (PMMA) is also used as matrix material [16]. Preparation of cobalt hexacyanoferrate nanoparticles-PMMA composites has been described in [17] using commercially available methylmethacrylate (MMA, employed after removing the inhibitor) and 2,2-diethoxyacetophenone as initiator for

radical polymerization. Adding MMA to tetraethoxysilane-ethanol-water mixture with HF (as hydrolysis catalyst), low dielectric constant PMMA-SiO₂ hybrid films have been produced [18].

The PMMA (molecular weight 950 K) in the form of 7 % anisole solution (preventing unraveling the PMMA particles into molecular chains) has been used for preparation of nanocomposite thin films containing Al₂O₃ and TiO₂ nanoparticles [19].

Preparation of PMMA based composite films containing Si nanocrystallites using toluene as polymer solvent and investigation of their luminescence properties has been reported. Si nanoparticles have been suspended in a toluene solution and after reflux for 10 min, films have been deposited on quartz substrates by spin coating and following heating at 80 °C for 30 min to evaporate the solvent [20].

PMMA is used for embedding Ln³⁺ (mainly Eu³⁺) chelates for production of different optical devices [21, 22-27]. The polymers (including PMMA) are also applied for preparation of inorganic (silica)/organic polymer hybrids [27-31]. A valuable review of the papers on complexes blended with polymers and covalently bonded to the polymer matrix, including PMMA is made by Binnemans [32]. Atomic force, scanning and transmission electron microscopy and photoluminescence spectra have been used to study the influence of the polymer nature, synthesis conditions, optically active component concentration on the fluorescence properties of the latter. The application of PMMA as immobilization matrix in the optical oxygen sensors is reviewed in number of papers (see for instance [16, 33, 34]) but the examples especially for embedding of Rudpp in PMMA are not available.

In the present work the so called host-guest [32] Rudpp-PMMA system is studied applying the both

possible synthetic techniques: dissolution of the Rudpp into the monomer solution and initiating polymerization or dissolving the polymer and the complex in a cosolvent and evaporation of the latter, obtaining doped polymer [32]. The morphology of the so prepared films and membranes, the influence of the immobilization of the chromophore on its optical properties and evaluation of the ability of Rudpp-PMMA composites to be applied as active component of optical oxygen sensors are studied.

2. Experimental

Materials. MMA (99 %, Sigma-Aldrich), PMMA ($M = 120\,000$, Sigma-Aldrich), CHCl_3 (>99.9 %, Sigma-Aldrich, as solvent of the polymer), benzoyl peroxide (Sigma-Aldrich) were used for matrices preparation. Rudpp (100 %, delivered by Alfa Aesar) was used as chromophor dissolved in dimethylformamide (DMF, p a. LAB-SCAN).

Matrices preparation and films deposition. Two preparation modes for matrix production were used:

a) Poly(methylmethacrylate) matrix was prepared by a catalytically induced polymerization of the monomer similarly to the method described in [27]. To 5.3 cm^3 of the latter 3 mg of benzoyl peroxide (used as catalyst) was added and after stirring was mixed with 2 cm^3 DMF solution (0.038 g/cm^3) of the complex. The polymerization proceeds at $80\text{ }^\circ\text{C}$ for 30 min. Films were deposited after aging at $50\text{ }^\circ\text{C}$ for 12 h. A 24 h of aging was applied when thicker membranes were prepared. It is supposed that the final product after evaporation of the solvent will contain 1.5 % Rudpp.

b) To 25 ml chloroform solution of PMMA (0.067 g/ml), 5 ml of chloroform solution of the 0.02 g complex was added and magnetically stirred vigorously for 30 min at ambient temperature. Films were deposited immediately after the end of the treatment. Membranes were prepared after 1 h aging at room temperature. The complex concentration in the final matrix is 1.0 %.

Films were deposited by dip-coating at withdrawn rate of 0.4 mm/s using the device described in [35]. Membranes (0.4 – 1.5 mm in thickness) were prepared casting of the PMMA solution or partially polymerized MMA in Teflon® mould. Both types of samples were dried at $50\text{ }^\circ\text{C}$ for 24 h.

Films characterization. The films thickness was measured by profilometer Talystep and their morphology was studied by a fluorescence (N-400M), scanning electron (Jeol JSM 5510) and atomic force (Veeco MultiMode and Agilent 5500) microscopy.

The excitation and emission photoluminescence spectra were recorded by Cary Eclipse Fluorescence Spectrometer (Varian).

The films stability against water was tested after 240 h soaking in distilled water at ambient temperature.

Response to oxygen. The photoluminescence response of the films to oxygen in a gas mixture was measured by the equipment described in [36] under the illumination by blue LEDs with maximum of the spectral output band at 450 nm. The device ensures measurements to be made in gaseous medium with controlled composition under reproducible conditions. The compressed gases (from

bottles) pass through flow-meters (to adjust the desired gas mixture composition) and mixing vessel and enter the measurement camera at a pressure of 101 kPa. The concentration of O_2 in the so obtained mixture is followed by measuring with Crowcon Detection Instruments Ltd. oxymeter mounted just before the described camera. The relative mean square deviation of the photoluminescent signal intensity was determined by five parallel measurements with one and the same film in a gas mixture with constant composition at full shutdown and 15 min interval between the measurements and was found to vary within the limits 0.2 % (0 % O_2) – 1.1 % (100 % O_2); 0.65 % is taken in the calculations of the detection limit.

The photoluminescent response of the fabricated films to oxygen in liquids was measured by Cary Eclipse device. The relative mean square deviation of the photoluminescent signal intensity (determined by measuring of 5 parallel samples containing $7.3 \cdot 10^{-4}\text{ } \%$ O_2) is 0.5 %. Distilled water boiled and bubbled with N_2 or O_2 to adjust different oxygen concentration was analyzed. The oxygen-free water was prepared by bubbling of high-purity N_2 for 90 min through water (previously boiled for 20 min) put in closed vessel with a hydraulic gate, and fully oxygenated water – by bubbling of O_2 for 50 min through ice-cold water, put in the same vessel. The O_2 concentration was measured in N_2 -filled glove box by an oxymeter Hanna Instruments 9145 with a precision of $\pm 1.5\text{ } \%$ of the full scale.

3. Results

Films morphology. Images from fluorescence, scanning electron and atomic force microscopy of the dip-coated films and membranes with different thickness prepared from catalyst-induced polymerization of MMA or from solution of PMMA are shown on Figs. 1, 2.

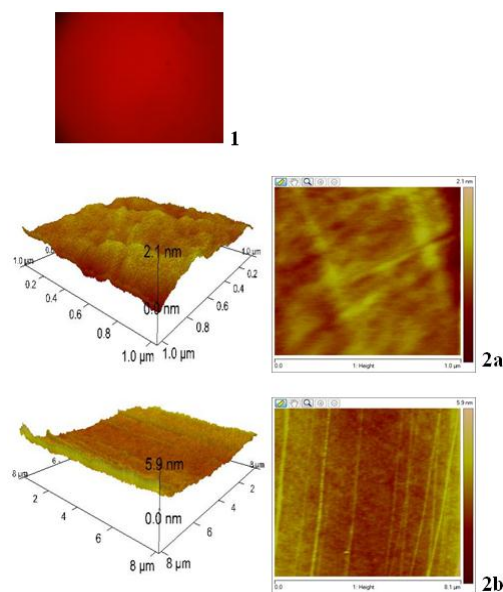


Fig. 1. Fluorescence, ($\times 160$, 1) and AFM (2, at different scanning area) images of dip-coated films from Rudpp-containing composite prepared from catalyst-induced polymerization of methylmethacrylate.

Poly(methylmethacrylate) films produced from monomer are dense with a smooth surface and uniform distribution of the complex. The morphology of the samples from PMMA solution is influenced by the polymer solution concentration, stirring and drying conditions and thickness. Applying more concentrated solutions (~ 0.1 g/ml) thicker membranes (>1.5 mm) can be obtained but “valleys” and cracks can be formed (Fig. 2.1). The drying at temperatures above 50 °C can cause protuberance-like (Fig. 2.2) and holes (Fig. 2.3) roughness due to the too fast evaporation of the solvent. The stirring

during the polymer - complex co-dissolving has to be rather energetic. Otherwise some nano- (Fig. 4c) and microcrystallization (Fig. 5a,b) and cluster formation (Fig. 5c) of the complex is observed. Cluster formation is also observed embedding of Nd-diketonates in PMMA matrix [32]. Following conditions described in the Experimental,

smooth films with uniform complex distribution (Fig. 2.7) are produced. [32]. Following conditions described in the Experimental, smooth films with uniform complex distribution (Fig. 2.7) are produced.

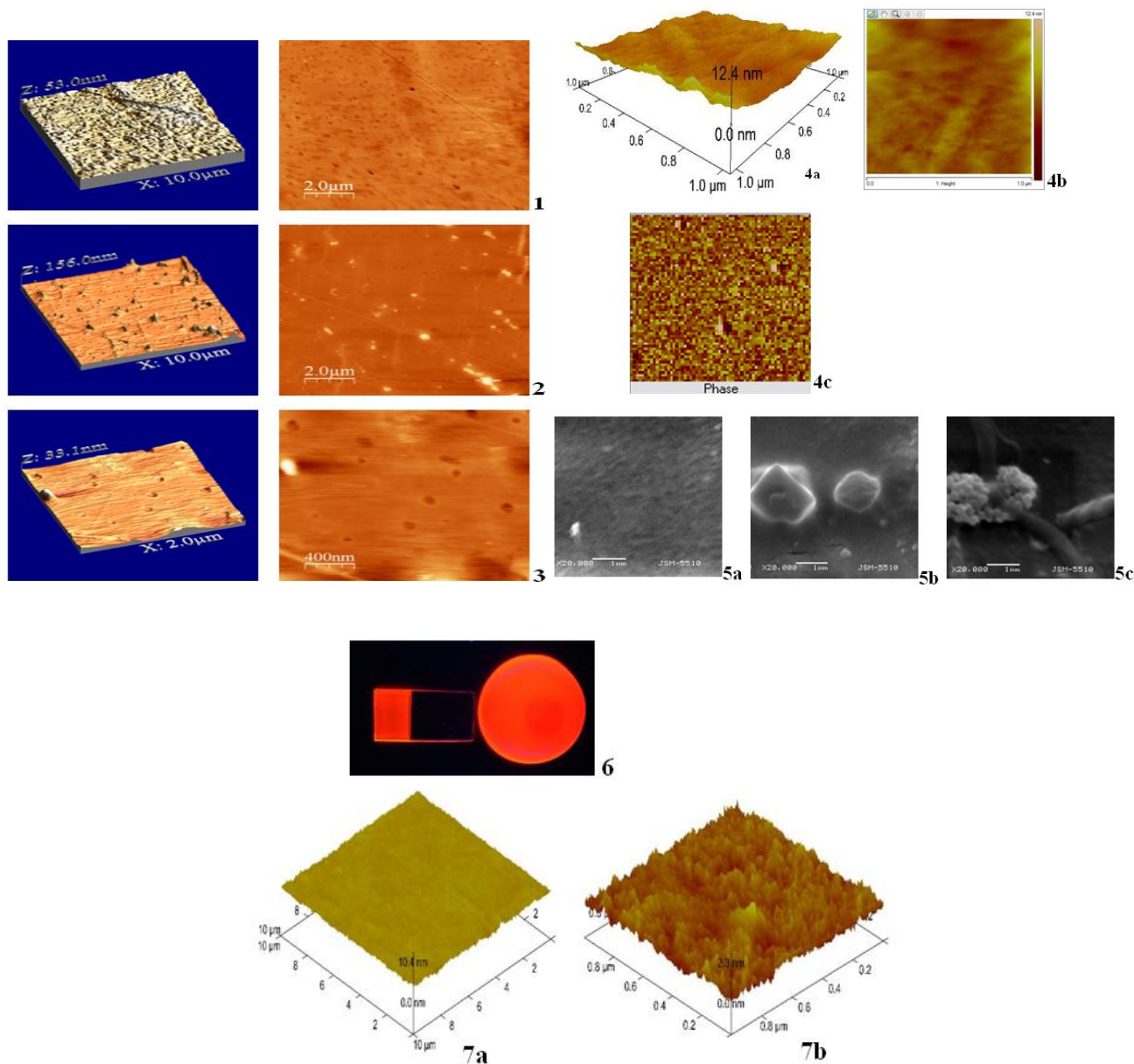


Fig. 2. AFM images of *RuDpp*-containing composite prepared from solution of PMMA: membrane with thickness ~ 1.5 mm, dried at 50 °C (1), the same, dried at 50 °C (2, 3), prepared by the conditions described in the Experimental (4), SEM images of the same sample (5), film and membrane (~ 1 mm in thickness) under UV irradiation - general view (6), film (~ 500 nm in thickness) prepared by the conditions described in the Experimental part (7, at different scanning area).

Fluorescence properties. The immobilization of the chromophore in films/membranes produced from MMA or PMMA solution does not change the fluorescence properties of the complex. The excitation and emission (Fig. 3) spectra of the two types of samples are practically identical. No significant broadening of the emission peaks are observed suggesting lack of interaction of the complex with the matrices. The position of the maximum of the emission spectrum (609-610 nm) is slightly shifted compared with the pure complex (605 nm [37]) and Rudpp-SiO₂ composite (612 nm).

However, the fluorescence emission intensity from films produced by polymerization of the monomer is significantly (2.5 fold) weaker due to partial destruction of the complex. To check this supposition a Ru-free matrix prepared from the monomer (by the method described in point **a** of § Matrices preparation and films deposition of the Experimental part but without Ru-complex) was dissolved under stirring at ambient temperature in chloroform (0.067 g/ml). Then the procedure described in point **b** of the same paragraph was followed. The fluorescence emission intensity from films produced by this way is practically equal to the one prepared from the commercially available polymer.

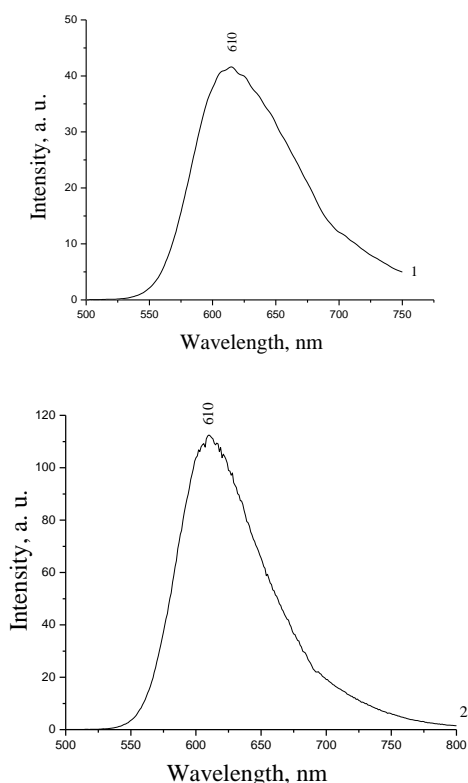


Fig. 3. Emission spectra of a Rudpp-containing membrane (excitation at 450 nm) prepared from catalyst-induced polymerization of methylmethacrylate (1) and from PMMA solution (2).

Response to oxygen. The response to O₂ of the microcomposites produced from MMA or PMMA with

equal thickness is shown on Fig. 4 through the well known Stern-Volmer's law $I_0/I = 1 + K[O_2]$, where I_0 and I are the emission intensities in the absence and presence of oxygen, respectively (fully deoxygenated water is used for determination of I_0 when the dissolved O₂ is measured), $[O_2]$ is the concentration of O₂ and K - the Stern-Volmer quenching constant. The values of the latter are shown in Table 1. The linearity of all of the produced samples is very good but the constant value of the film produced from monomer is more than 6 times lower than the membranes produced from PMMA solution.

The oxygen detection limit was evaluated from the Stern-Volmer plot as the oxygen concentration producing fluorescence signal equal to $I_0/[I_0 - 3\sigma]$ [38], where σ is the mean square deviation. The data shown in Table 1 confirm the much better performance of the material produced from PMMA solution. The values of the constant and detection limit of the film produced from solution of the monomer-produced polymer are rather close to the ones obtained by commercially available PMMA.

Composite stability. The soaking of the samples (prepared from PMMA) in solution distilled water for two weeks at ambient temperature does not change the excitation and emission spectra. No significant difference in the samples morphology is observed. However, the photoluminescence intensity of the treated samples decreases with approx 15 % suggesting significant leaching of the chromophore.

4. Discussion

The results reported show that the specimens' morphology depends on the nature of the starting material for matrix production. Conditions of matrix preparation from PMMA such like polymer concentration in the chloroform solution, stirring during the polymer-complex co-dissolving and temperature of the solvent separation are of significant importance for the obtained samples morphology. At the optimal conditions (shown in the Experimental) smooth, dense films and membranes (up to 1 mm in thickness) with uniform distribution of the complex and without cracks can be prepared.

The study of the composites fluorescence properties leads to the following main conclusions: (i) No significant interaction of the complex with the matrices takes place and the emission spectra of the complexes are practically not changed as a result of immobilization in both types of studied matrices. (ii) Due to the partial destruction of the Ru-complex during the polymerization of the monomer, the intensity of the so prepared samples is significantly lower (than that of the composites obtained from PMMA). Most probably, some disturbance of the complex distribution in the matrix volume can also be a result of the degradation process. Accordingly, the performance of these specimens as oxygen sensing device is much poorer.

The films exhibit a very good linearity of the Stern-Volmer dependence. However, acting as O₂ sensor, the produced composites, especially those from monomer,

have a relatively low sensitivity and high detection limit. This is due to the small quenching constant, most probably because of impeded penetration of the analyte in the matrix. The values of the same parameters along with relatively easy leaching of the chromophore in water do not permit films obtained from polymer solution to be recommended for dissolved oxygen measurements. Accounting for the easy production and relatively satisfactory performance, these composites can be considered as possible materials for measurement of O_2 at its medium and high content in a gas phase.

Table 1. Stern-Volmer constant K_{SV} for oxygen measurement and correlation coefficients for linear fitting

№	Matrix	O_2 in	K_{SV}	Correlation coefficient	Detection limit
1	PMMA from MMA	gas	$(1.66 \pm 0.03) \cdot 10^{-3} \%^{-1}$	0.994	13%
2	PMMA from solution of sample 1	gas	$(8.57 \pm 0.12) \cdot 10^{-3} \%^{-1}$	0.990	6%
3	PMMA	water	$(10.47 \pm 0.25) \cdot 10^{-3} \%^{-1}$	0.998	5%
4		water	$6.23 \pm 0.32 \text{ ppm}^{-1}$	0.995	13 ppm

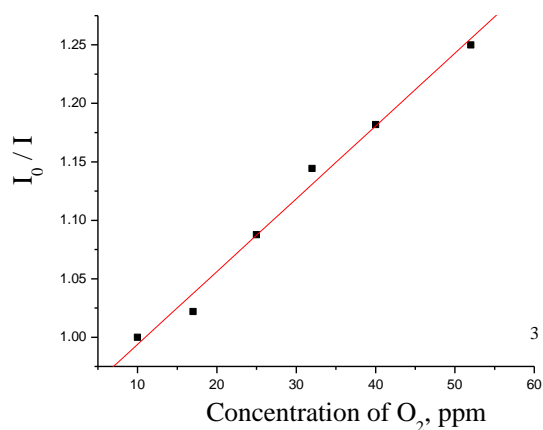
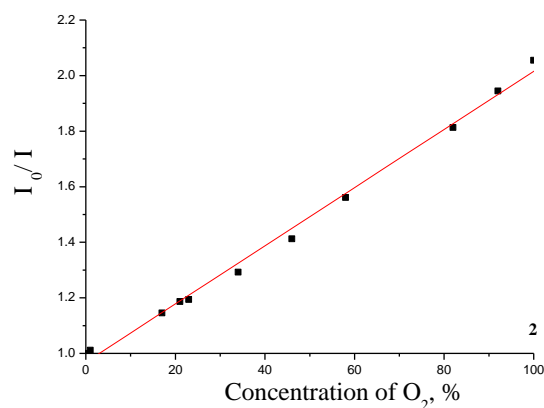
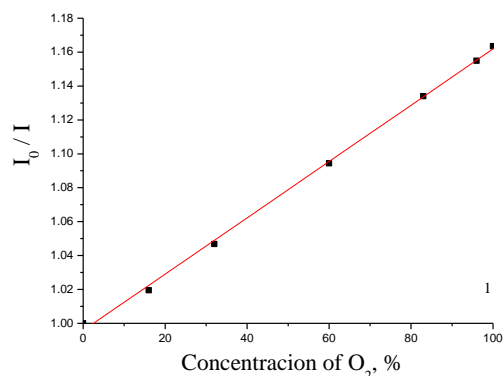


Fig. 4. Stern-Volmer dependence of composites Rudpp – PMMA: O_2 in gas phase (1, 2) and dissolved in water (3); PMMA produced from polymerized MMA (1) or from PMMA solution (2, 3).

5. Conclusion

The reported results show that the production of PMMA by the polymerization of the monomer in the presence of benzoyl peroxide as a polymerization initiator is not a suitable method for production of Rudpp-PMMA composite due to a partial destruction of the complex and the following significant decrease of the Stern-Volmer constant. Most probably the negative effect will be observed at the attempts other similar complexes to be embedded by the same method.

Using polymer solution, membranes and thin films of good quality can be obtained. The main advantages of PMMA as immobilization matrix are: not expensive and easy to be applied composite preparation method ensuring production of dense, smooth specimens with uniformly distributed optically active dye, possibility for preparation of membranes up to 1 mm in thickness, good linearity of the Stern-Volmer dependence and clear red color of the emitted light. However, acting as O₂ sensor, the produced composite has a relatively low sensitivity and high detection limit. The obtained material is not suitable for long-term permanent monitoring of O₂ dissolved in water due to the relatively easy leaching of the dye causing significant worsening of the sensor properties. The composite may be considered as possible material for measurement of O₂ at its medium and high content in a gas phase.

Acknowledgment

The study is performed with the financial support of the Bulgarian Fund for Scientific Investigations (contract VUH 05/05).

References

- [1] J. Zaharieva, M. Milanova, D. Todorovsky, *J. Optoelectronics Advanced Materials* **12**, 1247 (2010).
- [2] P. Douglas, K. Eaton, *Sens. Actuators B* **82**, 200 (2002).
- [3] Y. Amao, Y. Ishikawa, I. Okura, *Anal. Chim. Acta* **445**, 177 (2001).
- [4] V. V. Vasil'ev, S. M. Borisov, *Sens. Actuators B* **82**, 272 (2002).
- [5] P. Hartmann, M. J. P. Leiner, M. E. Lippitsch, *Anal. Chem.* **67**, 88 (1995).
- [6] P. Hartmann, M. J. P. Leiner, M. E. Lippitsch, *Sens. Actuators B* **29**, 251 (1995).
- [7] I. Klimant, Ph. D. Thesis. Karl-Franzens-Universitat. Graz, Austria, 1993.
- [8] S. Draxler, M. E. Lippitsch, I. Klimant, H. Kraus, O. S. Wolfbeis, *J. Phys. Chem.* **99**, 3162 (1995).
- [9] Y. Amao, I. Okura, *Sens. Actuators B* **88**, 162 (2003).
- [10] P. Hartmann, W. Trettnak, *Anal. Chem.* **68**, 2615 (1996).
- [11] T. E. Brook, R. Narayanaswamy, *Sens. Actuators B* **51**, 77 (1998).
- [12] X. M. Li, F. C. Ruan, K. Y. Wong, *Analyst* **118**, 289 (1993).
- [13] J. R. Bacon, J. N. Demas, *Anal. Chem.* **59**, 2780 (1987).
- [14] B. Meier, T. Werner, I. Klimant, O. S. Wolfbeis, *Sens. Actuators B* **29**, 240 (1995).
- [15] M.-C. Chow, C.-H. Yeung, K.-Y. Wong, Xi Chen, X. Wang, H.-L. Pang, N.-Y. Kwok, *Sens. Actuators B* **123**, 120 (2007).
- [16] A. Mills, M. Thomas, *Analyst* **122**, 63 (1997).
- [17] A. Zanotto, R. Matassa, M. L. Saladino, M. Berrettoni, M. Giorgetti, S. Zamponi, E. Caponetti, *Materials Chem. Physics* **120**, 118 (2010).
- [18] B. N. Joshi, A. M. Mahajan, *Materials Sci. Engin.* **B 168**, 182 (2010).
- [19] S. Lewis, V. Haynes, R. Wheeler-Jones, J. Sly, R. M. Perks, L. Piccirillo, *Thin Solid Films* **518**, 2683 (2010).
- [20] W. Lu, Y. Bian, H. Liu, Li Han, W. Yu, G. Fu, *Materials Letters* **64**, 1073 (2010).
- [21] C. Wang, Y. Zhang, X. Pei, T. Wang, Q. Wang, *Appl. Surf. Sci.* **256**, 2818 (2010).
- [22] X. Sun, H. Liang, H. Ming, Q. Zhang, J. Yang, Z. Zheng, H. Ma, Y. Zhang, J. Zhang, J. Xie, Li Cao, Z. Zhang, *Optics Commun.* **240**, 75 (2004).
- [23] T. U. Kobayashi, S. Nakatsuka, T. Iwafuji et al., *Appl. Phys. Lett.* **71**, 2421 (1997).
- [24] Z. Zheng, H. Liang, et al., in: *Proceedings of the 2nd Asia-Pacific POF Workshop, Hong Kong, China, 2003*, p. 58.
- [25] M. Mitsuishi, S. Kikuchi, T. Miyashita, Y. Amao, *J. Mater. Chem.* **13**, 2875 (2003).
- [26] B. B. J. Basu, N. Vasantharajan, *J. Luminescence* **128**, 1701 (2008).
- [27] P. A. Tanner, B. Yan, H. Zhang, *J. Mater. Sci.* **35**, 4325 (2000).
- [28] S. Kohjiya, K. Ochiai, S. Yamashita, *J. Non-Cryst. Solids* **119**, 132 (1990).
- [29] L. Mascia, A. Koul, *J. Mat. Sci. Letters* **13**, 641 (1994).
- [30] R. Tamaki, Y. Chujo, *J. Mater. Chem.* **8** 1113 (1998).
- [31] N. Yamada, I. Yoshinaga, S. Katayama, *J. Mater. Chem.* **7**, 1491 (1997).
- [32] K. Binnemans, *Chem. Rev.* **109**, 4283 (2009).
- [33] R. Ramamoorthy, P. K. Dutta, S. A. Akbar, J. *Materials Sci.* **38**, 4271 (2003).
- [34] S. M. Grist, L. Chrostowski, K. C. Cheung, *Sensors* **10**, 9286 (2010).
- [35] C. Dushkin, S. Stoyanov, A. Bojinova, S. Rusev, *Ann. Univ. Sofia, Fac. Chim.* **98 – 99**, 73 (2006).
- [36] S. Anastasova, M. Milanova, S. Rangelov, D. Todorovsky, *J. Non-Crystalline Solids* **354** 4909 (2008).
- [37] H. J. Kim, Y. C. Jeong, J. Il Rhee, T. H. Kim, *Bull. Korean Chem. Soc.* **27**, 2084 (2006).
- [38] N. Velasco-García, M. J. Valencia-González, M. E. Diaz- García, *Analyst* **122**, 1405 (1997).

*Corresponding author: JZaharieva@wmail.chem.uni-sofia.bg