Preparation of pH Sensors by Covalent Linkage of Dye Molecules to the Surface of Polystyrene Optical Fibers

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SYNOPSIS

Functional Bromothymol Blue dyes containing amino groups in position 3 have been immobilized on the surface of chlorosulfonated polystyrene fibers and characterized by ESCA. Upon laser irradiation, a modified fiber has been used as an antenna fiber in a twisted pair of plastic optical fibers immersed in aqueous solutions having various pH. The light transmitted to the receiving fiber depends on pH values. This device can be used as a pH sensor.

INTRODUCTION

There is an increasing interest in the application of fiber-optic sensors for continuous *in vivo* monitoring of physiological parameters such as blood pH, oxygen, and carbon dioxide content. Our main interest is to develop a fiber-optic sensor for *in vivo* pH measurements.[1-3] The existing sensors use membranes with a dye entrapped by cross-linking of the hydrophilic polymers, which have been attached to the glass fibers.[4-9] One of the disadvantages of these methods is that the reagent is not covalently bound to the fiber and may be leached out. Some applications may require the fibers to have high flexibility and to resist breakage upon bending and twisting, a requirement that prevents the use of glass fibers.

Recently, it has been shown that a pair of twisted polystyrene fibers immersed in a solution of a pH-sensitive dye is suitable for sensor applications.[10] In this configuration, one fiber behaves as a radiator and the other one as an antenna. The intensity of light detected at the end of the antenna fiber depends upon the pH. The curvature associated with the twist gradually converts a guided mode into a radiated mode in the first fiber, whereas a radiated mode entering the antenna fiber becomes a guided mode back to the detector. As a result, the pair behaves like a cuvette with the absorption of the radiated modes occurring in the medium of a dye solution between radiator and antenna elements. Using Bromothymol Blue solution, an excellent sensitivity of output voltage detected by photomultiplier versus pH was found.

Our objective has been to develop pH sensors based on covalent attachment of dyes to flexible plastic optical fibers. The use of a plastic optical fiber allows a high degree of mechanical flexibility combined with very small size and low-cost disposable construction. Covalent bonding of a dye molecule to microspheres, films, or fibers requires the introduction of a reactive site on the matrix support as well as on the dye itself. Since functional Bromothymol Blue dyes are not commercially available, we have synthesized and characterized functional bromothymol sulfonephthalein dyes containing amino, isothiocyanato, and maleimido groups on the sulfonated ring.[2] The spectral properties of the functional dyes do not change upon modification.[1] Dyes can be covalently attached to fibers having on the surface such functional groups as amino, thiol, and sulfonyl chlorides for the construction of a fiber-optic pH sensor.

In this paper, we describe sulfonation of polystyrene fibers and attachment of dyes containing amino groups by formation of the covalent sulfonamide linkage. The sulfonation can be carried out using SO_3 gas in air, sulfuric acid, or chlorosulfonic acid. Sulfonation only requires the presence of CH bonds

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and has been successfully applied to polyolefins, poly(vinyl chloride), polystyrene and its copolymers, polyimides, polyamides, polycarbonates, polyurethanes, etc.[11,12] We decided to apply chlorosulfonation to obtain sulfonyl chloride groups that rapidly react with primary amines to form sulfonamides. This approach leads to transparent coating, essential for twisted pair fiber-optic probe measurements.

EXPERIMENTAL

Chemicals were purchased from Aldrich Chemical Company (Milwaukee, WI). Fluoresceinamine and amino Bromothymol Blue were used in the surface attachment experiments. Fluoresceinamine was used as received, and amino Bromothymol Blue was synthesized starting from saccharin.[2] Optical fibers were supplied by General Fiber Optics Inc. (Cedar Grove, NJ). A 500 μm optical fiber consisted of a polystyrene core and poly(methyl methacrylate) cladding. The cladding of the fiber was removed by dipping in 55% sulfuric acid solution for 24 h and washing with distilled water, then methanol, and subsequently drying under vacuum.

In a typical experiment, the clad-removed fibers were wrapped around a glass cage. The cage was placed in a 500 mL resin flask and exposed to chlorosulfonic acid vapors. Argon was used as carrier gas to transport the vapors. The temperature of the chlorosulfonic acid flask was kept at 50°C for different periods of time ranging from 15 min to 1 h. After chlorosulfonation, the fiber was immediately immersed in a 10 mmol solution of amino Bromothymol Blue dye containing an excess of alkali for 15 min while stirring at room temperature. Fibers were washed several times with distilled water. The surface of the fiber developed a yellow coloration, the intensity of which depended upon the time of exposure to the chlorosulfonic acid vapors.

The IR spectra were recorded on a Nicolet FTIR model 5 DXB spectrometer. ESCA measurements were made on an AEI Model ES 200 electron spectrometer. UV spectra were obtained with an IBM 9430 spectrophotometer. A Fisher Accumet Model 805 MP pH meter was used for pH measurements.

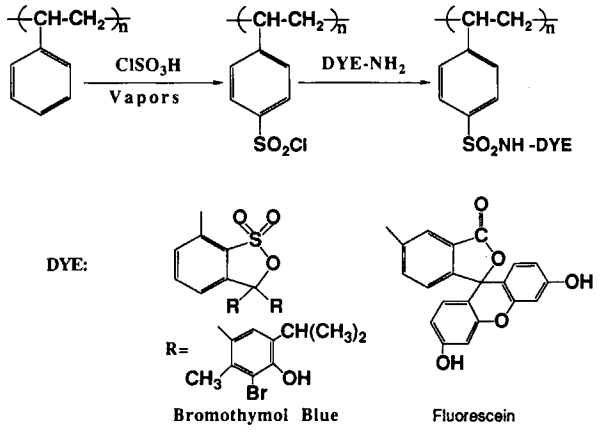
RESULTS AND DISCUSSION

Surface modification of optical fibers has to be carried out under heterogeneous conditions in order to avoid significant damage to the surface that could result in the fatal loss of the optical transmittivity. On the other hand, the modification and dye attachment should take place in a useful time scale. Prolonged chlorosulfonation led to fibers with poor optical properties with a partially destroyed surface. Since the fibers were 500 μm thick, they retained their dimensional integrity. However, some fibers demonstrated a loss of light transmittance due to surface modification. The additional loss of transmittance occurred in the second step, when dyes were attached to the fibers.

The optical loss (α) for an optical fiber in the transparency region is expressed as $\alpha = \mathbf{A}/\lambda^4 + \mathbf{C}(\lambda) + \mathbf{B}$. The first term represents Rayleigh scattering, which is caused by microscopic density fluctuations inherent in the formation of the fiber.[13] The $\mathbf{C}(\lambda)$ term accounts for loss peaks due to absorption caused by various impurities in the fiber core. The **B** term is due to waveguide imperfections such as bubbles in the core and microbending. This term increases in the twisted fiber system. The $\mathbf{C}(\lambda)$ term is probably the most important of the three types of optical losses, because the modified surface also acts as an impurity and absorbs strongly.

The structure of the chlorosulfonated fiber and the subsequent reaction with amino Bromothymol Blue and fluoresceinamine are shown in Scheme 1. Fluoresceinamine modification was intended to develop a fluorescence-based sensor, whereas Bromothymol Blue modification was attempted for an absorption-based sensor. The surface-modified fibers showed repeated color change with change of pH, from yellow to blue in the case of Bromothymol Blue, whereas a yellow to orange transition was observed for fluorescein.

The IR spectra showed characteristic features indicative of sulfonyl groups. Bands at 1364 and 1172 cm^{-1} correspond to the asymmetric and symmetric



Scheme 1.

stretching of SO_2 groups of sulfonyl chloride in aromatic systems. The two peaks at 590 and 640 cm^{-1} are considered to be due to the C—S and S—O stretching absorptions. Sulfonic acid and sulfone group formation accompanies sulfonyl chloride formation during chlorosulfonation. The broad absorption at 3460 cm^{-1} and the weak absorption at 1650 cm^{-1} are due to water adsorbed by the hygroscopic sulfonic acid groups.[14] The signal at 1420 cm^{-1} was associated with the asymmetric stretch of the sulfone moiety. The sulfone formation may be due to cross-linking, which occurs during chlorosulfonation. In both spectra of the dye-modified fibers, the peak due to sulfonyl dye-modified fibers and the peak due to sulfonyl chloride were found to be absent as a result of the reaction between sulfonyl chloride and primary amine, leading to the formation of sulfonamide. The sulfonamide band appeared at 1348 and 1180 cm^{-1} in the case of the Bromothymol Blue-modified fiber. The fluorescein-modified fiber demonstrated peaks at 1332 and 1180 cm^{-1}.

X-ray photoelectron spectroscopy (XPS or ESCA) is capable of identifying elements present on the surface of materials by means of the binding-energy distribution of core-level electrons displayed by the incident X-rays up to a depth of about 50 Å. Examination of the dye-bound polystyrene fibers by XPS yielded spectra containing signals due to oxygen 1*s* electrons at 535 eV binding energy, sulfur 2p electrons at 180 eV binding energy, and nitrogen 1S at 403.7 eV binding energy in the case of the Bromothymol Blue-modified fiber and 403.5 eV binding energy in the case of the fluorescein-modified fiber, in addition to the carbon 1*s* signal at 288 eV binding energy. The untreated polystyrene fiber shows no nitrogen and no sulfur presence. The XPS analysis of the fibers confirm the presence of sulfur, oxygen, and nitrogen. Together with the IR spectra, the XPS confirms the introduction of dye molecules into the polystyrene core surface.

We were not able to study sensors by the measurements of the fluorescence changes as a function of the pH, since the unmodified polystyrene core itself showed an intense emission in the 650 nm region. The background signal has been many times stronger than the fluorescence response due to fluoresceinamine-modified fibers. Therefore, we report only the pH studies of an absorption-based sensor. A 1.5-foot-long optical fiber bearing amino Bromothymol Blue was used in combination with an unclad optical fiber as a twisted optical fiber probe. This pair was placed in a vertical tube containing acidic or alkaline solution, and output voltages at a photomultiplier tube (PMT) were measured with respect to changes in pH using an optical arrangement as shown in Figure 1. A light beam of 632.8 nm from a He—Ne laser is passed through a chopper, and the reference signal produced is fed into the refer-

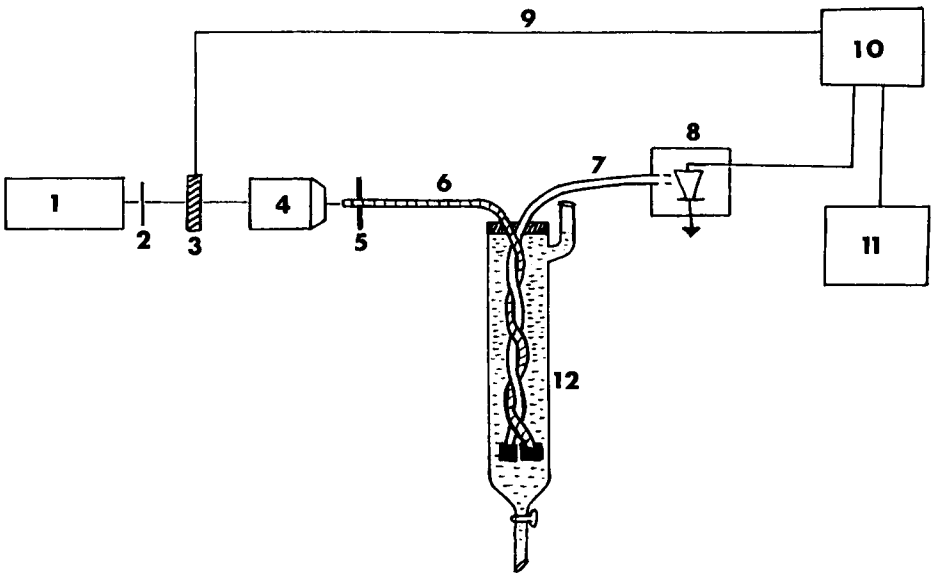


Figure 1 Schematic diagram of the experimental setup for pH measurements in a twisted pair of optical fibers: (1) He—Ne laser; (2) band pass filter; (3) chopper; (4) microscopic objective lens; (5) fiber holder; (6) modified antenna fiber; (7) receiver fiber; (8) photomultiplier tube; (9) reference signal; (10) lock-in amplifier; (11) digital voltmeter; (12) flask with solution of different pH.

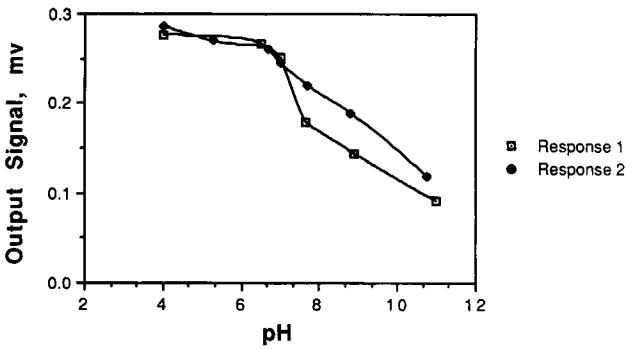


Figure 2 Dependence of the response of the voltmeter on pH. Response 1 measured after 5 min. Response 2 measured after 24 h.

ence channel of a lock-in amplifier. The laser beam is passed through a band pass filter and then is focused onto the plastic fiber using a 40× objective lens. The antenna fiber of the probe is connected to the PMT detector. The PMT detector output is fed to the lock-in amplifier, which is transmitted to a voltmeter for a digital readout (V_0). Examination of V_0 versus pH (Fig. 2) for this twisted fiber pair showed that over a pH range from 4 to 11 the output voltage decreased gradually, and in the physiological pH range (6.5–7.5), the change was significant. Higher voltage values were obtained with a band pass filter. The measurements performed after 24 h indicate small changes in the physiological pH range due to leaching by partial hydrolysis.

The presented studies indicate the possibility of the immobilization of pH-sensitive dyes onto the surface of the optical fibers and the feasibility of the detection of the change in pH by the twisted polystyrene fiber probe containing dye covalently attached to the surface.

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