Optical constants of azopolymer PAZO thin films in the spectral range 320 – 800 nm

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Abstract. Azo benzene containing polymers (azopolymers) have been investigated for a number of applications – holographic data storage, polarization optical elements, diffractive gratings, etc. Herein we report on the optical characteristics of films obtained from the commercially available water soluble azopolymer PAZO (poly[1-[4-(3-carboxy-4-hydroxyphenylazo) benzenesulfonamido]-1,2-ethanediyl, sodium salt). Thin films were deposited by spin coating and their thickness was determined by a Talystep precision profilometer. The FTIR spectra of PAZO were measured between 3000 cm⁻¹ and 500 cm⁻¹. For the first time, to the best of our knowledge, we evaluated the PAZO complex refractive index continuously in a broad spectral range (320 – 800 nm) based on transmission and reflection spectrophotometric data. The wavelength dependence of the complex refractive index of organic dyes layers cannot be readily described with dispersion models used for crystals, metals or semiconductors. This is why we used a derivative approach on a wavelength-by-wavelength basis to solve a set of two nonlinear equations with two unknowns – the real and imaginary parts of the refractive index. The determination of the optical constants of PAZO films is effective and robust.

1. Introduction
Azobenzene containing polymers (azopolymers) have been investigated for a number of applications – holographic data storage, polarization optical elements, diffractive gratings etc. [1-6]. All these applications are based on an important property of the azocompounds – the reversible trans-cis photoisomerization observed in them.

In many cases it is essential to know the complex refractive index (RI) of the azopolymer. For example, in the case of thickness measurement using thin-film interference, the measurement precision can be increased significantly if the thin film RI is provided for the entire spectral range used.

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However, data about the RI of azocompounds are given rarely and even in such a case, usually for fixed wavelengths [7,8].

Herein we report on the optical characteristics of films obtained from a commercially available azopolymer PAZO (poly[1-[4-(3-carboxy-4-hydroxyphenylazo) benzencesulfonamido]-1,2-ethanediy1, sodium salt). The spectrum of the complex refractive index of PAZO in the range 320 – 800 nm was calculated from transmission and reflection spectrophotometric data at normal incidence.

Our approach was based on the use of incoherent partial waves. The inverse problem was solved on a wavelength-by-wavelength basis. Further, the numeric procedure was based on the so-called “trust-region-dogleg” algorithm that is specially designed to solve nonlinear equations. The calculated transmission and reflection spectra with the evaluated optical constants of PAZO film match the experimental results to a negligible uncertainty.

2. Experimental procedures, model and computational approach

The chemical structure of PAZO is shown in figure 1. This azopolymer is commercially available from Sigma Aldrich. The main advantage of PAZO is its water solubility.

Thin layers were prepared by spin coating for 30 s at 1500 rpm of a PAZO water solution with concentration 100 mg/ml on 1.96-mm-thick quartz substrates. The film thickness was measured by a high-resolution TaLystep profilometer. The experimental data reported below were acquired from a 440-nm-thick PAZO sample.

The transmittance and reflectance spectra of azo-films were measured by a UV-Vis-NIR Cary 5E spectrophotometer (Varian) at normal incidence. The spectral range of evaluation covered 320 nm to 800 nm. The results are presented in figure 2.

![Figure 1. Chemical structure of the azopolymer PAZO.](image)

![Figure 2. The transmittance (a) and reflectance (b) spectra of the 440-nm-thick PAZO film.](image)

The powdered PAZO polymer was studied by a Varian 600 Series FTIR Spectrometer with a spectral resolution of 0.07 cm⁻¹ (figure 3) using a method described earlier [9]. The strong absorbance at 1750 cm⁻¹ in the IR spectrum could be explained with the presence of a carbonyl group (C=O). The peak at 1523 cm⁻¹ could be related to stretching vibrations of azo compounds bearing the functional group R¹=N=N–R², namely to phenyl rings linked by an N=N double bond. The peak at 1195 cm⁻¹ shows the presence of an S=O double bond. The absorbance at 867 cm⁻¹ and 761 cm⁻¹ could be related to deformation vibrations of aromatic rings with two neighboring hydrogen atoms [10-13]. This deformation suggests the presence of certain inhomogeneities in the deposited thin film that could lead to light scattering or functional dependence of the layer’s refractive index on the film depth. For this
reason, we will treat the complex refractive index evaluated as an effective index of equivalent homogeneous isotropic non-corrugated film with a predetermined physical thickness.

Our goal was to determine the wavelength dependence of the PAZO layer’s real refractive index $N$ and extinction coefficient $K$ from experimental data by mathematical minimization techniques. Usually, the estimation of the unknown parameters $N$ and $K$ is regarded as a heavily over-determined inverse problem, i.e. 6 to 20 unknowns (describing $N$ and $K$) in a set of 300 to 500 wavelength-dependent equations. Besides, the spectral dependence of the complex refractive index of layers containing organic dyes, as the azo-polymer PAZO, cannot be readily described with dispersion models used for crystals, metals, semiconductors: Drude, Lorentz, Farouhy and Bloon, Lorentz and Tauc models, to name a few. This is why we used a derivative approach to solve a set of two nonlinear equations, related to the measured transmission ($T$) and reflectance ($R$), on a wavelength-by-wavelength basis. The procedure was based on the so-called ‘trust-region-dogleg’ algorithm [14]. The evaluation was focused on computing a trial step to a global minimum. This step was constructed from a step along the steepest descent direction and a step in the Gauss-Newton direction [14]. The leading idea of this method is to define a region in the parametric $N$-$K$ space (trust-region), where the optical response can be approximated by a simpler function.

3. Results and discussion
We tried two different procedures for the construction of the minimization goal function. In the first one, the Abelès characteristic matrix approach, the complex-amplitude reflection and transmission coefficients were calculated from $2 \times 2$ matrix elements. The physical picture behind this is the coherent superposition of multiple reflected partial waves within the film. This is the “classical” way for thin-films optical response estimation. If, for some reasons, the coherence of the partial waves is destroyed, the optical response is estimated by multiple reflections of partial wave’s intensities, not complex field amplitudes. This was the second method, namely the incoherent approach [15]. The overall layer reflectance and transmittance were calculated by the elements of the product of three $2 \times 2$ matrices, whose elements themselves are functions of the complex refractive index, physical thickness, angle of incidence and wavelength. All this is easily generalized for a multilayer stack. Details can be found in ref. 15. The results obtained showed that the incoherent approach is by far more appropriate for our problem. As a measure for the goodness of the estimation, we calculated the root-mean-square uncertainty (RMSU), normalized by the number of degrees of freedom. Thus, RMSU gives the error per one point of the observations. It is a statistical measure of the discrepancy between the measured spectra of $T$ and $R$, and the estimated transmission and reflectance. RMSU is compared to the experimental uncertainty.

First, we estimated the optical constants of the uncoated substrate. Then we considered the stack PAZO layer on the substrate and constructed its optical response. Then, with the “trust-region-dogleg” algorithm, we calculated the optical constants of the 440-nm-thick PAZO film as functions of the wavelength. The estimation of the optical constants $N$ and $K$ by means of the proposed model and the described minimization technique resulted in RMSU $\sim 0\%$. This is much lower than the experimental error, which was $\sim 10^{-4}$ in $T$ and $\sim 5 \times 10^{-4}$ in $R$. The results are presented in figure 4.

Figure 3. FTIR characterization of PAZO polymer.
Figure 4. Wavelength dependence of the calculated optical constants. (a) polymer refractive index $N$ and (b) extinction coefficient $K$.

4. Conclusions
The complex refractive index of a PAZO layer was evaluated from transmission and reflection spectrophotometric data at normal incidence between 320 nm and 800 nm. For determination of the spectral dependence of the refractive index of azopolymer thin films, we proposed a minimization procedure based on solving a set of two nonlinear equations on a wavelength-by-wavelength basis. The equations were related to experimental data under the assumption of multiple incoherent wave propagations within the thin layer. A solution of the inverse optical problem was obtained by the so-called “trust-region-dogleg” algorithm. The evaluation of the optical constants of PAZO films is effective and robust. Although there is a significant number of publications on optical properties of azopolymers, to the best of our knowledge, this is the first time that spectra of complex refractive index are reported. We regard the proposed approach as sound and reliable that could be applied to other azopolymer layers as well, even in the case of a photo-induced anisotropic optical response. This approach could promote the research on organic-dye sensitized polymers and the design of new types of optical devices.

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