



Dedicated to Professor Alexandru T. BALABAN
on the occasion of his 90th anniversary

INVESTIGATION OF SURFACE RELIEF GRATINGS ON AZO-COPOLYIMIDE FILMS USING ATOMIC FORCE MICROSCOPY

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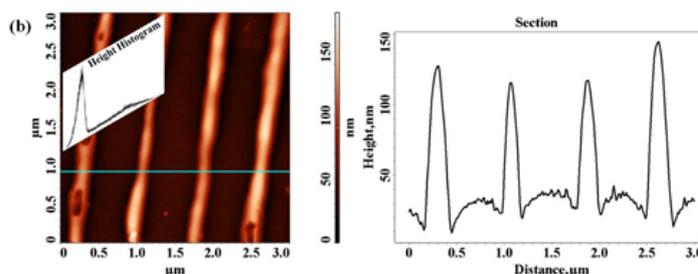
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Azo-copolyimide films were explored regarding the surface relief gratings formation under the action of pulsatory laser irradiation. The azo-copolyimides have been synthesized by the polycondensation reaction of benzophenonetetracarboxylic dianhydride and a mixture of two diamines, one of which contains substituted phenyl groups and the other one contains two pendent substituted azobenzene group, taken in the molar ratio 3 : 1, respectively. Atomic force microscopy was used to investigate the surface relief gratings characteristics in different conditions and for different structures of the azo-copolyimide films.



INTRODUCTION

Considerable interest have been made in the development of materials that are optically responsive and have the potential to be useful in photonic technology. Azobenzene and many of its derivatives are promising materials for such applications. The utility of these materials is based on multiple *trans-cis-trans* isomerization cycles of azobenzene groups accompanied by their movement and rearrangement of the macromolecular chains to the laser polarization beam.^{1,2} Polymers with such properties have shown potential technological applications such as

optical information storage and processing, optical switching devices, holographic gratings, fabrication of diffractive elements with specific polarization properties, waveguides and many others.¹⁻⁸ For advanced practical applications, the azopolymers should fulfill other requirements like short response time, long-term chemical and orientational stabilities at the operating temperatures, good film forming ability, high thermal stability and good processability. The physical and photoinduced properties are strongly associated, with both the chromophore and polymer matrix architecture. The more vulnerable part in such materials is the azobenzene group. To

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increase the thermal stability of optically induced birefringence the combination of high glass transition temperature (T_g) polymers, such as polyimides, was used by many authors.⁹⁻¹⁴

The incorporation of azobenzene chromophore into the polymers can introduce structural diversity and processability into the functional materials. Laser-induced surface relief gratings on azobenzene polymer films have attracted considerable attention since first reported by different authors.^{3,4} The formed surface relief gratings are stable when kept below glass transition temperature. They will be erased by laser or heating.^{15,16} The atomic force microscope (AFM) is a powerful device to characterize and image the nanomaterial surfaces. AFM as a unique tool not only can be used to study the topography and morphology of films, but also applied to probe the local mechanical behavior of films, especially the force response to approach. Many researchers have been focused on the progress in AFM techniques to characterize the films, single cells and single molecules in nano-scale.^{17,18}

The investigation of surface relief gratings (SRG) was performed by using atomic force microscopy to analyse the nanochannels characteristics which were obtained on the film surfaces. This work studies by AFM the structuring behaviour of polymer films which contain in the same macromolecular chain a rigid part and a flexible part. The rigid part consists in a matrix of aromatic polyimide and a flexible part was introduced in a side azobenzene group containing different lengths of alkyl units.

RESULTS AND DISCUSSION

Surface relief gratings of azo-copolyimide films

The parameters used for obtaining surface relief gratings (SRG) on azo-copolyimides films were chosen based on our previously study performed on other azo-polyimides and azo-copolyimides.^{11-14, 16,19,20} The investigations of surface structuring capacity have been performed by using a laser field with an energy density of 45 mJ/cm^2 and two different numbers of pulses, 10 and 100. We try to use a lower energy density (*i.e.* 10 mJ/cm^2) but no SRG were obtained on the surface of the polymer films. Surface irradiation was realised under the action of a pulsed laser field, with a controlled

distribution of energy represented by an interference pattern after passing through the phase mask. The energy source is represented by 6 ns Nd:YAG laser pulses working on its third harmonic at 355 nm.

Atomic force microscopy was used to characterize the resulted structured surfaces. The bimodal distribution of heights (height histograms) corresponding to the AFM morphological images from Figs. 1-4 indicates the existence over the surface of two different entities, *i.e.* the two regions of the SRGs. The lengths of the alkyl chains have established the pattern depth, calculated using the cross-section profiles corresponding to the AFM morphological images (Figs. 1-4). The obtained results presented in Table 1 show that by increasing the number of alkyl chains in the macromolecular chain of the azo-copolyimides, the modulation depth decreases, irrespective of the number of pulses used. Thus, by using 10 pulses, for azo-copolyimide **CPI 1,3** which incorporates in the azobenzene side linkage three methylene units, the modulation depth was $134 \pm 8 \text{ nm}$. For azo-copolyimide **CPI 1,4** which contains four methylene units the modulation depth was $96 \pm 6 \text{ nm}$ and for **CPI-1,5** having five methylene units and **CPI 1,6** which incorporates six methylene units the modulation depth decreases to $91 \pm 5 \text{ nm}$ and $88 \pm 7 \text{ nm}$, respectively. It seems that the flexibility of the azo-copolyimide with a small number of alkyl chains is greater, inducing a greater structuring capacity, and thus a more pronounced relief. By increasing the number of pulses to 100, the generated channels were even and uniform as can be seen in Figs. 1-4, the modulation depth being significantly higher. By analyzing a profile diagram it was observed that the homogeneity of the surface features is satisfactory, the deviations being in the domain of 15-30 nm. Also, it was observed that the values of modulation depth decrease with increasing the number of methylene units in the side chains of the azobenzene groups, as can be seen in Table 1. The surface morphology has a preferential orientation, indicated by the texture direction index (Stdi), as can be seen in the AFM images presented in Figs. 1-4. A good anisotropy of the morphology of the SRG of the azo-copolyimide films is evidenced by a low value of Stdi.²¹ As can be seen in Table 1 the values of Stdi are in the range of 0.183 – 0.367.

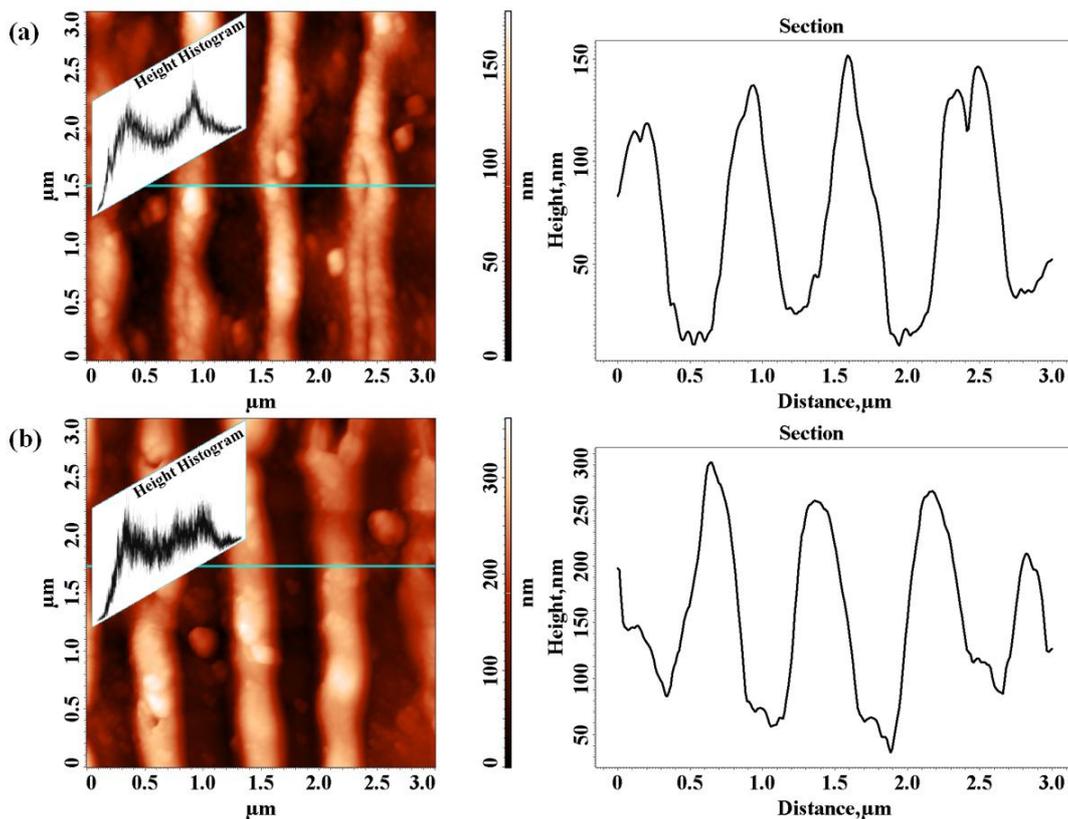


Fig. 1 – SRG of azo-copolyimide CPI 1,3 at 10 (a) and 100 (b) irradiation pulses.

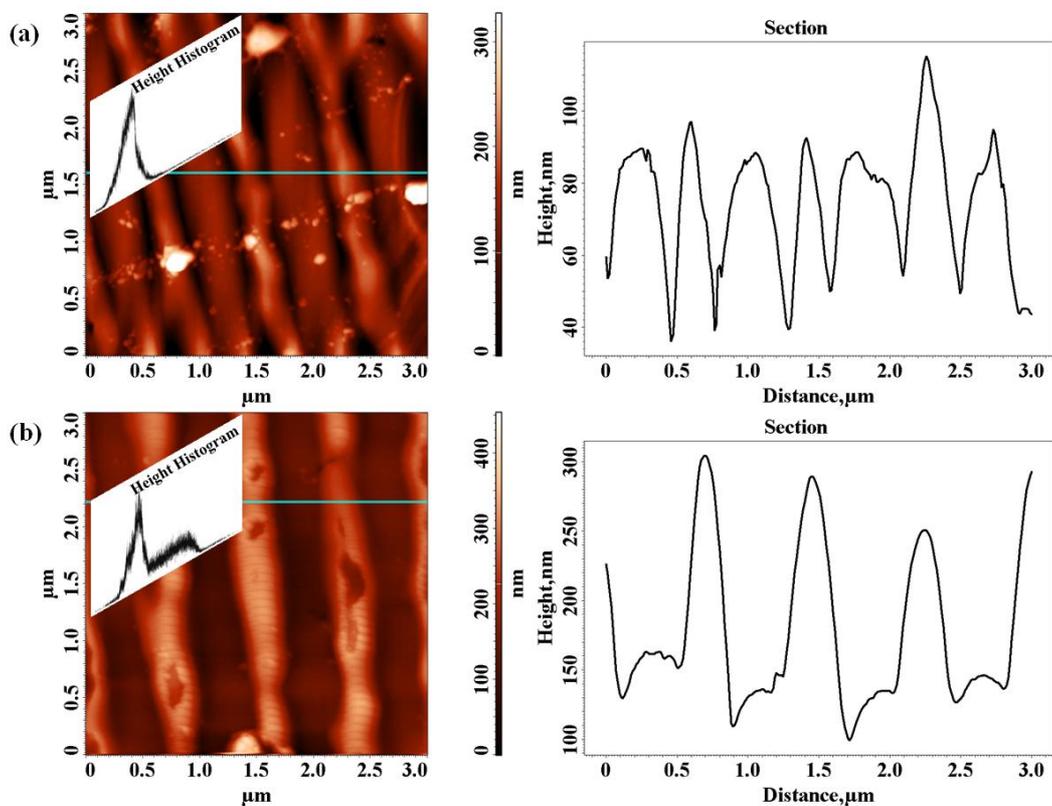


Fig. 2 – SRG of azo-copolyimide CPI 1,4 at 10 (a) and 100 (b) irradiation pulses.

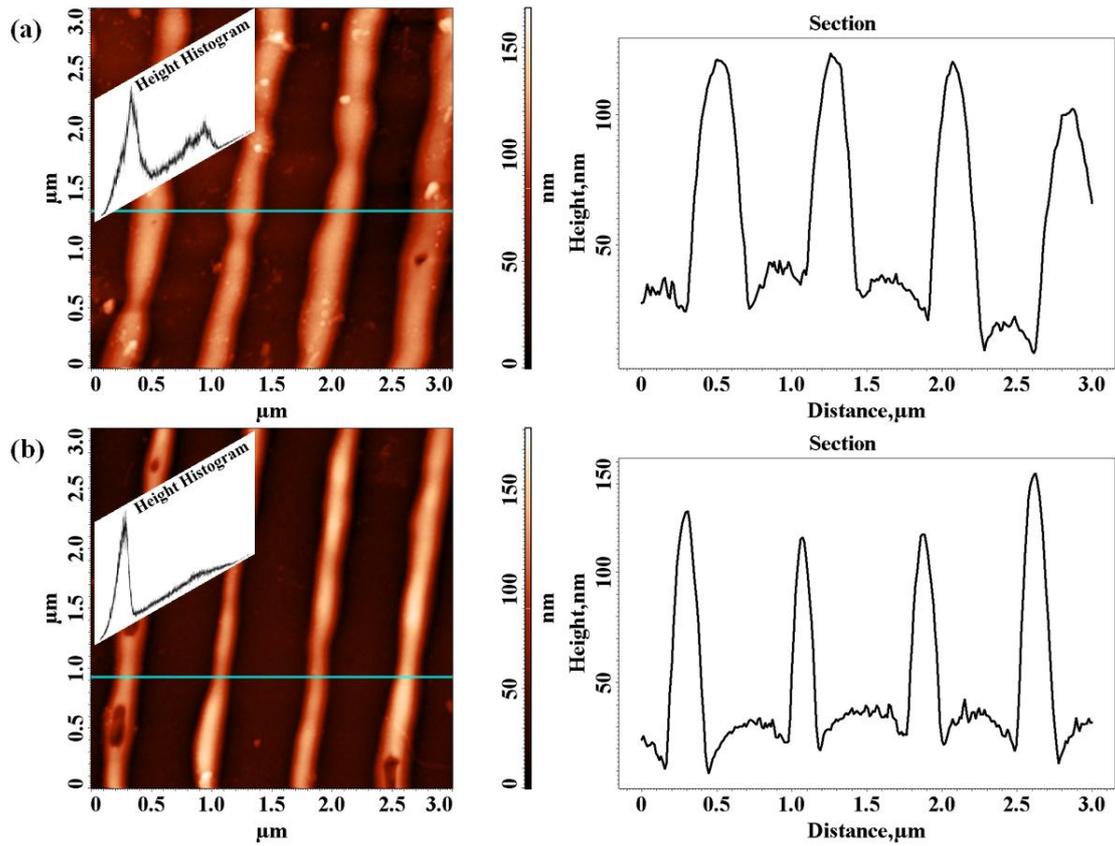


Fig. 3 – SRG of azo-copolyimide CPI 1,5 at 10 (a) and 100 (b) irradiation pulses.

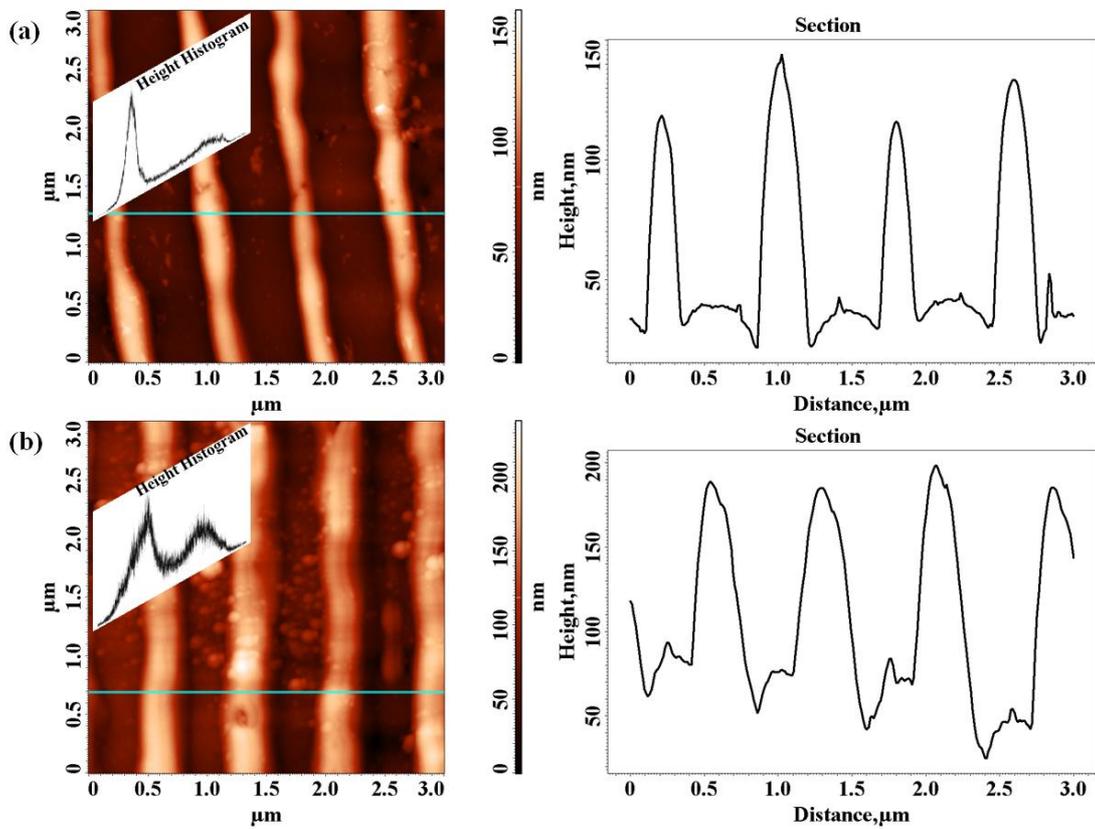


Fig. 4 – SRG of azo-copolyimide CPI 1,6 at 10 (a) and 100 (b) irradiation pulses.

Table 1

The modulation depth and texture direction index of the azo-copolyimides

Pulses number	Azo-copolyimides							
	CPI 1,3		CPI 1,4		CPI 1,5		CPI 1,6	
	Z*, nm	Stdi	Z*, nm	Stdi	Z*, nm	Stdi	Z*, nm	Stdi
10	134 ±8	0.274	96 ±6	0.367	91 ±5	0.299	88 ±7	0.244
100	221 ±31	0.266	162 ±22	0.310	145 ±14	0.210	143 ±16	0.183

Z* – Modulation depth; Stdi – texture direction index

The presence of two side azobenzene groups determined the structuring ability of these azo-copolyimides. The presence of the BTDA units in the macromolecular chain of the azo-copolyimides slightly increase the rigidity of the chains but the presence of two side azobenzene units in the chain connected by ether and alkyl units improve the flexibility. The presence of MMDA have a small influence of the structuring capacity of the polymer films compared to aromatic diamines which contain ether linkages connected in *meta* or *para* position.^{11,16}

EXPERIMENTAL

The structure of azo-copolyimides used to investigate the behavior to the laser patterning is shown in the Scheme 1. These azo-copolymers have been synthesized by the polycondensation reaction of benzophenonetetracarboxylic dianhydride (BTDA) and a mixture of two diamines, one of which contains substituted phenyl groups, namely 4,4'-diamino-3,3'-dimethyldiphenylmethane, (MMDA) and the other one contains two pendent substituted azobenzene group, namely 2,2 bis-(3-amino-4-alkoxy-phenyl-4'-methylazobenzene) hexafluoropropane. The molar ratio between the two diamines was 3 : 1, respectively. The polycondensation reaction of these monomers and the details of the synthesis and characterization was carried out by using a procedure previously reported.^{22,23}

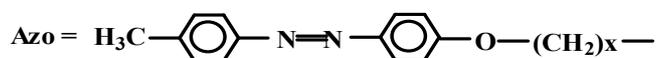
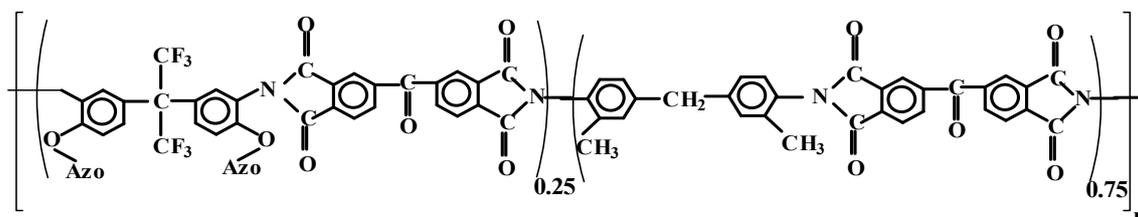
The third harmonic (355 nm wavelength) of a pulsed Nd:YAG laser (Brilliant B from Quantel, 6 ns pulse duration, 5 mm diameter) was selected to generate an interference field in the proximity of a phase mask (1000 grooves per mm), placed prior to the azo-copolyimides samples. The incident

fluency on the grating was kept constant to 45 mJ/cm², while the laser pulses number was set to 10 and 100.

The surface relief gratings were investigated by Atomic Force Microscopy by using a Scanning Probe Microscope Solver PRO-M (NT-MDT, Zelenograd, Russia). The film topography was analyzed in tapping mode, in air, using a rectangular cantilever NSG10/Au (NT-MDT, Zelenograd, Russia) with a resonant frequency of 277 kHz. Different scan sizes were analyzed by means of Nova v.1.26.0.1443 for Solver software, but the morphological features were easily observed when the scan length of 3 μm was utilized. The tridimensional parameters were calculated using Image Analysis 3.5.0.18542 software.

CONCLUSIONS

Atomic force microscopy was used to investigate surface relief gratings formation under the action of pulsatory laser irradiation of the azo-copolyimide films. All the azo-copolyimide films showed a good surface structuration capacity irrespective of pulses number at 45 mJ/cm². The azo-copolyimides with a small number of alkyl chains have presented a more pronounced relief due to their flexibility. By using a high number of pulses, the surface relief grating became much more regular and the modulation depths in these cases were around 140-250 nm, while in the cases using only 10 irradiation pulses, the modulation depths were in the range of 80-150 nm. The surface morphology has a preferential orientation, indicated by the low value of the texture direction index.



CPI 1,3: x = 3; CPI 1,4: x = 4; CPI 1,5: x = 5; CPI 1,6: x = 6

Scheme 1 – Structure of azo-copolyimides.

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