Surface Plasmon Resonance of Azobenzene-Incorporated Polyelectrolyte Thin Films as an H$^+$ Indicator

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ABSTRACT: An azo-dye-incorporated polyionene was spin-coated as thin films on silver evaporated glass substrates. The films were used in conjunction with surface plasmon resonance (SPR) spectroscopy to examine the utility of combining these techniques for optical H$^+$-ion sensing. A method suggested by Kano and Kawata was used to enhance the sensitivity of the classical SPR measurements toward absorption detection. With the exposure of the composite polyionene films to HCl vapor, changes in the reflectivity signal were obtained in proportion to the concentration of H$^+$ ions and according to the analyzing wavelength. The transformation of the parent azobenzene into the azohydrazone polar form determined the displacement of the absorption band and was the basis for the absorption-enhanced SPR measurements. The difference in the SPR signals for the neutral sample and that exposed to interaction with HCl was most demonstrated for the wavelength at which the sample spectrum changed from being nonabsorbing to absorbing. The results show that chromophoric polyionenes are good materials for the production of sensitive substrates and can be combined with SPR spectroscopy for the optical sensing of aggressive gaseous species. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 86: 1459–1464, 2002

Key words: polyelectrolytes; sensors; thin films

INTRODUCTION

Film-forming polymers doped with active organic compounds for the optical sensing of various analytes such as nitrogen dioxide,[1,2] carbon oxide or dioxide,[3] oxygen,[4] chlorine,[5] H$^+$,[6–10] humidity,[11] and different organic vapor molecules[12,13] create interesting alternatives with respect to other thin-film techniques, such as Langmuir–Blodgett deposition.[14] In particular, such composite materials have proven to be powerful for the fabrication of thin films with different thicknesses, architectures, and properties that vary with the concentration of the analyte to be sensed. Optical methods that are based on reversible changes in absorption,[1] fluorescence,[7,9] or reflectance[15] of the sensing layer offer many advantages over other sensing techniques (e.g., electrochemical[16] and conductance[17] techniques) because the measured signal is insensitive to electrical contacts. Surface plasmon resonance (SPR) belongs to optical techniques for studies of thin films and interfaces and attracts attention because of its high sensitivity and simple construction.[18] It is based on very small refractive-index changes ($<10^{-4}$) and thicknesses that can be monitored in real time by reflectance measurements of the incident light. In addition, the SPR sensors have the potential for miniaturization and easy fixation with optical fibers.[19] There are numerous reports on SPR ultrahigh-sensitivity chemical sensor applications, especially in the field of biosensors.[20,21] Recently, the SPR method has been proposed for the detection of optical absorption changes in switching[22,23] or sensing techniques.[24,25] This methodology, in turn, uses changes in the imaginary part of the complex refractive index of the sensing layer, which reflects the extinction coefficient of the sample.

In optical chemical sensors, the sensing layer is usually composed of organic dyes covalently bound or doped to a polymer matrix. The choice of solid supports and the immobilization of the indicator in the supports have important effects on the performance of the sensor. Physical immobilization may lead to the migration and agglomeration of organic molecules, which limit sensor stability in long-term use. However, chemical attachment has the advantage of not suffering from the indicator leaking out but requires usually complex synthesis that may change the desired optical properties. Interesting alternatives to both methods are matrices based on polycations with anionic dyes as counterions.[26,27] In this article, we report the development of an absorption SPR sensor for H$^+$ ion with an azobenzene derivative incorpo-

rated into an ionene polymer as the counterion. The ionenes are ionic polymers with charged groups in the main chain. When modified by anionic dyes, they give us an opportunity to fabricate thin films with different functions appropriate for electronic,[28] nonlinear optical,[29,30] fluorescent,[31] and electroluminescent devices. Cast films, even with a high loading of dyes, show useful parameters suitable for optical studies because of their transparency, mechanical stability, and chemical inertness. An azo dye, 4-(4-diethylaminophenylazo)benzenesulfonic acid (EO), was chosen as the indicator. Azo dyes display many attractive features because azobenzene systems posses two types of reversible processes, photochemical cis–trans isomerization and electrochemical oxidation reduction.[32] Tautomeric azohydrazone transformations connected with color changes are used as indicators in acidimetry.[33] Although azo compounds are widely presented in systems that undergo large changes in structure,[34–36] conductivity,[37] or transmission[38,39] with photoisomerization, there are few examples of azo sensors tested by various sensing methodologies.[1,13,40,41]

This article presents results for SPR as a sensor for absorption measurements with azo-incorporated polyionene (I-EO) as an analyte. This system offers a simple route for the production of optically active films for effective H^+-ion sensing. SPR of polyionene/ azo systems has not been reported as a sensing technique for H^+.

EXPERIMENTAL

Materials and sample preparation

The synthesis and optical properties of the materials used in this study are described in detail elsewhere.[26] Structural formulae of the polyionene (I) and azobenzene derivative are given in Figure 1. An azo-dye-substituted polyelectrolyte (I-EO) was obtained by a metathetical counterion exchange in dimethylformamide (DMF) starting from statistical polyionene prepared as a bromide and sodium salt of ethyl orange. A cationic polymer containing 69 wt % dye was precipitated from water at 30°C and dried in vacuo. The I-EO salt was dissolved in DMF and provided an optically clear and film-forming product. H^+-sensitive samples for both SPR and ultraviolet–visible absorption spectroscopy were made by the spin coating of 1 wt % solutions of the polymer in DMF onto bare or silver-coated microscope glass slides. The films were typically about 20 nm thick. Absorption spectra of I-EO films were taken on a Specord M-40 spectrophotometer (Carl Zeiss Jena, Germany). All the measurements were performed under ambient conditions at room temperature (20°C).
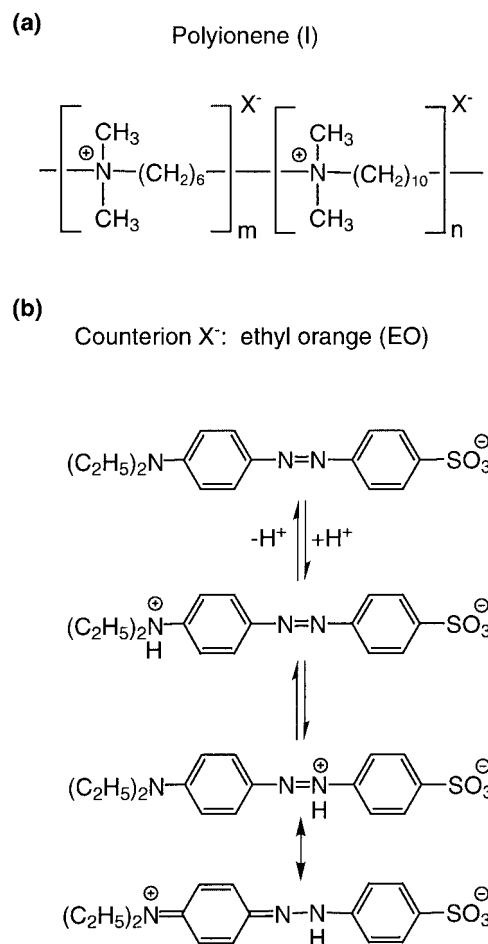

Figure 1 (a) Structures of polyionene and (b) a scheme of tautomeric azohydrazone transformation responsible for color changes in ethyl orange.

Principle of surface plasmon spectroscopy

A surface plasmon is a surface charge density wave that may propagate along the interface between the metal and dielectric as surface plasma waves (SPWs). Oscillations of free electrons at a smooth metal surface can be optically excited via coupling to the evanescent field of an internally reflected light beam by the attenuated total reflection (ATR) method in a Kretschmann configuration (Fig. 2). The coupling is observed as a sharp drop in the reflected light intensity with a minimum at the resonance angle θ_{SP}. The light that passes by a dispersive medium, such as a high-refractive-index prism, increases a component of a wavevector parallel to the prism base, $\mathbf{k}_x$, by the factor n_0:

$$\mathbf{k}_x = n_0 \cdot \mathbf{k} \cdot \sin\theta \qquad (1)$$

where n_0 is the refractive index of the prism, $\mathbf{k} = \omega/c$ is the wavevector of light in a vacuum, and θ is the angle of incidence on the prism base. The energy transfer from the light to SPWs occurs under resonance conditions when the light wavevector $\mathbf{k}_x$ be-
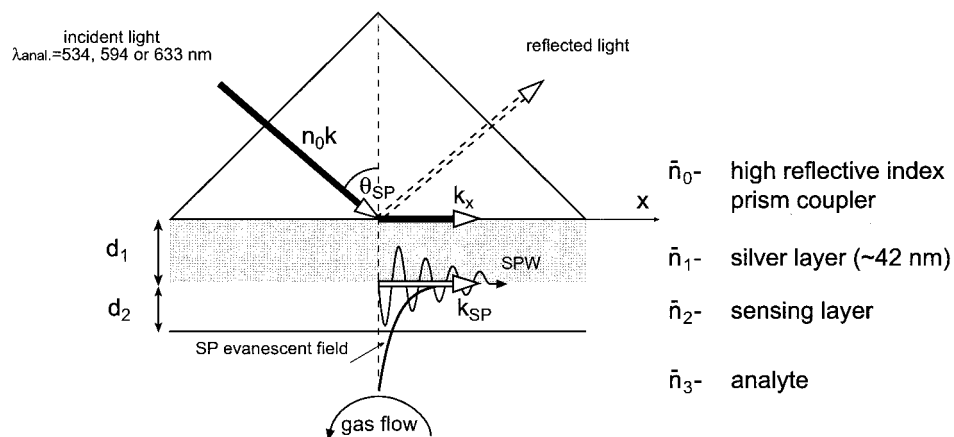
Figure 2 Schematic configuration used to generate the SPR signals for a sensing effect of a flowing vapor over a polyionene film containing azobenzene counterions.

comes equal to the surface plasmon wavevector $\mathbf{k}_{SP}$. SPWs are created on the opposite side of the silver film and cause a loss in the intensity of reflected light. The electromagnetic field associated with SPR perpendicular to the interface shows characteristic exponential decay in both layers, thereby sampling the interface region. Outside the metal, an evanescent electric field penetrates dielectrics and can optically interact. Changes in the optical properties of this region will influence the SPR signal. From the shift and shape of the resonance curve, one can calculate the thickness of the overlayer and its index of refraction. The intensity of the dip in the reflectance curves for an absorbing coating depends also on the film thickness of a metal. Although, theoretically calculated, the optimal thickness for refractive-index measurements, characterizing the deepest resonance curve, is for 51.5-nm-thick silver films, the best enhancement of absorption sensitivity in SPR is expected for thinner 48.2-nm (positive enhancement) or thicker 52.5-nm films (negative enhancement). The calculated enhanced factor is expected to be 28.9.[24] This points to the usefulness of SPR as a technique for the design of optochemical sensors.

Vapor sensing with SPR

The ATR unit for exciting the surface plasmon, consisting of a BK7 prism and a glass slide with a thermally evaporated silver film (42 nm thick), was mounted on a motorized θ–2θ rotating stage. The table rotates the dispersive unit by θ while rotating the detector at 2θ. The reflectivity for a fixed wavelength was recorded as a function of the incident angle with a silicon photodiode. The analyzing beam was p-polarized laser green (543 nm), orange (594 nm), or red (633 nm) light. First, SPR curves were obtained from the bare silver layer for the three incident wavelengths. Geometrical and optical thickness parameters

of the silver film were calculated from the fitting of the SPR profile to Fresnel reflecting formulae according to the transfer matrix method.[42] On the silver layer, a film of I-EO was spin-coated at 2000 rpm for 10 s and at 5000 rpm for 50 s and dried. For such prepared samples, the SPR curves were measured in the same way as for the silver. In particular, the film thickness (d) and real (n) and imaginary (α) parts of the complex refractive index of the I-EO film were obtained. Then, the I-EO sample was subjected to hydrogen chloride (HCl) vapor in an ambient atmosphere, and the reflectance signal was again measured as a function of the incident angle. The polyelectrolyte contained traces of water molecules either from synthesis or from the surroundings; therefore, HCl was hydrated after diffusion into the matrix. After the H^+ concentration measurement, the sample was flushed with air so that the I-EO film could recover to its baseline, as checked by the SPR response signal.

RESULTS AND DISCUSSION

The sensing properties of I-EO films are due to the H^+-concentration-dependent tautomerism of the azo dye (Fig. 1). The transformation occurs within a pH range of 3.1–4.4.[33] Figure 3 shows the visible absorption spectra of the I-EO thin film before and after interaction with HCl vapor. Before interaction with H^+, the absorption spectrum shows a maximum at 427 nm and a shoulder at 475 nm. These bands of high intensity have π–π^* character. A low-intensity n–π^* transition, typical of the —N=N— bond, is not visible in the spectrum and probably is hidden under the broad π–π^* band. Subjecting the sample to HCl vapor causes a change in the color from orange to maroon, with the maximum shifted to 491 nm and a shoulder at 562 nm. This change is due to the protonation of the azo group. The energy of nonbonding electrons is, therefore, reduced, allowing a strong bathochromic
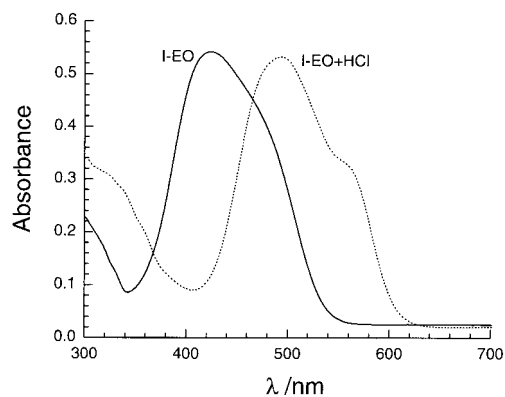
Figure 3 Ultraviolet–visible absorption spectra of an I-EO thin film (—) before and (- - -) after interaction with HCl vapor.

shift of π–π^* transitions. In other words, protonation increases the electron-withdrawing effect of the acceptor group (the benzene ring and —N=N— group). The tautomeric structure containing a proton on the amino nitrogen does not seem to contribute to color changes because a proton reduces the electron-donating properties of the amino group, leaving the acceptor group unchanged. The separation of H^+ from the film by the application of an air atmosphere reverses the shift to the absorption spectrum of the neutral sample. This finding indicates that a weak associative chemisorption process between the electron-rich aminoazobenzene molecule and the electrophilic hydrogen ion is responsible for the tautomerism.

Figure 4 shows SPR reflectivity curves of I-EO obtained with the ATR technique at different wavelengths of the analyzing beam. The dips on each graph show the SPR spectra for a silver layer and for a silver-coated, polyionene-containing azobenzene thin film before and after exposure to HCl. A shallow resonance for the uncoated silver is due to the coupling of an evanescence field of the surface plasmon with the light. As expected, the minimum in the reflected intensity shifts toward lower angles with the increasing wavelength of incident light. From the mode shape and position, it is possible to calculate the complex refractive index and film thickness. The optical parameters of the sensing film for the three examined wavelengths are given in Table I. For the neutral I-EO sample [Fig. 4(B)], the deepest resonance is for 543-nm light, the result of a considerable extinction coefficient (α) of EO at this wavelength. With the exposure of I-EO to HCl, the shape of all reflectivity curves is changed. The curve at 543 nm becomes shallower and broader in appearance with a slight decrease in the angle of the resonance minimum. In turn, the dip for the 594-nm beam, originally at an angular position of 42.5°, moves to higher angles, considerably increasing the depth. This enhancement effect in resonance is similar to that previously observed for a
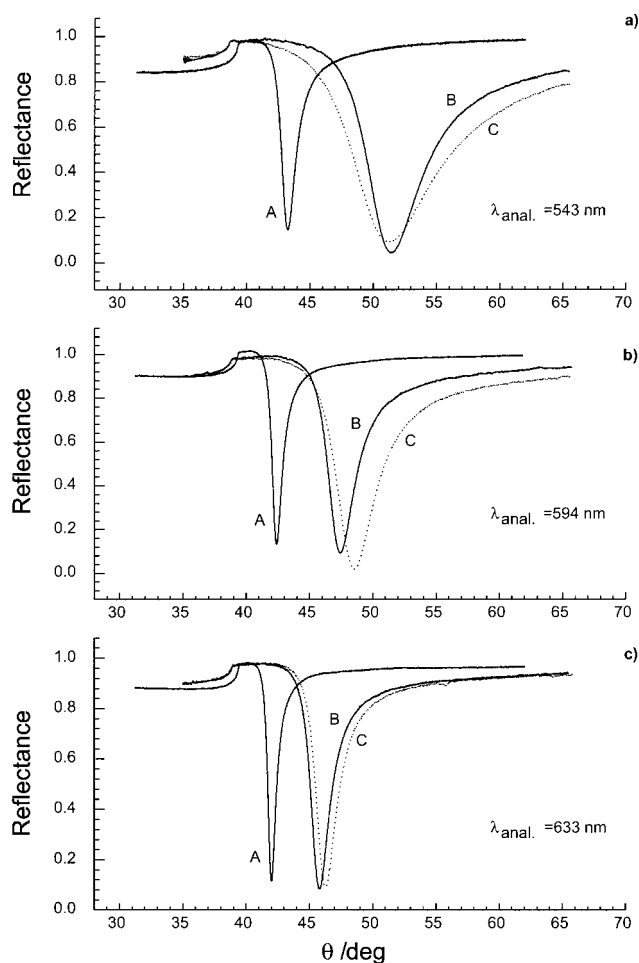
Figure 4 SPR reflectivity profiles as a function of the incident angle for (A) a silver layer, (B) a silver-coated I-EO thin film before interaction with HCl vapor, and (C) a silver-coated I-EO thin film after interaction with HCl vapor. SPR was generated by p-polarized light at (a) 543, (b) 594, and (c) 633 nm.

neutral sample excited by a 543-nm beam. It is associated with a new intense absorption of the protonated form of EO at 594 nm and a decrease in the refractive index of the sensing layer. For the 633-nm light, the shape of the SPR profile has changed slightly in com-

TABLE I
Complex Refractive-Index Data $\bar{n} = n + i\alpha$ and Film Thickness Values d Obtained by SPR Spectroscopy for Neutral and Acidified I-EO Samples

Analyzing wavelength [nm]	n	α	d [nm]
543	1.680	0.045	20.5
	1.665[a]	0.150[a]	
594	1.620	0.007	20.5
	1.690[a]	0.065[a]	
633	1.610	0.004	20.3
	1.620[a]	0.005[a]	

[a] Acidified sample.
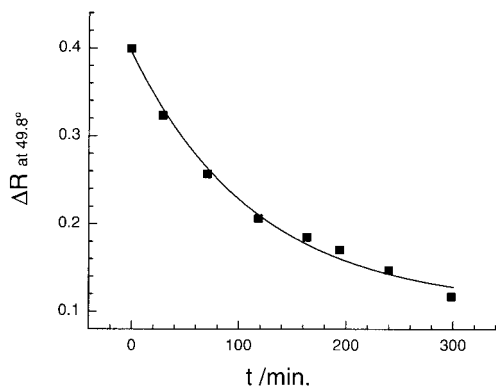
Figure 5 Temporal changes in the reflectance of I-EO measured at 49.8° after exposure of the sample to HCl vapor.

parison with those at 543 and 594 nm, showing once again similar changes in n and the residual absorption of the sample from the red side band of the EO dye. The observed opposite changes in refractive index n at 543 and 594 nm for exposure to the acidic vapor can be deduced from Kramers–Kronig relations and are concomitant with any absorption as a function of wavelength. They are negative at the blue side and positive at the red side of the absorption maximum.

The response time and recovery time of the I-EO sensor to the HCl vapor are dependent on the gas concentration. For a fully saturated I-EO sample, the recovery kinetic constant is $k = 105$ min^{-1}. Complete recovery to the initial state requires 300 min. The reversible nature of the SPR signal on interaction with HCl suggests that a chemisorption interaction with EO is occurring. The changes in optical thickness parameters can be followed in real time by the recording of reflectivity at a fixed angle of incidence (e.g., $\theta = 49.8°$). Figure 5 shows a plot of the reflectance versus time for an I-EO film initially exposed to HCl vapor. The analysis wavelength was 594 nm. The solid line is fit for a simple first-order rate low. Kinetic analysis can give information about equilibrium changes and reversibility. The reaction cycles can be conducted many times.

CONCLUSIONS

For the development of optical sensors, the production of a very thin film should provide a fast response for a particular analyte. Polyionenes with incorporated azo chromophores were used to investigate potential optical sensing through reflectivity changes of the surface plasmon signal. Experiments were conducted with three different analyzing wavelengths to establish changes in the SPR signal in response to HCl vapor flowing over an active polymer surface.

In conclusion, the research presented in this report shows that an acidic environment can be readily detected by SPR with glassy polyionene thin films,

which offers a novel form of chemical sensing technology. Moreover, high optical quality, chemical resistivity, and a broad range of dye concentrations with homogeneously distributed counterions in polyionenes prove that this polymer is a perfect material for use in sensor devices. Azobenzene-substituted polyionenes form homogeneously thin films that are 20 nm thick, giving large refractive-index changes and thereby providing an excellent alternative to Langmuir–Blodgett-deposition thin-film techniques. Recent studies on optical gas sensing using a polysiloxane matrix with an incorporated azobenzene chromophore[1] show that the polyionene can be used as an indicator of NO_2 as well.

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