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# Surface-relief formation in azo-polyelectrolyte layers with a protective polymer coating

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**Abstract:** Azobenzene-modified photosensitive polymers offer the possibility to reshape flat films upon UV-Vis irradiation. The photochemical isomerization between trans-cis configurations is the key mechanism for surface relief grating (SRG) formation on the free surface of thin azo-polymeric films illuminated by structured illumination. In the present work, we consider a sandwich configuration wherein an azopolymeric film (PAZO) is coated by a plasma-deposited polyacrylic acid (PPAA). It is demonstrated that the PPAA coating protects the PAZO against dissolution in aqueous environment. More interestingly, light-induced SRG can still be formed in the PAZO film, and the resulting modulation is transferred to the PPAA coating above. Results obtained open the possibility of exploiting water-soluble azopolymers in bio-oriented applications.

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## 1. Introduction

Azobenzene polymer systems have been studied for over 80 years [1]. During time the aims are deeply changed, from light absorbers to light controlled photo responsive systems. Azopolymers, doped or covalently attached, represent a class of light-responsive systems in which the rapid and reversible photoisomerization reaction (trans  $\rightarrow$  cis  $\rightarrow$  trans) of azobenzene molecules can actuate mass transport phenomena at molecular, mesoscopic, and even macroscopic length scales [2–4]. In particular, azopolymer films exposed to a suitable interference light pattern can form stable Surface Relief Grating (SRG) at the polymer-air interface [5–8]. Nowadays scientists efforts has been concentrated on exploiting their potential technological applications such as optical switching, responsive materials and growth support for cell adhesion applications [9–15]. It is widely acknowledged that the polymer structure (e.g. chemical structure, degree of functionalization, link to backbone) can have significant effect on SRGs formation, both on inscription rate and saturation level [16,17].

In the present work, we consider a photosensitive polymer consisting of azo-polyelectrolyte poly[1-[4-(3-carboxy-4-hydroxyphenyl-azo)benzenesulfonamido]-1,2-ethanediyl, sodium salt] (PAZO). PAZO is a highly light-responsive material showing efficient SRG formation upon visible irradiation during short illumination time [19,18]. Unfortunately PAZO is water soluble, therefore its applications to bio-oriented applications (e.g. for cell-culture conditioning) has been rather limited. In order to overcome such a limitation, we consider here PAZO thin films coated with a protective polyacrylic acid layer that is plasma-deposited. In this way, we aim at preventing PAZO dissolution in aqueous environments whilst maintaining its effective mass-migration capabilities.

## 2. Experimental

The PPAA-coated PAZO film has been prepared and characterized as described below.

### 2.1 Chemicals and Film preparation

The azopolymer considered here is an azo-polyelectrolyte (poly{1-[4-(3-carboxy-4-hydroxyphenylazo)benzenesulfonamido]-1,2-ethanediyl,sodiumsalt}) briefly named as PAZO, supplied by Sigma-Aldrich. PAZO films are prepared by spin casting on thin glass surface (thickness of 130-160  $\mu\text{m}$  from Bio-Optica, Germany) soaked for 15 min into piranha solution (75%  $\text{H}_2\text{SO}_4$ : 25%  $\text{H}_2\text{O}_2$ ) to remove organic contaminants. 500 $\mu\text{l}$  of PAZO solution

in methanol (concentration 25 mg/mL) is spin-casted (500 rpm) on the glass surface in order to have a polymer thickness of 1.5  $\mu\text{m}$ . The sample is dried overnight at dark, under controlled condition of humidity and temperature.

Plasma-Polymerized Acrylic Acid (PPAA) is deposited on PAZO films by a plasma-assisted polymerization process from pure acrylic acid, 99% (AAc) monomer (Sigma-Aldrich). The PPAA films are obtained in a 13.56 MHz Radio Frequency-Plasma Enhanced Chemical Vapour Deposition (RF-PECVD) reactor by means of a pulsed plasma discharge. Thicknesses can be precisely controlled upon a previous calibration [20,21]. When needed, PAZO films are physically masked before PPAA deposition, in order to obtain a selective coating on specific regions only. This arrangement is useful in Atomic Force Microscopy analysis.

## 2.2 Optical setup

PAZO films on glass are irradiated and optically characterized according to the setup shown in Fig. 1. A collimated, circularly polarized Nd:YAG laser ( $\lambda = 532 \text{ nm}$ ; 250 mW) is incident on an amplitude-type photomask wherein a linear grating pattern is formed. The linear grating has a period  $\Lambda_0 = 10 \mu\text{m}$ . The 0th-order transmitted light is blocked. The two first diffraction orders are collected by a 25.5 mm focal length lens in such a way that an image is produced onto the sample surface. The photomask-lens distance is  $d_0 = 57 \text{ mm}$ , the lens-sample distance is  $d_i = 46 \text{ mm}$  and a resulting magnification of about 0.8 is obtained. The projection reduction, together with the 0th-order blocking, allows to obtain a linear grating with effective period  $\Lambda_i = 4 \mu\text{m}$  over a spot area of roughly  $1 \text{ mm}^2$  on the image plane, corresponding to an overall inscription power of about 8 mW.

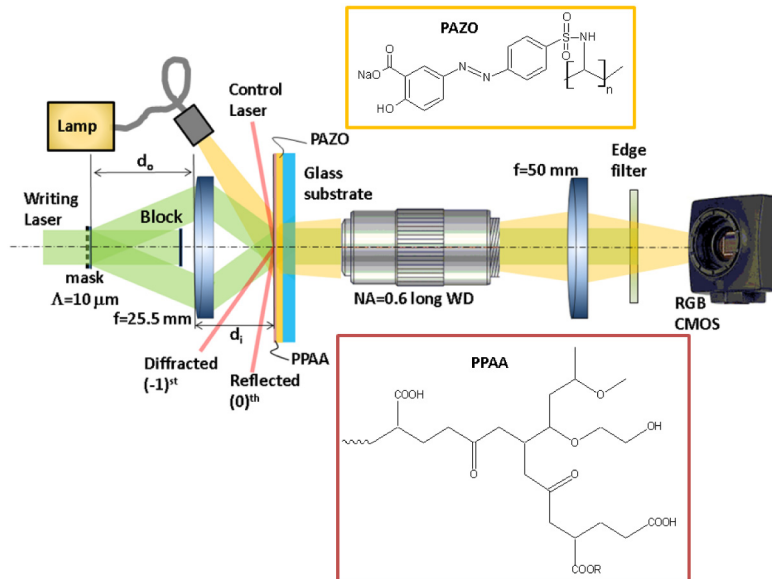


Fig. 1. Optical setup for azopolymer irradiation and monitoring.

A wide-view imaging system is implemented in such a way that SRG formation on the PAZO film can be directly detected as an optical image. A fibered halogen lamp is used as a tilted source for illuminating the sample. Partially transmitted and scattered light from the sample is collected by a long-working distance objective (Mitutoyo, Japan), with 0.42 Numerical Aperture and imaged onto a RGB CMOS camera (Thorlabs) through a telescope lens. In order to filter out the laser light used for PAZO inscription, an edge filter (Semrock) is employed. In addition to the imaging system, a diffractometric means is also employed for time monitoring of the SRG formation. A He-Ne laser beam ( $\lambda = 633 \text{ nm}$ ) is incident on the

sample surface at a grazing angle. The  $-1$ -st-order diffracted light is collected and detected by means of a photodiode.

### 3. Results and discussion

As previously discussed, the goal of PPAA-coating PAZO films is to prevent dissolution in aqueous environments. Nominally identical samples of PAZO thin film spun on glass are prepared and then coated with PPAA with different thicknesses (30 – 50 – 80 – 100 nm). A water droplet (250  $\mu$ l) is delivered on the sample surface and kept in controlled atmosphere to prevent evaporation. After 24 hours the water droplet is dried and the sample surface is visually inspected. In Fig. 2(a) a representative set of samples is shown. We observe that the bare PAZO film has been almost completely dissolved by water, whilst PAZO removal is partially or completely prevented when PPAA is used as a protective coating. As the PPAA thickness increases to 100 nm, the PAZO dissolution seems to be completely avoided.

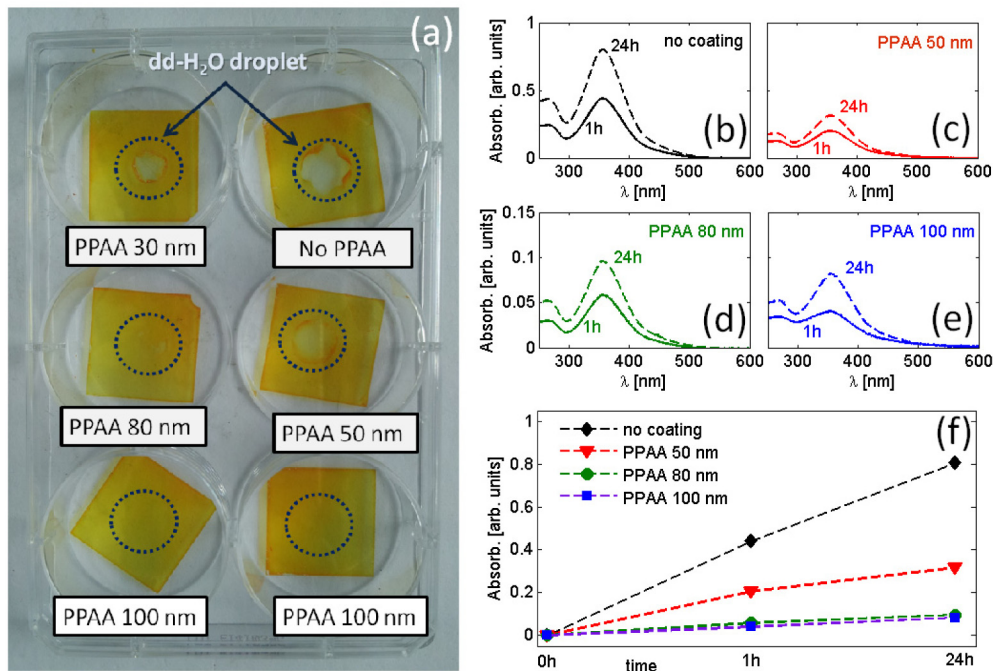


Fig. 2. (a) picture of a set of bare and PPAA-coated PAZO films after a 24h incubation of a water droplet on the surface; (b-e) absorbance spectra of PAZO released in water after 1h and 24h since sample immersion; (f) PAZO absorbance peak ( $\lambda = 360$  nm) after 1h and 24h immersion showing the progressive release of PAZO in water.

In order to assess the PAZO dissolution in water more precisely, fresh PAZO films are prepared (bare and PPAA-coated) and then immersed in identical wells containing dd-H<sub>2</sub>O (4 ml). The time-monitoring of the PAZO release in water is performed by detecting the PAZO main absorption peak in the solution. A small amount (250  $\mu$ l) of solution is collected from each well after 1h and 24h since sample immersion and then put into a quartz cuvette with a 1 mm optical path for UV-Vis measurements (Varian Cary 500 UV-Vis-NIR spectrophotometer). Spectra are collected in transmission, and the corresponding absorbance is derived. Figure 2(b)-2(e) shows representative absorption spectra related to bare PAZO and coated PAZO with 50 nm, 80 nm and 100 nm PPAA thickness respectively. All spectra are normalized, in such a way that they can be directly comparable. It is found that the most relevant release of PAZO in water occurs in samples with no PPAA-coating. Instead, in coated samples, the PAZO dissolution is progressively reduced as the PPAA thickness increases. For a PPAA-coating 100 nm thick, a 90% reduction in PAZO concentration in

water is observed thus demonstrating the effectiveness of the coating in preventing dissolution. After 24h the PAZO film reaches a stable condition, with almost no additional release in the solution (Fig. 2(f)).

The ability of the PAZO to form SRG from a flat film configuration is investigated in the case wherein a PPAA coating 100 nm thick is deposited on a limited portion of the sample surface. After a few minutes irradiation, a SRG is clearly observed on both the coated and the uncoated regions, as shown in the wide-field optical image in Fig. 3(a). More specifically, a linear corrugation corresponding to the amplitude photomask is formed across the edge of the PPAA-coating.

During laser irradiation, the SRG formation is monitored in real-time upon detection of the first-order diffraction intensity of the control beam. In both coated and uncoated regions, the maximum diffracted power is reached after roughly 4 minutes of irradiation. We assume such a final condition as indicative of the complete formation of the SRG, corresponding to a diffraction efficiency between 8% and 10%. However, due to the PPAA layer ( $n = 1.56$ ), the diffraction efficiencies of SRG in either the coated or the uncoated PAZO SRG are slightly different. For this reason, we normalized the measured diffracted power to the maximum diffracted power obtained when SRG reach a complete inscription. The time evolution of SRG shows systematic and reproducible differences between the bare and the coated case, as illustrated in Fig. 3(b). The SRG formation follows a roughly exponential dynamics, with the SRG on bare PAZO being characterized by a smaller time constant as compared to the SRG on the coated region. We explain such a difference by invoking a stronger overall surface interaction of the PAZO film when sandwiched between glass and PPAA. In previously published works, the role of the surface interaction of the azopolymer film with the underlying substrate in affecting the maximum height of inscribed SRG has been reported [22,23]. More specifically, in very thin layers, the interaction with the substrate can be dominant over the light-driven mass-migration effects in the azopolymer, thus resulting in very shallow SRGs [24]. Here, the interaction of the PAZO film with the PPAA provides an additional surface constraint, resulting in an increased overall stiffness of the polymeric assembly, thus slowing down the SRG formation process.

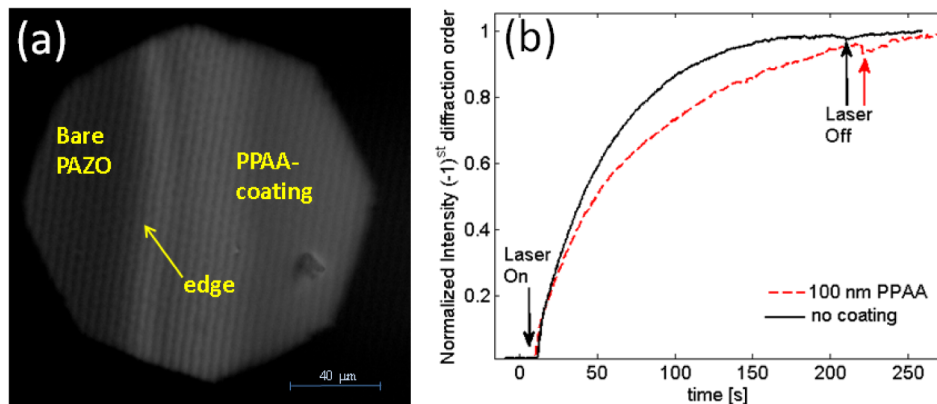


Fig. 3. (a) wide-field white light optical image of a SRG formed upon irradiation (duration about 4 minutes) of a partially coated PAZO film. A linear grating is observed across the edge of the PPAA coating; (b) time-resolved diffracted intensity ( $-1^{\text{st}}$  order) detected during SRG formation on a bare and a PPAA-coated (100 nm) PAZO film.

Although diffractive effects have been detected on the coated azopolymer, an Atomic Force Microscope (AFM) analysis is performed to get insights on the effective topography of the sample after irradiation. AFM is operated in contact-mode on the partially coated PAZO film. In Fig. 4(a), a three-dimensional representation of the surface topography in the neighbourhood of the PPAA edge region is shown. As expected, a surface modulation is formed on the bare PAZO portion. More interestingly, such a light-induced modulation is also

transferred from the PAZO film to the PPAA coating above. The cross-sectional topographic profile in Fig. 4(b) reveals that the SRG modulation amplitude is slightly reduced on the PPAA coating (65 nm) as compared to the PAZO film (80 nm). This can be reasonably expected because of the role of the PPAA in constraining the mass-migration of the underlying azopolymer. Since mass is conserved, the difference in the relief modulation amplitudes on bare and coated PAZO should result in a non-uniform height of the PPAA coating across the grating. As a demonstration, we show in Fig. 4(c) that the PPAA edge height (nominally, 100 nm as set by the deposition parameters) is larger when evaluated along the grooves (110 nm) as compared to the ridges (90 nm).

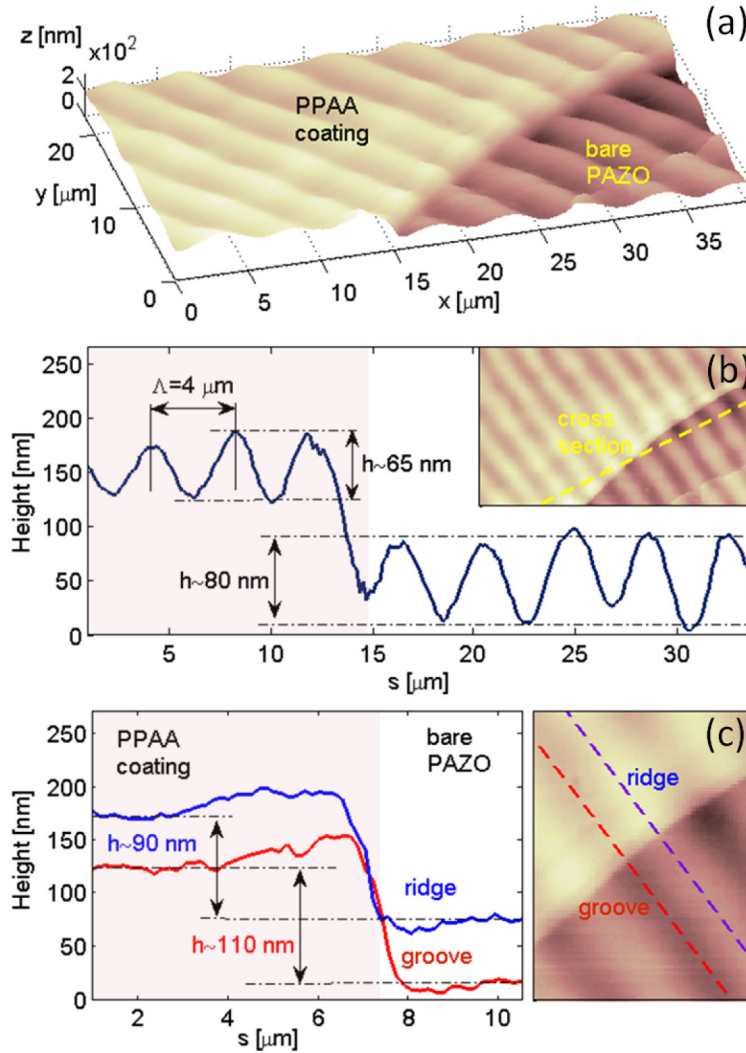


Fig. 4. (a) three-dimensional representation of the SRG obtained on a PAZO film partially coated with PPAA 100 nm thick (edge region); (b) cross-sectional topographic profile of SRG across the PPAA edge along the yellow dashed line in the inset; (c) cross-sectional topographic profile of the PPAA edge as considered along either a ridge or a trench of the SRG (blue and red dashed lines in the 2D map on the right, respectively).

#### **4. Conclusion**

To conclude, in this work we investigated the SRG-formation capabilities of an azo-polyelectrolyte polymer (PAZO) coated by a plasma-deposited polyacrylic acid (PPAA) with different thicknesses. It is experimentally demonstrated that the PPAA prevents the PAZO dissolution in water yet enabling SRG to be formed on the surface, upon proper irradiation with structured light. Surface modulations up to 80 nm are obtained with few minutes irradiation at  $\lambda = 532$  nm. The proposed approach makes PAZO an interesting light-responsive material in biological applications [17,25] wherein dynamic modifications of planar substrates are required to be performed in aqueous environments.

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