Polymer Track Membranes as a Trap Support for Reagent in Fiber Optic Sensors

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SYNOPSIS

The article presents a new idea of the application of polymer track membranes (PTM) for immobilization of a reagent in fiber optic chemical sensors. PTM was made of a poly(ethylene terephthalate) foil (10 μm in thickness, pores of 0.2 μm in diameter). The usefulness of membranes additionally covered by poly(vinyl chloride) was tested in a fiber optic redox titrator. The titrator utilized *N,N'*-diphenylbenzidine as a reagent which changes its absorbance in dependence on the redox potential. The measuring system is based on a light-emitting diode and a silicon photodiode connected to a bifurcated fiber optic bundle. The gain is in price and availability of the membrane. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Fiber optic sensors have been introduced simultaneously with the development of fiber optics and optoelectronics technology which was stimulated mainly by telecommunication. The advances in technology provide new fibers with lower losses. There are many visible and infrared semiconductor light sources. Highly sensitive photodiodes and low-noise amplifiers allow one to detect a very low level of optical signals. Thus, fiber optic sensors and systems, which include these components, are finding an increasing number of applications in industry, environmental monitoring, medicine, and chemical analysis. They can be used for sensing both physical and chemical phenomena such as pressure, stress, displacement, ion concentration, and detection of compounds.[1] Fiber optic chemical sensors (FOCS)[2] are often called remote spectrophotometers because, in this case, a sample is not delivered to a laboratory but the measurement can be done *in situ*. An optical signal can be guided over several or even hundreds of meters to an electronic system where it is converted into direct readouts of measured species.

Many of the advantages of FOCS are due to the characteristics of fiber optics.[1,2] In comparison with to the electrochemical sensors, they do not require a reference electrode or cell. They can be designed as a very small and flexible device. There is no possibility to generate an electric spark or electric shock. This is very important particularly from a medical point of view. The transmitted optical signal is not subject to electric and magnetic interferences. The measurements can be done in real time with an extremely low consumption of measured species. Notwithstanding, there are several limitations and disadvantages of FOCS. One of the major limitations is an ambient light. The system should be preserved from the possibility of interference from the laboratory light, or the light source used should be modulated. The long-term stability of the sensor is limited by photodecomposition of a transducer material, aging, and washing out process. More details about FOCS can be found in several reviews published over the last decade.[2-4]

FOCS usually utilize a chemical indicator which changes its optical properties in the dependence on the analyte, which can be absorbance, luminescence, fluorescence, fluorescence decay time, etc. Each sensor consists of two main parts, i.e., an optoelectronic system (light source, fiber optics, photodiode, electronic circuit for signal processing, etc.) and a

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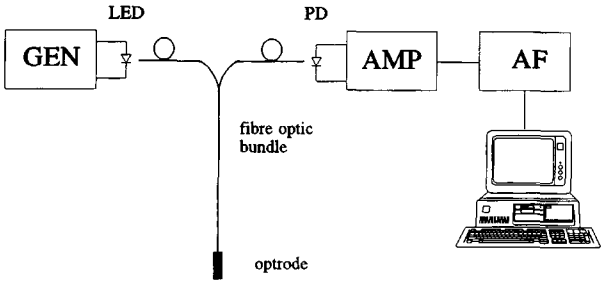


Figure 1 Experimental setup. GEN, square wave generator; LED, light-emitting diode; PD, photodiode; AMP, transimpedance amplifier; AF, active filter.

so-called optrode. The optrode is this part of the fiber optic sensor where an appropriate indicator is immobilized and its basic task is to convert the information about measured species into the change of light delivered. The most popular fiber optic chemical sensor investigated in many laboratories so far is a pH meter.[5–7] It is based on the use of an acid–base indicator such as phenol red, bromothymol blue, or fluorescein. The main problem in the design of the optrode is an immobilization procedure of the reagent. It occurs since the fiber optic sensors have been developed. Many techniques such as adsorption or chemical binding are widely utilized.[2,8] The indicator can be immobilized directly on a fiber optic or on a polymeric support. It should be pointed out that the immobilization procedure should meet several requirements. The indicator used cannot be washed out during the measurements. The optical properties of the indicator should not be changed (e.g., sometimes a red shift of the absorption spectrum is observed), and the indicator should still work properly after immobilization.

In this work, we propose a new method of indicator immobilization in the micropores of polymer track membranes (PTM). Preliminary results of our work were presented in Ref. 9. A membrane made of poly(ethylene terephthalate) (PETP) was chosen for tests in the fiber optic redox titrator. The system is based on *N,N'*-diphenylbenzidine (DPB) which changes its absorbance in dependence on the redox potential. Two ions were used as oxidant and reductant, Ce(IV) and Sn(II), respectively. Our current work was focused on PTM as a polymeric support and recent results of work on optimization of immobilization are presented.

EXPERIMENTAL

The most basic version of the experimental setup is shown in Figure 1. Modulated light from a light emitting diode (LED) is transmitted to the optrode by one arm of the fiber optic bundle. The light matched to the maximum of the molar absorbance of DPB (560 nm) is reflected in dependence on the redox potential variations and then it is transmitted to a photodiode by the second arm of the bundle. The photodiode is connected to a transimpedance amplifier and active filter. The electrical signal obtained is acquisited and processed by a pc-lab card with 12-bit A/D converter. The optrode was manufactured on the surface of the common end of the bundle according to a procedure described in Ref. 9. The PETP membrane (10 μm in thickness, with pores 0.2 μm in diameter) was soaked in a solution of DPB and poly(vinyl chloride) (PVC) in tetrahydrofurane (THF). Next, the membrane was dried. It was assumed that the addition of PVC should seal the pores. In such a way, the molecules of the reagent should be trapped in the micropores. It was verified by photographs obtained from a scanning electron microscope. Figure 2 presents a schematic cross section through the membrane based on the photographs observed.

Because the molecules of the indicator are too small to see, the original photograph is not presented here. Unfortunately, PVC gives a nonhomogeneic covering layer. Some pores are not sealed by PVC. We assumed that the indicator is immobilized inside the pores and part of DPB may be on the PETP surface partially covered by PVC.

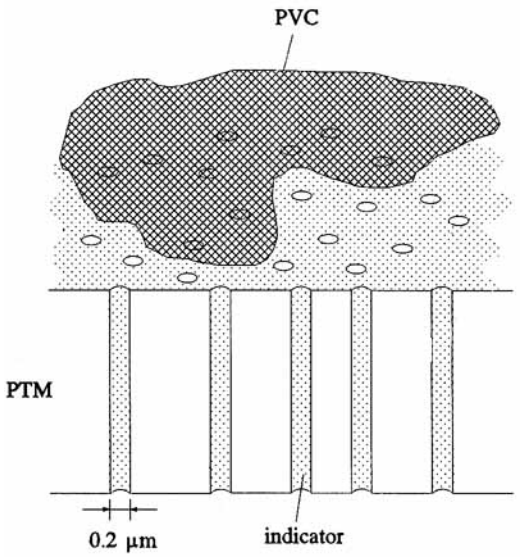


Figure 2 Schematic cross section of the membrane made of PETP and PVC.

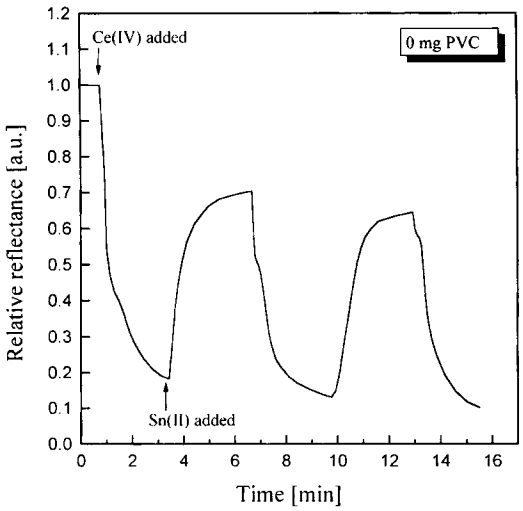


Figure 3 Time response of the optrode with PETP membrane (without PVC).

RESULTS

The measurements were carried out by alternate addition of solutions $Ce(SO_4)_2$ ($0.1M$) and $SnCl_2$ ($0.06M$). The membranes were kept in distilled water before tests. It is worth noting that the molecules of DPB were not washed out by water, which is shown as a constant value of the reflectance in each beginning of the curves observed. Even a long time of wetting (2 weeks) has no influence on the shape of the signal. It may prove that the reduced form of DPB (present in the membrane in a water environment) is immobilized by physicochemical sorption to the PETP. Since the usefulness of the membrane in redox titrations is determined by the shape of the signal observed, only time characteristics are presented. The reflectance signals are drawn in arbitrary units because the relative changes are important. The values were normalized against its maximum.

We have also checked a redox membrane prepared exclusively from PETP foil (without PVC) in order to observe the efficiency of immobilization by the pores and response of the membrane. Figure 3 shows response of the membrane in dependence on the redox potential variations.

The solution of Ce(IV) was added to a beaker with the optrode immersed into distilled water. After that, the reflectance signal decreases due to the membrane's color change from colorless to violet. Unfortunately, if the oxidized form of DPB is present, a washing-out effect occurs. Addition of reductant Sn(II) restores the redox potential and the reflectance increases. Two-step response occurs after addition of Ce(IV) (decreasing part of the curve). The first step is quite rapid and it can be related to the response of easier accessible part of the indicator which is on the surface of PETP membrane. The second one is much slower, and in our opinion, this is caused by diffusion of the ions inside the pores. The relation between rapid and slow response changes. It may be attributed to the washing out of the indicator from the surface of PETP. It is not clear for us what is the origin of asymmetrical response between the decreasing and the increasing part of the curve. A two-step response is useless for applications in redox titrations because the endpoint cannot be determined precisely. Different amounts of PVC were added to optimize the response. Figure 4 shows responses for membranes containing 10, 25, and 50 mg PVC in the solutions for membrane preparation.

The amount of 10 mg of PVC is too small to improve the response of the membrane. There is also two-step response. The relative reflectance is almost on the same level as for the membrane without PVC. When the amount of PVC was increased up to 25 mg, the relative change of the reflectance decreased. However, the optrode has quite stable levels in the oxidizing and the reducing environments and a smooth curve was observed. One possible explanation may be that the PVC layer does not allow one to react DPB immobilized inside the micropores. The change observed is caused by the surface part of DPB. The PVC layer is thick enough and there is no observable washing out. The response time of the optrode is a few minutes. Such a membrane is suitable for the endpoint determination as was presented in Ref. 9. The addition of 50 mg of PVC has no further influence on the shape of the signal. The

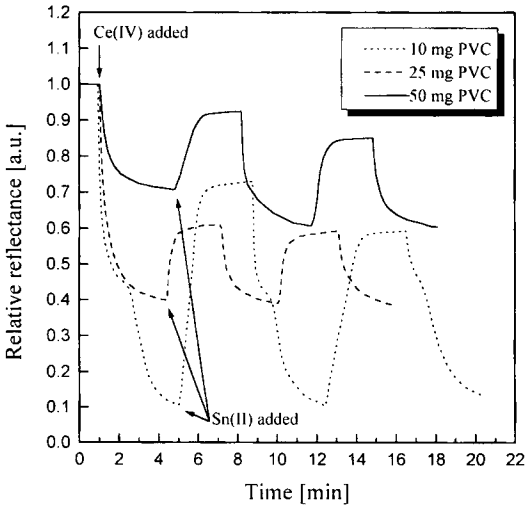
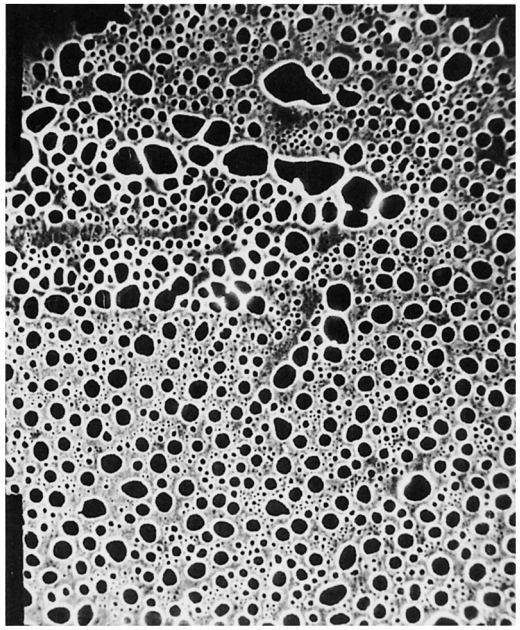
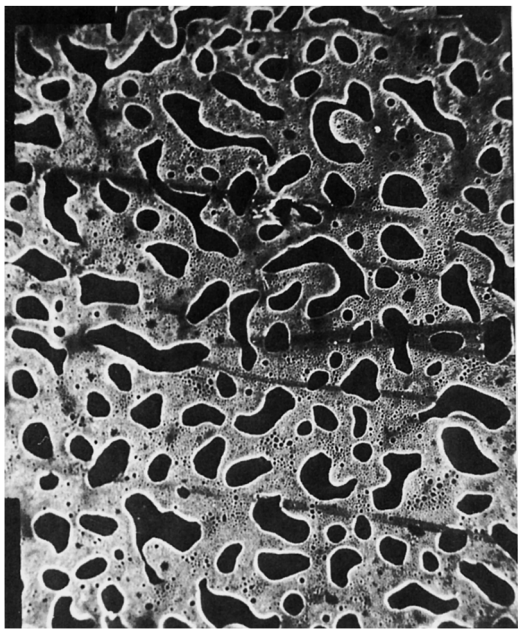


Figure 4 Response curves for different additions of PVC.



(a)



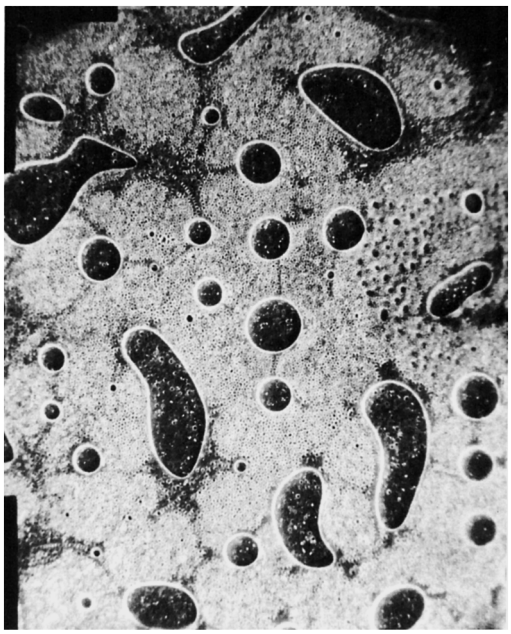
(b)

Figure 5 Photographs of the PETP membranes (magnification: ×250). Addition of PVC: (a) 10 mg; (b) 25 mg; (c) 50 mg.

relative change of the reflectance is similar to the membrane with 25 mg of PVC, but there are different levels of the signal for oxidized and reduced forms of DPB. It can be related to the thicker PVC layer, which leads to the larger reflectance. Moreover, for the membrane with 50 mg of PVC, a slight drift is observed. So, the optimal membrane is the one with 25 mg of PVC. Such a membrane has a good response and can be repeatedly used in the titrations.

The tested membranes were observed in a scanning electron microscope. Figure 5 presents microscopic top views of the membranes. Irregular black stains represent the surface of PETP and white ones depict the PVC layer. The light dots in Figure 5(c) are micropores of PETP.

One common conclusion can be reached from the photographs and the measurements. PVC does not cover well the surface of PETP. There are some uncovered places of PETP independent of the amount



(c)

Figure 5 *(Continued from the previous page)*

of PVC added. It seems that PVC and PETP are not satisfactorily matched. The smallest amount of PVC [10 mg, Fig. 5(a)] gives many small holes. The holes are linked together by thin chains of PVC. The shape of the response (see Fig. 4) is similar to that of the membrane without PVC (Fig. 3) because PETP is not sufficiently covered by PVC. A greater amount of PVC [25 mg, Fig. 5(b)] forms larger holes, but it seems that the PETP surface is more efficiently covered. Addition of 50 mg of PVC [Fig. 5(c)] covers PETP by a thicker layer. There are only a few big holes but the response is worse as compared with 25 mg of PVC. It suggests that we should continue our work with a focus on PTM as a support and a more matched polymer as a covering layer.

SUMMARY

The polymer track membranes made of PETP have been tested in redox titrations. It has been shown that an additional covering layer of PVC on the surface of PETP allows one to obtain a membrane with an appropriate response. The optimal amount of PVC added was 25 mg. The membrane obtained in that way is applicable in redox titrations. The response of the optrode is smooth and the endpoint of titrations can be determined precisely. It seems that further studies should be carried out to improve the surface properties of PTM and additional covering polymer. One of the possible solutions of that problem may be a change of solvent used for membrane preparation or a change of polymer [e.g., cellulose, poly(vinyl alcohol)]. Additional pretreatment of the PTM surface could be useful as well.

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