

# Fabrication of surface-relief gratings on an azobenzene-containing epoxy-based polymer film using atomic force microscopy

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## Abstract

Many studies have been reported on the photo-fabrication of surface-relief gratings (SRGs) in azo-polymer films using the interference of two laser beams of appropriate polarization. However, there are few reports in the literature concerning the electro-fabrication of SRGs on such types of polymer films. The goal of the work reported was the electro-patterning of an azobenzene-containing epoxy thermoplastic film. An epoxy-based polymer functionalized with an azo-chromophore was synthesized and characterized using thermal analysis. The reversible optical storage properties and photo-induced dichroism were studied. SRGs were fabricated on a film of the synthesized azobenzene-containing polymer using contact mode current-sensing atomic force microscopy which locally applied an electric field that aligned the azobenzene moieties. The anisotropic mass transport of the azo-polymer film was observed after applying an electric field. Additionally, the effect of the relief formation in the polymeric film surface was investigated by means of atomic force microscopy and electrostatic force microscopy.

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**Keywords:** azo-polymer; epoxy; birefringence; dichroism; atomic force microscopy; surface relief gratings

## INTRODUCTION

Light-induced motions in azobenzene-containing polymer films<sup>1,2</sup> have attracted much attention because of possible application in micro- and nanoscale fabrication, waveguides<sup>3</sup> and optical data storage.<sup>4–7</sup>

As illustrated in Fig. 1, illumination of an azobenzene-containing polymer film with linearly polarized light generates changes of local orientation of the azobenzene molecules. The underlying mechanism is based on selective excitation of those azobenzene groups whose dipole moment vectors have a component parallel to the light polarization plane. At the molecular level, these groups can undergo repeated *trans*–*cis*–*trans* photo-isomerization cycles. As a result, the direction perpendicular to the light polarization, excluded from optical activation, will become enriched in azo-chromophores. The concentration of the azo-chromophores aligned perpendicular to the light polarization steadily increases under illumination with polarized light, until a saturation level is attained. When the azobenzene groups are bonded to a polymer matrix, especially when it has some degree of intrinsic order (liquid crystalline or Langmuir–Blodgett), a cooperative motion at the domain level, generally nanoscale level, can be achieved. The movement of the photo-active groups results in a change of local optical properties such as absorption, refractive index, polarization properties, etc. This reorientation also forms the primary step in the remarkable light-induced mass-transport process exhibited by azobenzene-functionalized polymer films, which can be considered a macroscopic motion.

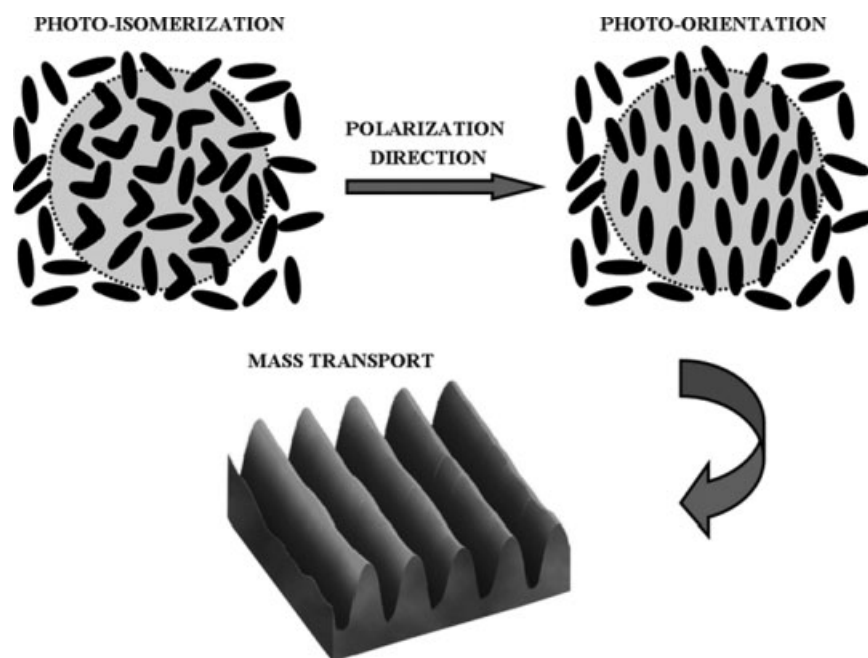
Optical patterning involves very large material transport on a micrometre and submicrometre length scale. This mass trans-

port provides a unique opportunity for nanostructure formation. Many studies have been reported on the photo-fabrication of surface-relief gratings (SRGs) in azo-polymer films using the interference of two laser beams of appropriate polarization,<sup>8–23</sup> and several models and mechanisms have been presented to explain the laser inscription of high-efficiency SRGs.<sup>24–29</sup> In almost all cases such SRGs are photo-inscribed at room temperature in azo-polymers substantially below the glass transition temperature ( $T_g$ ). Therefore, this process can only be possible due to a local plasticization experienced by the azo-polymer molecules that undergo *trans*–*cis*–*trans* isomerizations, which is followed by molecular reorientation and mass transport.<sup>30</sup> However, at present, no mechanism appears to provide an entirely complete and satisfactory explanation to account for the microscopic origin of the driving force in azobenzene optical patterning. In general, proposed mechanisms take into account thermal gradients, diffusion considerations, isomerization-induced pressure gradients

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**Figure 1.** Schematic of the various levels of light-induced motions in an azobenzene-containing polymer.

and interactions between azo dipoles and the electric field of the incident light. Recently, a photo-mechanical effect occurring in films of azo-polymers has also been proposed as a new candidate mechanism to explain SRG formation.<sup>31,32</sup>

External electric field-induced alignment of azobenzene molecules is of interest in molecular manipulation and nonlinear optical (NLO) applications.<sup>26,33,34</sup> The requirement for NLO behaviour in any material is an asymmetric response of the electronic system. Azobenzenes with push–pull substituents have a strongly asymmetric electron distribution, which makes them ideal NLO molecules. For a bulk NLO response, one requires an overall non-centrosymmetric material. This requirement is achieved in many inorganic crystals. In organic systems, the broken symmetry is typically obtained by applying an electric field at a temperature sufficient to allow for the molecular dipoles to align with the field. Azo-polymers have been shown to be excellent NLO materials.<sup>33</sup>

In previous studies, we analysed the phenomenon of perpendicular orientation of azobenzene groups to the polarized light of a laser beam in thermoplastic epoxy matrices with the azobenzene groups covalently attached, and we compared the results with those obtained for thermoplastics with azobenzene molecules physically dispersed as a guest in the polymer host.<sup>35</sup> In addition, we also investigated the optical anisotropy behaviour of epoxy thermosetting matrices as a function of several variables and we observed that some of the systems studied provided good results in terms of optical storage and stability.<sup>36</sup> In the work reported in the present paper, a step towards advancing the study of epoxy-based azo-polymer properties was taken by analysing the SRG-forming behaviour of a thermoplastic epoxy polymer containing azobenzene units using AFM electric field-induced nanolithography. As found in the literature, some researchers, such as He *et al.*,<sup>12,13</sup> have reported the photo-induced formation of SRGs on epoxy-based azo-polymer films by investigating the correlation between the polymer structure and the SRG photo-fabrication properties. In particular, they investigated the effect of backbones, substituents and degrees of functional-

ization on SRG inscription rate for epoxy systems modified with azo-chromophores. Nevertheless, to the best of our knowledge, this is the first contribution concerning the electro-fabrication of SRGs on an azobenzene-containing epoxy-based polymer film by means of contact mode current-sensing AFM, which locally applies an electric field. Electro-patterning can be achieved since the dipole moment of the azo-chromophore can be aligned using an external electric field.<sup>37</sup>

## EXPERIMENTAL

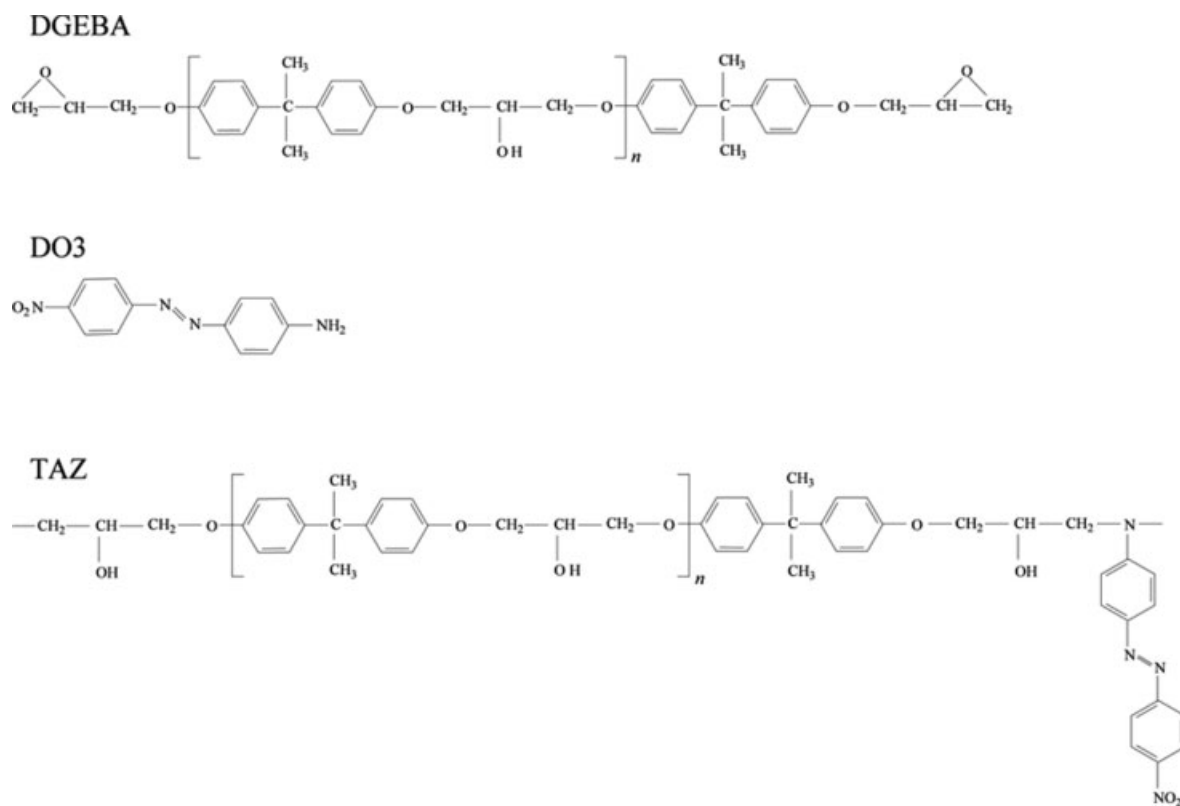
### Materials

A bifunctional epoxy resin, diglycidyl ether of bisphenol A (DGEBA; DER 332,  $n = 0.03$ ), with an epoxy equivalent of  $175 \text{ g eq}^{-1}$  was kindly provided by Dow Chemical. The azo-chromophore Disperse Orange 3 (DO3) was supplied by Aldrich and tetrahydrofuran (THF) was purchased from Panreac. Both reactants and solvent were used as received without further purification.

### Sample preparation

A thermoplastic epoxy polymer modified with azobenzene groups (TAZ) was synthesized by reaction between DO3 and DGEBA, in a stoichiometric ratio  $r = \text{DO3 eq/DGEBA eq} = 0.5$ , following a procedure described elsewhere.<sup>38</sup> The chemical structures of the resulting TAZ, having a chromophore concentration relative to the polymer backbone of 26 wt%, and the reactants DGEBA and DO3 are shown in Fig. 2.

For optical birefringence and dichroism measurements, films were prepared by spin coating using a P6700 spin-coater from Cookson Electronics, with solutions of 5 wt% TAZ in THF. The spinner cycle programme was as follows: 1000 rpm for 30 s, 4000 rpm for 10 s and 8000 rpm for 20 s. Residual THF was removed by evaporation at room temperature. Films were heated above  $T_g$  and subsequently stored at room temperature. All the films had comparable thicknesses of the order of 400 ( $\pm 50$ ) nm, which were



**Figure 2.** Chemical structures of the epoxy resin DGEBA, the azo-chromophore DO3 and the azo-polymer TAZ.

determined from the topographic profiles of the scratched films obtained using AFM.

SRGs were fabricated on films of TAZ prepared onto mica substrates coated with a layer of gold, Au (111), of at least 1500 Å thickness, by dip coating using a DC Multi-8 dip-coater from NIMA Technology. The gold surface was dipped for 1 min in a solution of 5 wt% TAZ in THF at a rate of 40 mm min<sup>-1</sup> and subsequently pulled out from the solution at a rate of 5 mm min<sup>-1</sup>. Residual THF was removed by evaporation at room temperature.

### Techniques

DSC was performed using a Mettler Toledo DSC 192 822 differential scanning calorimeter equipped with a sample robot (193 TSO 801 RO). Nitrogen was used as purge gas (10 mL min<sup>-1</sup>).  $T_g$ , defined as the onset of the change in specific heat, was determined from the thermograms obtained in heating scans at 10 °C min<sup>-1</sup>.

Optical storage experiments were carried out at room temperature and under ambient conditions. The experimental set-up used was similar to that previously reported.<sup>38</sup> Optical birefringence was induced in the TAZ films using a linearly polarized argon laser operating at 488 nm (writing beam) with a polarization angle of 45° with respect to the polarization direction of a low-power He–Ne laser operating at 632.8 nm (reading beam). The power of the writing beam used in the experiments was 6 mW on a spot of 0.4 mm<sup>2</sup> and the change in the transmission of the reading beam, which passed through the sample between two crossed polarizers, was measured with a photodiode. The induced birefringence ( $\Delta n$ ) was determined by measuring the reading beam transmission ( $T = I/I_0$ ) according to

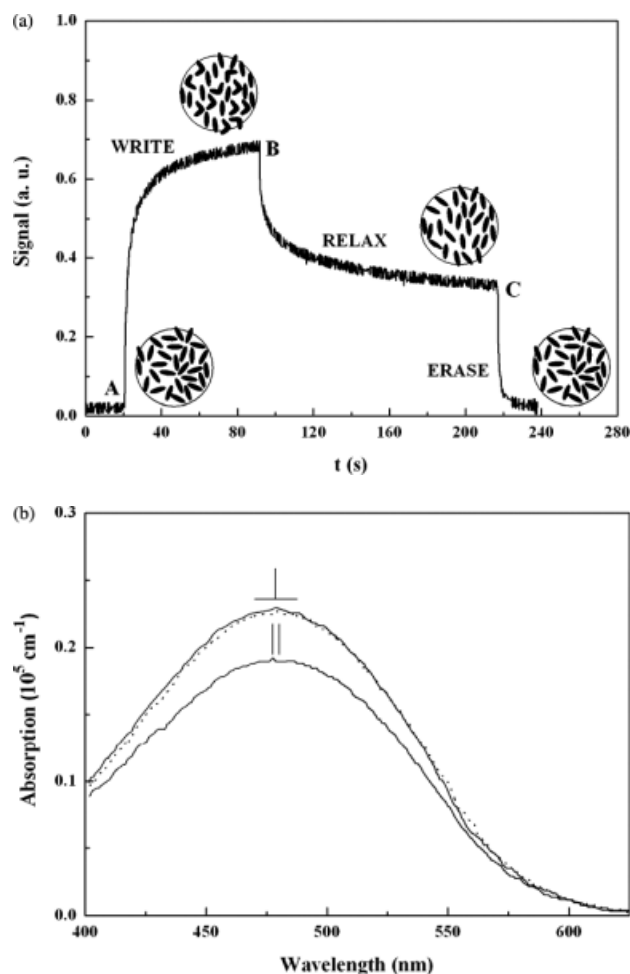
$$\Delta n = \frac{\lambda}{\pi d} \sin^{-1} \left( \frac{I}{I_0} \right)^{1/2} \quad (1)$$

where  $\lambda$  is the wavelength of the reading beam,  $d$  is the film thickness,  $I$  is the intensity of the reading beam after the second polarizer and  $I_0$  is the transmitted intensity of the reading beam between parallel polarizers in the absence of anisotropy.

UV-visible spectra of TAZ films were recorded using a Milton Roy Spectronic Genesys 5 spectrophotometer fitted with polarizing optics. Firstly, the sample was exposed to a linearly polarized argon laser beam at 488 nm (6 mW) for enough time to reach saturation and, subsequently, UV-visible spectra for light polarized parallel and perpendicular to the writing polarization direction were recorded. The dichroism ratio ( $D$ ) of the samples was calculated from the measured absorbance at maximum wavelength ( $\lambda_{\max}$ ) parallel ( $A_{\parallel}$ ) and perpendicular ( $A_{\perp}$ ) to the electric vector of the writing beam:

$$D = \frac{A_{\perp}}{A_{\parallel}} \quad (2)$$

AFM was employed in tapping mode (TM) for the acquisition of topographic images and in contact mode (CM) for electro-patterning, using a Dimension 3100 NanoScope IV (Veeco) microscope. Measurements were performed using a Co/Cr-coated MESP tip having a nominal radius of 25 nm and a resonance frequency around 75 kHz. SRG formation was achieved applying a negative voltage (–6 V) to the AFM tip with respect to the TAZ film at a scan rate of 0.01  $\mu\text{m s}^{-1}$ . Electrostatic force microscopy (EFM) was also performed in order to measure the electric field gradient distribution above the sample surface, using the same microscope operating in lift mode (lift scan height was 50 nm) by applying a tip voltage of –3 V. All experiments were carried out at room temperature (ca 25 °C) with a relative humidity of ca 50–60%.



**Figure 3.** (a) Typical writing, relaxing and erasing curves for TAZ. (b) UV-visible spectral changes of a TAZ film irradiated with a linearly polarized argon laser beam at 488 nm (6 mW). Solid curves correspond to spectra obtained using probe light with the electric vectors parallel,  $\parallel$ , and perpendicular,  $\perp$ , to that of the writing beam; the dotted curve corresponds to the spectrum of TAZ film before irradiation.

## RESULTS AND DISCUSSION

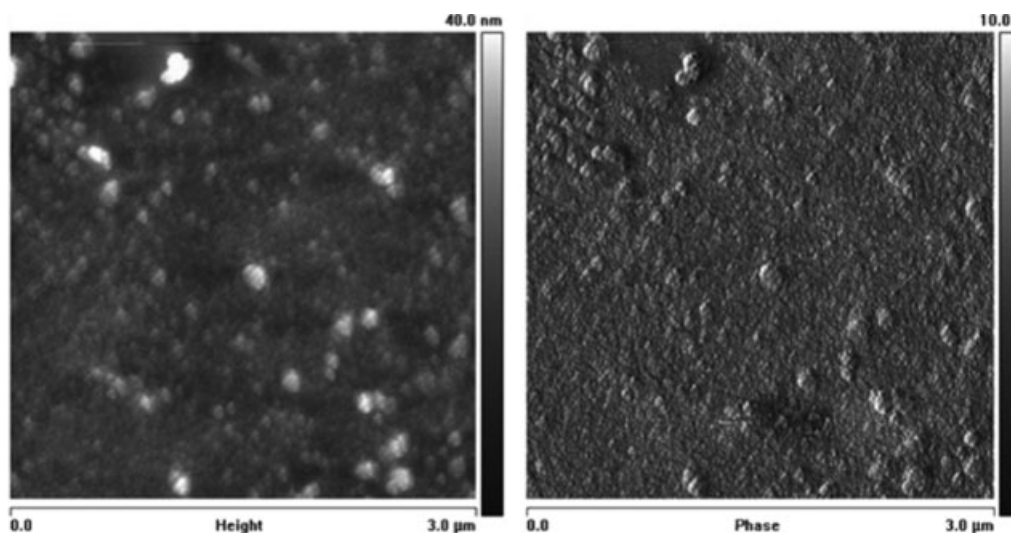
The thermal behaviour of TAZ was studied using DSC; its  $T_g$  value, estimated using this technique, is 28 °C. The photo-induced birefringence and dichroism properties of this thermoplastic epoxy polymer containing azobenzene groups were also evaluated. Values of maximum and remaining birefringence were determined from optical storage experiments. Figure 3(a) shows writing, relaxing and erasing sequences obtained for a TAZ film. The reading beam continuously illuminates the sample. At the beginning of the experiment there is no transmission of the reading beam, since the azo-chromophores in *trans* form, which is the more stable configuration, are randomly distributed, the TAZ film being isotropic. At point A, the writing beam is turned on and the reading beam is transmitted through the polarizer-sample-polarizer system due to the optical anisotropy induced in the TAZ film as a consequence of *trans-cis-trans* photo-isomerizations that lead to the orientation of *trans* molecules perpendicular to the polarization vector of the writing beam. In fact, it is observed that the photo-induced birefringence is rapidly built up to the saturation level, where a large number of azobenzene groups aligned perpendicular to the polarization vector of the writing

beam is achieved. This optically induced birefringence represents a writing mechanism in an optical storage device. Quantitatively, an optical birefringence of  $\Delta n = 0.028$  is determined for TAZ from the value of maximum transmitted signal obtained. When the writing beam is turned off at point B, the signal rapidly falls off initially. This is probably due to thermally activated dipole reorientation which would tend towards randomization of the anisotropy.<sup>39</sup> Immediately after, it is observed that the signal becomes stable in a relaxed level, where the rate of change of anisotropy is very small. After a preferred orientation is photo-induced in the azo-polymer film and irradiation is interrupted, this orientation may be conserved or not depending on the nature of the azo-polymer. In particular, the birefringence conserved after relaxation, i.e. the remaining birefringence, for TAZ is of the order of just 50%, probably due to the high molecular mobility at room temperature of this azo-polymer with  $T_g = 28$  °C. This stable birefringence pattern corresponds to the storage step. Finally, at point C, in order to remove the remaining birefringence, circularly polarized light is introduced, which completely randomizes the azo-chromophore orientation.

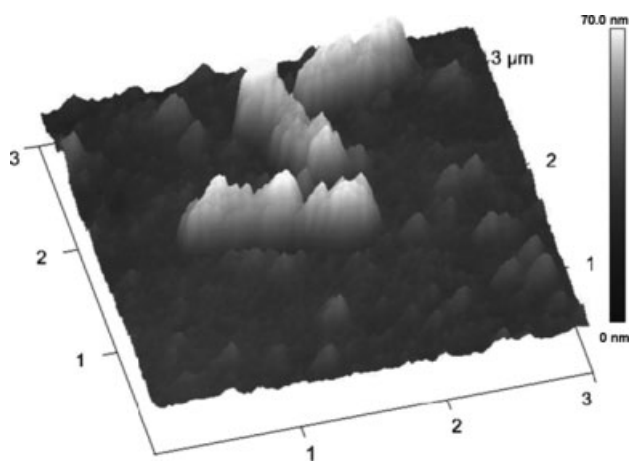
In Fig. 3(b) typical examples of optically induced dichroism are presented, where the polarized UV-visible absorption spectra of a TAZ film are shown. The absorption coefficient for light polarized parallel to the writing direction is lower than that for light polarized in the perpendicular direction, which is reflected in a small  $D$  value of about 1.2. This low value achieved could be related to the fact that the dichroism is measured when the writing beam is turned off, i.e. in the relaxed level. Therefore, taking into account the low  $T_g$  of TAZ (28 °C), an easy mobility of the azo-chromophore around its molecular axis is expected and, consequently, a low remaining birefringence, as previously shown, which is directly related to the dichroism value obtained. The lower the remaining photo-orientation, the lower is the attainable dichroism value. However, the spectra of written films (parallel and perpendicular) and the unwritten one do not show significant shape and  $\lambda_{\max}$  differences. This can be taken as evidence of a negligible aggregation of azo-chromophores, since a significant shift would be expected otherwise.<sup>40</sup> Moreover, this would indicate that the mechanism responsible for the dichroism is the reorientation of the azobenzene molecules.

Once the optical birefringence and dichroism properties of TAZ had been analysed, the fabrication of SRGs on this azo-polymer, which is a dielectric material with high dipole moment from the azo-chromophore, was investigated. Figure 4 shows TM-AFM height and phase images of the TAZ film before the electro-patterning experiments. It is observed that the polymeric film presents certain roughness. As mentioned in the introductory section, the azobenzene molecules can be aligned using an external electric field. Taking this into account, the SRG formation process was carried out as follows. Firstly, a voltage of  $-6$  V was locally applied to the AFM tip with respect to the TAZ film by means of CM-AFM. As a result, the azo dipoles are oriented parallel to the tip direction and, consequently, perpendicular to the film surface in the area of voltage application. Subsequently, TM-AFM height images of the manipulated TAZ film were obtained. Figure 5 shows a three-dimensional view of the height of the TM-AFM image of TAZ. This topographic image confirms surface relief formation, which highlights the film areas where the AFM tip voltage was applied. As can be observed, a large mass transport is achieved in the scanning direction, with relief of ca 50 nm of height being obtained. In particular, the patterned lines are not parallel in order to observe various writing directions and to prove that by means





**Figure 4.** TM-AFM height (left) and phase (right) images of TAZ before electro-patterning ( $3\ \mu\text{m} \times 3\ \mu\text{m}$ ).



**Figure 5.** Three-dimensional view of the height of an AFM image of TAZ after electro-patterning ( $3\ \mu\text{m} \times 3\ \mu\text{m}$ ).

of the procedure employed to obtain the surface relief almost any shape can be inscribed. Furthermore, it was verified that the obtained surface relief on the TAZ film is a consequence of the application of the voltage, and not due to the fact that the tip alters physically the film surface, by acquiring images under identical experimental conditions, but with a voltage of 0 V. In this case, TM-AFM images similar to those shown in Fig. 4 are obtained, which confirms that the AFM tip does not scratch the surface, but rather just makes enough contact with the film to apply the voltage. However, slight differences in roughness between Figs 4 and 6 can be observed, which could be attributed to a deterioration of the AFM tip probably because the Co/Cr conductive coating flakes off leading to the tip becoming less sharp. This would cause the acquisition of images with lower and lower resolution. In addition, it was proved that when using voltage values higher than  $-6\ \text{V}$  the tip is more quickly damaged. The differences between both images due to the variation in heights on the polymeric film surface before and after electro-patterning should also be taken into account, which implies different image scale adjustments.

As previously reported by Baba *et al.*,<sup>37</sup> a possible mechanism that would explain the formation of the relief is as follows. First, the

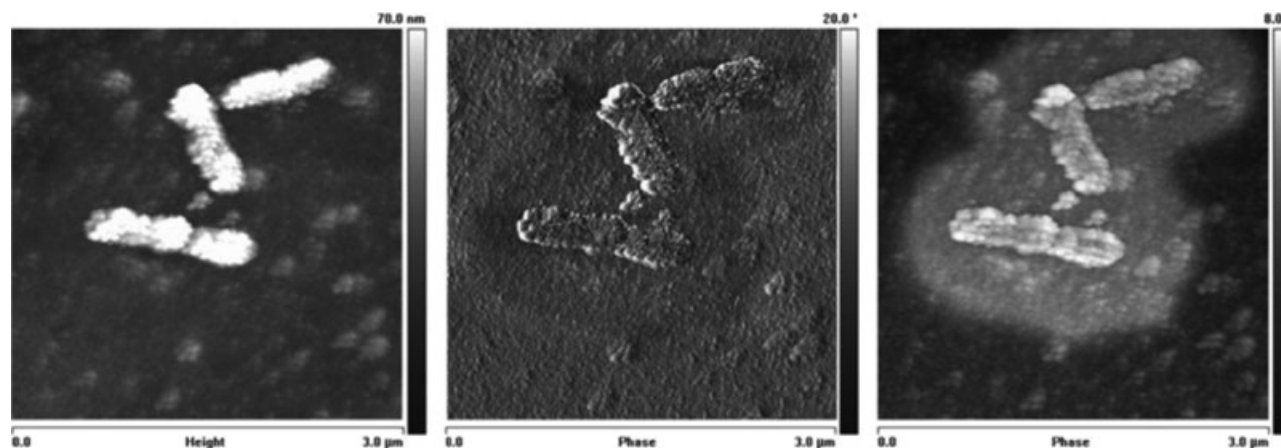
azo-polymer is softened to  $T_g$  by Joule heating and then aligned to the direction of the moving electric field. The softened TAZ is then realigned to the direction of the moving AFM tip, so that the mass transport is observed in this direction. Joule heating causing TAZ softening is produced by ionic currents where a water meniscus acts as a bridge, providing a steady medium for electrical conduction and polymer mass transport.<sup>41</sup>

Figure 6 shows TM-AFM height and phase images and an EFM phase image of the TAZ film after electro-patterning. In the TM-AFM height image a raised surface caused by the electrical field effect is observed. TM-AFM phase images give information on properties like rigidity, among others. Based on this knowledge, it is supposed that relief formation induces a change of rigidity in the surroundings of the relief formed, possibly as a result of the topographic change in the TAZ film surface which would cause film stretching in the relief surroundings, as well as by film softening due to the Joule heating effect. In the EFM phase image the change induced in the surroundings of the surface relief formed in TAZ is even more obvious. EFM is a versatile method for studying the electric field gradient distribution on sample surfaces. Thus, from the obtained EFM image it is inferred that there is a concentration of electrostatic charges in the area of the film in which the relief is formed, as well as in the surroundings. Here, it should be pointed out that the formation of the relief is a consequence of the orientation of the azo dipoles. Therefore, it is possible that in the relief surroundings the orientation of some azo dipoles is also induced, which could also contribute to the observed film surface changes.

## CONCLUSIONS

In summary, we investigated the photo-induced birefringence and dichroism properties and demonstrated electro-patterning of a thermoplastic epoxy polymer functionalized with azobenzene groups.

A large height change of the azo-polymer film was observed due to mass transport induced by the alignment of azobenzene molecules and Joule heating, as a result of the application of a local electric field using AFM. Additionally, in the surroundings of the surface relief formed, a change of material rigidity was observed



**Figure 6.** TM-AFM height (left) and phase (middle) images, and an EFM phase image (right) of TAZ after electro-patterning ( $3\ \mu\text{m} \times 3\ \mu\text{m}$ ).

by means of TM-AFM, and a concentration gradient of electrostatic charges was observed using EFM.

This novel method of electro-patterning might have future applications for fabricating three-dimensional structures and for nanoscale device applications, also opening up the possibility of electro-nanolithography of azo-polymer films.

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