

# Laser microstructuring of azopolymers via surface relief gratings: controlling hydrophobicity

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In this paper the large-scale mass transport mechanism is used to microstructure azopolymeric films, aiming at controllable hydrophobic surfaces. Using an Ar<sup>+</sup> laser with intensity of 70 mW/cm<sup>2</sup>, we produced egg-crate-like surfaces with periods from 1.0 to 3.5 μm that present distinct wetting properties. The static contact angle of water was measured on the microstructured surfaces, and the results revealed an increase of approximately 9° for a surface pattern period of 2 μm. Our results indicate the use of the microstructuring method described here for the fabrication of devices with controllable hydrophobicity.

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## 1. Introduction

Polymeric materials have been proposed as interesting candidates for the development of a broad range of applications from photonics to biology, because they meet the ever increasing mechanical, thermal, electrical and optical properties required for novel devices [1-8]. As an additional advantage, polymers are cheaper and easier to manufacture than other materials. Several techniques have been used for machining and structuring polymers, such as conventional photolithography, electron beam writing and, more recently, laser micromachining [9-11]. Because of its ability to precisely structure material's surface and volume, laser micromachining has been used to fabricate a wide variety of devices such as, for instance, waveguides, optical couplers, resonators and superhydrophobic silicon surfaces [13-14]. Overall, in a laser micromachining process, intense laser light is focused into the sample, which is translated with respect to the laser beam. The light intensity at the focal volume is high enough to induce permanent changes or ablation in the material.

In this paper, we propose the use of the large-scale mass transport mechanism [15-17], which follows the photoisomerization in azopolymers, to microstructure the surface of a polymeric sample, aiming at the fabrication of surfaces with controllable hydrophobicity [18]. This process is entirely light driven and occurs when the sample is exposed to a moderate intensity laser pattern, without the need of focusing the laser light or translating the sample [15, 19]. Using an interference pattern from an Ar<sup>+</sup> laser operating at 488 nm, we were able to produce surfaces with distinct morphologies (regularly spaced) that exhibit different wetting properties. We observed an increase of up to 9° in the static contact angle of water on the surface, depending on the structure inscribed on the surface of the azopolymer.

## 2. Experimental

The azopolymer poly(1-methoxy-4-(O-disperse Red1)-2,5-bis(2-methoxyethyl)benzene) (PODR1), whose chemical structure is shown in Fig. 1, was dissolved in chloroform in a concentration of 1 wt.%. The solution was sonicated for 20 minutes and subsequently filtered through a 0.45 μm porosity filter. Films were prepared by casting this solution on glass substrates, yielding samples with thicknesses of approximately 1 μm. The UV-Vis absorbance of the samples was measured with a Varian Cary 17 spectrophotometer.

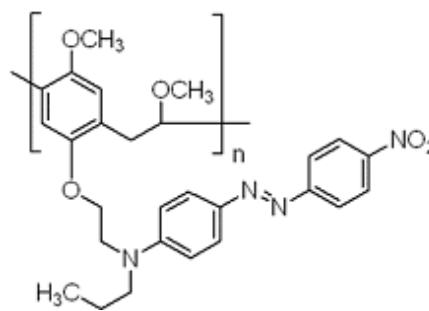


Fig. 1. Chemical structure of poly(1-methoxy-4-(O-disperse Red1)-2,5-bis(2-methoxyethyl)benzene) (PODR1).

The films were microstructured using the light-driven mass transport mechanism, which leads to the inscription of a surface-relief grating (SRG). A detailed description of the mechanism as well as the theory proposed to explain the SRG formation can be found in Refs. [15, 16]. From an experimental point of view, SRG are inscribed on the surface of an azopolymer film by the interference pattern produced by a p-polarized Ar<sup>+</sup> laser at 488 nm (70 mW/cm<sup>2</sup> and 50 minutes of exposition), as shown schematically in Fig. 2. In this setup (Lloyd Mirror), the

period ( $\Lambda$ ) of the interference pattern and consequently of the inscribed SRG can be tuned by varying the angle  $\theta$  between the laser beams, according to  $\Lambda = \lambda / [2 \sin(\theta)]$ , where  $\lambda$  is the wavelength of the laser. The SRG is inscribed in an area of approximately  $1 \text{ cm}^2$ . Two sets of gratings were recorded orthogonally to each other, resulting in an egg-crate-like structure [16, 20, 21]. In our experiment, the angle  $\theta$  was adjusted to produce SRGs with periods ( $\Lambda$ ) from 1.0 to  $3.5 \mu\text{m}$ .

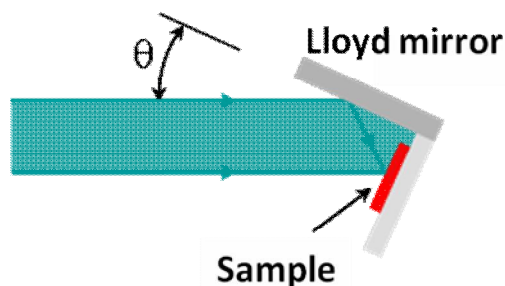


Fig. 2. Experimental setup used for SRG inscription.

After microstructuring, the samples were treated with (heptadecafluoro-1,1,2,2-tetrahydrodecyl)trichlorosilane for 24 hours in a low-pressure chamber in order to increase its natural hydrophobicity [22, 23]. The same treatment was performed for the flat samples which were not microstructured. The microstructures were analyzed by transmission optical microscopy (Olympus BX41) and atomic force microscopy using a Nanoscopy IIa system from Digital Instruments. To determine the surface's wettability, a home made goniometer with a CCD camera horizontal microscope was used for measuring the static contact angle of a water droplet. We used  $3 \mu\text{L}$  droplets (droplet radius of  $0.9 \text{ mm}$ ) and the contact angle was averaged over 20 measurements (5 droplets and 4 samples for a given  $\Lambda$ ). The measurements were carried out at room temperature ( $22^\circ \text{C}$ ). The relative humidity during the measurements varied between 40 and 50 %.

### 3. Results and discussion

Fig. 3 (solid line) shows the UV-Vis absorption spectrum of a cast film of PODR1. For comparison, the UV-Vis spectrum of PODR1 in a chloroform solution is also shown (dashed line). The absorption maximum at  $470 \text{ nm}$  for PODR1 in chloroform (dashed line), which corresponds to the  $\pi \rightarrow \pi^*$  electronic transition of the azochromophore, was red shifted to  $485 \text{ nm}$  in film. The red shift in the absorption maximum could be due to the anti-parallel-type of aggregation (J-aggregation) of the azochromophores in the film [24, 25]. Such aggregation, however, is not strong enough to hinder molecular movement preventing the SRG recording.

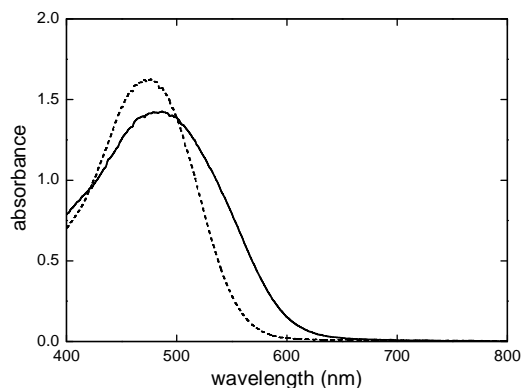


Fig. 3. UV-Vis absorption spectra of a chloroform solution of PODR1 (dashed line) and a cast film on glass substrate (solid line).

The inscription of SRG was monitored by measuring the intensity of the first-order diffraction of a probe beam (He-Ne laser). Such signal saturates after approximately 50 minutes, indicating that the SRG recording is ready. Fig. 4 shows optical microscopy images of egg-crate-like structures fabricated by recording two gratings orthogonally to each other at the same sample's spot, with periodicity  $\Lambda = 2.0$  and  $\Lambda = 3.5 \mu\text{m}$ . SRG produced under low laser intensities, as the case of the results presented here, are a light-driven mechanism [15] which is explained by the field-gradient model. In this model, mass transport is due to a force arising from the optical field gradient, which is only nonvanishing when the polarization direction of the optical field has a component in the direction of the field gradient (p-polarized light) [15, 19].

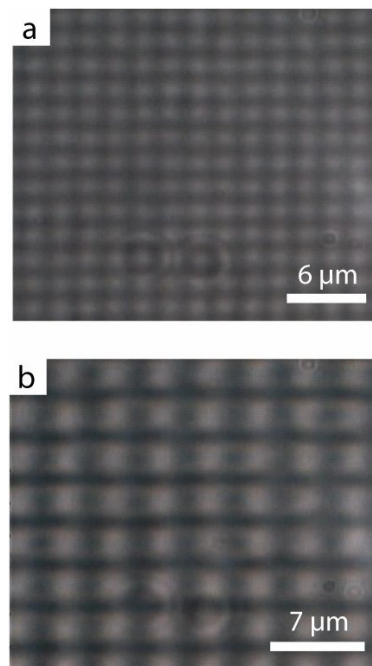


Fig. 4. Optical microscopy images of microstructures inscribed on PODR1 cast films with  $\Lambda = 2.0 \mu\text{m}$  (a) and  $\Lambda = 3.5 \mu\text{m}$  (b).

The modulation depth of surface relief gratings depends on the exposure time, chemical structure of the azopolymer and light intensity [17, 20, 21, 26]. The amplitude of the surface patterning we inscribed was obtained through atomic force microscopy. In figure 5a we show an atomic force micrograph of the microstructured surface ( $\Lambda = 2.0 \mu\text{m}$ ). The depth (peak-valley height) of the surface microstructure determined through the atomic force micrograph is approximately 200 nm, which is comparable to other values reported in the literature for distinct azopolymers. Fig. 5 (b) shows a three-dimensional atomic force micrograph picture of the surface. The peaks in this egg-crate-like structure present a full-width-at-half-maximum of approximately  $1.4 \mu\text{m}$ . It should be pointed out that the induced surface patterning is completely stable, remained unchanged for periods longer than one year after inscription.

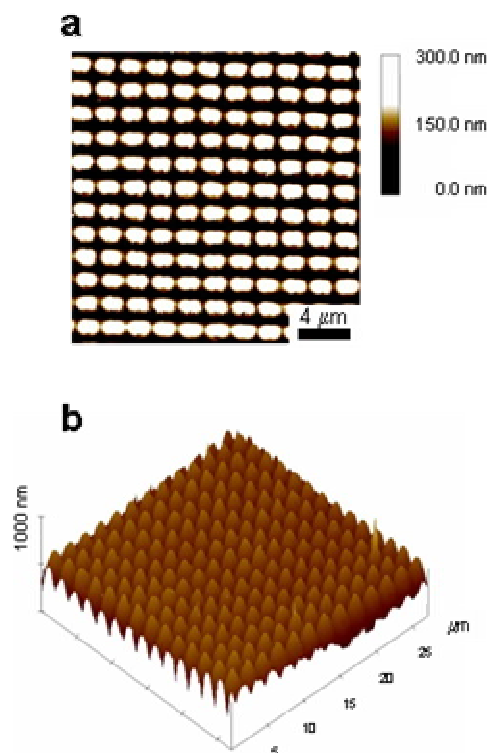


Fig. 5. Atomic force micrograph of the PODR1 film surface microstructured with  $\Lambda = 2.0 \mu\text{m}$  (a) and the three-dimensional rendering of the sample surface (b).

As mentioned in the experimental section, after microstructuring the samples were treated with fluorosilane to lower the surface energy [27], which allows us to study the changes in the surface hydrophobicity due only to the surface pattern inscribed through SRG.

Fig. 6 shows the change in the static contact angle as a function of the periodicity of the microstructures,  $\Lambda$ . These values were calculated relative to the contact angle of the flat surface (not microstructured). The contact angle we measured on the flat surface is  $108^\circ$ , indicating that water does not wet this surface (contact angle greater than  $90^\circ$ ). As seen in Fig. 6, the contact angle of the microstructured

surface increases by  $9^\circ$  at  $\Lambda = 2 \mu\text{m}$ , and then decreases as the periodicity,  $\Lambda$ , of the inscribed pattern increases. For the surface with  $\Lambda = 2 \mu\text{m}$ , we observed a small contact angle hysteresis – difference between the advancing and receding contact angle – a feature required in the engineering of hydrophobic surfaces.

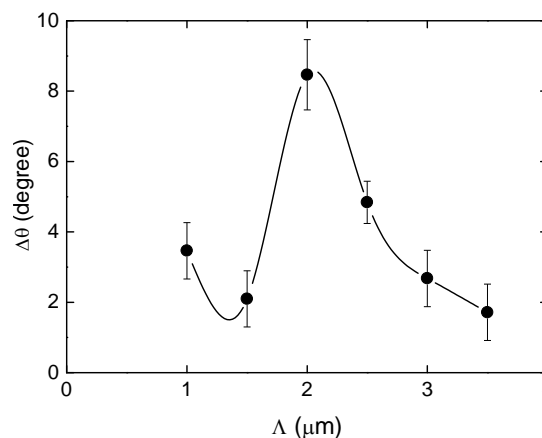


Fig. 6. Static contact angle change of water on microstructured azopolymeric surfaces as a function of the inscribed pattern periodicity  $\Lambda$ . The line was drawn only to guide the eye.

To comprehend the result observed in Fig. 6, it is necessary to understand the effect of the surface roughness on the hydrophobicity. Fundamental aspects on surface wettability have been carefully studied, and can be found in details in Refs. [28-30]. In general, according to the Cassie-Baxter model [31, 32], the liquid does not wet completely the roughened surface, because air pockets are trapped in the gaps of the rough surface. In this situation, the liquid interacts with a surface composed by the polymer and air, in a so called three-phase contact (solid-liquid-gas). According to this model, the smaller the contact area between the solid and the liquid the larger is the contact angle. Such situation seems to be optimized, for the azopolymer studied in this work, for a surface periodicity of about  $2 \mu\text{m}$ . For this periodicity, the aspect ratio of the structured surface is such that the entrapped air pockets lead to a small contact area between water and polymer and, consequently, to a larger increase in the contact angle. The depth of the grooves we inscribed by SRG peaks at  $\Lambda \sim 2 \mu\text{m}$  (grating amplitude 220 nm). Such behavior has also been observed by other research groups, and is explained by the interference pattern used for inscription [33, 34]. For smaller  $\Lambda$ , the interference pattern is blurred due to vibrations during inscription, while for larger  $\Lambda$  the field gradient is decreased (for a fixed light intensity). In both cases, a decrease on the grating amplitude is expected. Therefore, when the period of the pattern lays off  $2 \mu\text{m}$ , the contact angle decreases because the pockets created through the surface microstructuring are too wide to trap air. Consequently, the contact area between polymer and water increases, giving rise to a smaller increase in the contact angle. Similar results have been reported for a silicon surface roughened by femtosecond laser micromachining [22].

Although the surface structuring method described here seems to be interesting to control the surface wetting properties, it did not allow the fabrication of superhydrophobic surfaces, where the contact angle is higher than 150°. In order to obtain a higher increase in the contact angle with the method described here, it will be necessary to produce deeper surface microstructures, capable of trapping higher volumes of air. The height of the surface patterning produced, however, is intrinsic from the SRG approach employed. Even though the SRG amplitude can be modified by increasing the light intensity or choosing a different azopolymer, it is always in the range of a few hundreds of nanometers. Nevertheless, the use of the light-driven mass transport mechanism (SRG) does not require the use of intense lasers or translation stages, allowing the fabrication of large microstructures areas (~1 cm<sup>2</sup>) in a single step.

#### 4. Conclusions

We showed that the large-scale mass transport mechanism can be used to microstructure the surface of azopolymers, aiming at the fabrication of surfaces with different hydrophobic characteristics. The surface microstructure with a periodicity of 2 μm was shown to be the one that gives the larger increase in contact angle with water, a result that seems to be in agreement with the Cassie-Baxter model for the hydrophobicity of rough surfaces. The approach proposed here provides some advantages over other structuring methods that employ intense laser light. First, we used a moderated intense laser pattern, without the need of focusing neither translating the sample. Besides, the method described here allows the fabrication of larger microstructured area at once. Therefore, the large-scale mass transport mechanism seems to be an interesting option for the fabrication of devices with controllable wetting properties.

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