

Surface Relief Gratings Inscription in Linear and Crosslinked Azo Modified Epoxy-Isocyanate Polymers

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Received 17 November 2014; accepted 23 December 2014; published online 00 Month 2015

DOI: 10.1002/polb.23674

ABSTRACT: This work analyses the SRG forming ability of a linear and a crosslinked polymer, both based on the same azo chromophore (Disperse Red 19, DR19) and diisocyanate (4,4'-metileno-bis(ciclohexil isocyanato), DI) with similar glass transition temperature values. The effect of the experimental and geometrical parameters (such as beams polarization direction and interference pattern spacing) on the surface modulation process was examined as well. The absence of photodegradation or bleaching was corroborated by comparing Raman spectra inside and outside the SRG zone. Being a very important subject matter, the influence of crosslinking on the inscription

rates and thermal stability of SRGs was investigated. Crosslinked films with an interesting modulation and good grating stability, even at high temperatures (160 °C), were obtained. Gratings shape was retained, and significant diffraction was still observed even well above the T_g of the bulk sample. © 2015 Wiley Periodicals, Inc. *J. Polym. Sci., Part B: Polym. Phys.* **2015**, *00*, 000–000

KEYWORDS: azobenzene; azo polymers; crosslinking; epoxy-isocyanate polymer; surface relief grating; thermosets; thermoplastics

INTRODUCTION Light-induced surface modulation is a unique attribute of azobenzene-containing materials, based on which the photoisomerization of the azobenzene chromophores initiates mass transport over micrometer distances.^{1–4} This reversible process allows the construction of high-quality surface relief gratings (SRG) by a facile and single step procedure (a wet process is not required) with potential applications that range from optical technology (holographic memories, diffractive optical elements, photonic components)^{5–10} to nanotechnology (micropatterning, nanopatterning).^{11,12}

In a typical experiment, two coherent laser beams, with a wavelength in the azo absorption band, are intersected to generate an interference sinusoidal patterning at the sample surface (usually a thin spin-coated film) at a temperature well below the T_g of the polymer. The phenomenon is a reversible mass transport that does not include irreversible material ablation, since a flat film with the original thickness is recovered upon heating above glass transition temperature (T_g). The grating depths may approach several hundreds of nanometers, as it has been confirmed by AFM.^{2,13}

Over the last years, many research groups have delved into the inscription of surface relief gratings on a large variety of

thermoplastic azobenzene functionalized polymers with different chemical structure, molecular weight, T_g , and azobenzene content.^{1,2,13–18} They have postulated that intermolecular interactions are essential for the SRG formation process since the movement of the whole molecules is necessary, and hence, the matrix properties and morphology gain particular relevance.¹⁹

Regarding optical devices, the long-term stability of the optical properties is a prerequisite. Crosslinking or interpenetrating networks formation could be developed to fulfil this requirement.²⁰ However, despite the fact that several research groups have described the synthesis and inscription of SRG in azo thermoplastics polymers, only a few have centered on crosslinkable polymers. More often than not, SRGs have been developed by postcrosslinking strategies.^{20–25} This awoke our interest to study the formation of patterns in previously crosslinked polymers and to evaluate their thermal stability.

In a previous work, we studied the optical behavior of a series of epoxy-isocyanate based azo systems and obtained promising material with high maximum values and remnant birefringence, and also good thermal stability.²⁶ The aim of this new research was to study these epoxy-isocyanate

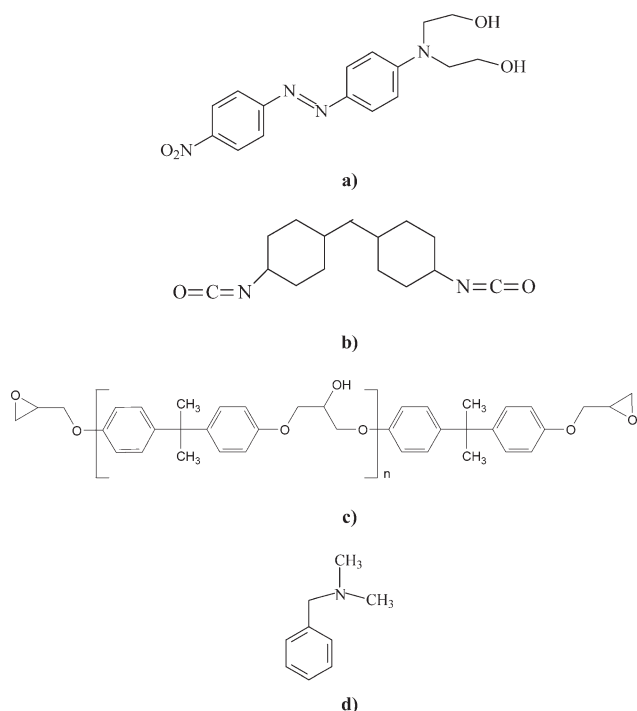


FIGURE 1 Chemical structure of the different reactives: (a) Disperse Red 19 (DR19), (b) 4,4'-methylene-bis(cyclohexyl isocyanate) (DI), (c) diglycidyl ether of bisphenol A (DGEBA), and (d) benzyltrimethylammonium chloride (BDMA).

systems and to analyze SRG forming ability by comparing a crosslinked system with a noncrosslinked one, both based on the same azo chromophore and diisocyanate. In particular, focus was on the effect of crosslinking on the inscription rates and thermal stability of SRGs. Also, the differences in the structuring process in these azo polymers were examined, and the influence of the experimental and geometrical parameters (such as beams polarization direction and interference pattern spacing) was analyzed.

EXPERIMENTAL

Materials

A push-pull azo chromophore, $C_6H_3(NO_2)N=NC_6H_4N(CH_2CH_2OH)_2$ (Disperse Red 19, DR19, Aldrich, $T_m = 300\text{ }^\circ\text{C}$, dye content 95%), was selected as photosensitive reactive. 4,4'-methylene-bis(cyclohexyl isocyanate) (DI, Aldrich, 85%) was employed in the synthesis of azo-urethane polymers. Dibutyltin dilaurate (DBTDL, Aldrich) was used as a catalyst for the synthesis.

Reactions were carried out in tetrahydrofuran (THF, Biopack, 99%) that was distilled from calcium chloride and stored over 3 \AA molecular sieves.

The diepoxide used was based on diglycidyl ether of bisphenol A (DGEBA, Der 332, Aldrich) with a mass per mole of epoxy groups equal to 174 g mol^{-1} . Benzyltrimethylammonium chloride (BDMA, Aldrich) was used as a catalyst for the epoxy-

isocyanate reaction. The chemical structures of the different reactants are shown in Figure 1.

Synthesis of Azo-Urethane Polymer Films (L-PUazo)

DR19 (0.330 g, 1 mmol) and DI (0.262 g, 1 mmol) were dissolved in about 20 mL of distilled THF. DBTDL (1.6 g of DBTDL/100 g of DI) was added as catalyst. The resulting solution was heated at $55\text{ }^\circ\text{C}$ and the reaction continued until isocyanate peak disappearance was checked in the infrared spectrum (24 h). Then the solution was cooled to room temperature (the reaction scheme is plotted in Fig. 2). Toluene was added to the solution, and a red precipitate was obtained. The precipitate was washed with toluene and recrystallized from THF. The procedure of precipitation and washing was repeated. The precipitate was dried first in air and then in a vacuum chamber for several hours to remove the traces of toluene. Then, it was dissolved in chloroform at concentrations ranging from 1 to 5 wt %. Thin films for all the solutions were prepared by spin coating on to cleaned glass substrates at 3000 rpm for 1 min. The films were dried in a vacuum chamber for 24 h to remove residual solvent.

Synthesis of Epoxy-Isocyanate Films (DGEBA-PUazo)

The crosslinked azopolymer was obtained following a two-step procedure:

Step (a) Synthesis of an Azo Prepolymer (PUazo)

DR19 (0.165 g, 0.5 mmol) and DI (0.262 g, 1 mmol) were dissolved in about 20 mL of distilled THF. DBTDL (1.6 g of DBTDL/100 g of DI) was added as a catalyst. The resulting

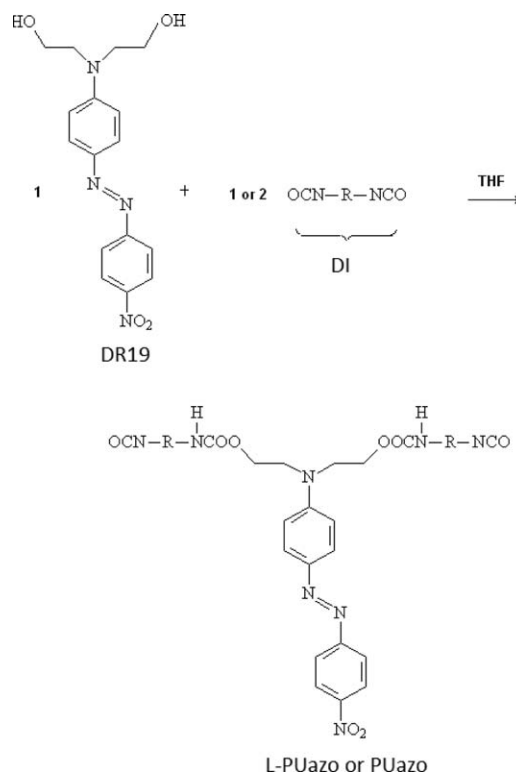


FIGURE 2 Synthesis scheme of the azo polyurethane L-PUazo and the azo-prepolymer PUazo.

solution was heated at 55 °C for 1 day and then cooled to room temperature (Fig. 2).

Step (b) Epoxy-Isocyanate Reaction (DGEBA-PUazo)

DGEBA in a stoichiometric ratio $r = \text{eq. NCO}/\text{eq. epoxy}$ ($r = I/E$) equal to 1 and 1% BDMA (mole per isocyanate equivalent) to initiate the reaction were added to the PUazo solution resulting from step (a). Films from the reactive mixture solution were prepared by spin-coating using a single wafer spin processor (Model WS-400E-6NPP-lite, by Laurell) on glass slides previously cleaned. The spinner cycle program was as follows: 1000 rpm for 30 s, 4000 rpm for 10 s, and 8000 rpm for 20 s. The films were cured at 100 °C for 1 h, 180 °C for 1 h, and 200 °C for 1 h in a vacuum oven.

Fabrication of Surface Relief Gratings (SRG)

A Lloyd interferometer, a widely employed interferometer for the generation of patterns from a coherent source (488 nm semiconductor laser), was used to generate the gratings. The experimental setup is illustrated in Figure 3.

The interferometer is essentially a mirror positioned perpendicular to a glass substrate where the sample is deposited. The interference pattern is projected on the sample by the combination of one half of the incident laser beam, and the other half of the beam reflected from the mirror.

Additionally, the fringe spacing Λ is easily controlled by varying the reference angle θ , calculating estimation based on eq 1

$$\Lambda = \frac{\lambda}{2\sin(\theta)} \quad (1)$$

where θ is the angle between the incident beam and the plane parallel to the mirror, λ is the laser wavelength, and Λ is the spacing between peaks. In this work, the spacing was determined at approximately 1.5 μm ($\theta = 9^\circ$).

The gratings were recorded at two different polarization conditions. The orthogonal linear one with the polarization planes oriented at an angle of 45° to the incidence plane (+45°:−45°), and the s-s one, in which the two interfering beams were linearly polarized in the vertical direction, perpendicular to the plane of incidence and parallel to the polarization planes.

The progression of the inscription was monitored by measuring the growth of the first diffraction order through a semiconductor laser emitting at 633 nm.

The diffraction efficiency was calculated by dividing the intensity of the first diffraction order by the intensity of the incident beam.

To evaluate the thermal stability of SRGs in the crosslinked and noncrosslinked samples, the films with gratings were heated at fixed temperatures and maintained for 30 min; then diffraction efficiency was measured. Afterwards, the same sample was heated and the procedure repeated.

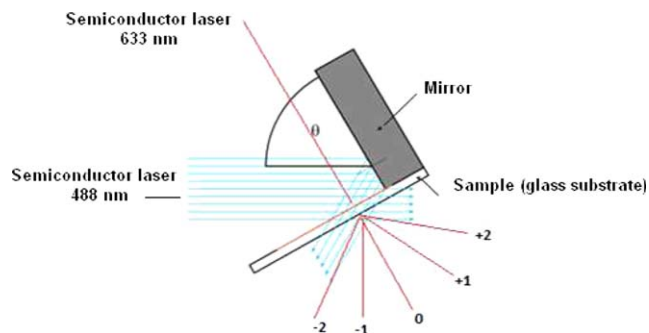


FIGURE 3 Experimental setup used for the inscription of surface relief gratings (Lloyd interferometer).

Characterization

A FTIR Nicolet 6700 Thermo Scientific device was employed to obtain infrared spectra (IR) in the mid-IR range (400–4000 cm^{-1}). Drops of the solution were deposited on NaCl windows.

Differential scanning calorimetry (DSC) was performed using a Pyris 1 device (Perkin Elmer). Glass transition temperature (T_g) was measured on the onset of thermograms obtained from second scans performed at 20 °C min^{-1} .

Atomic force microscopy (AFM), operated in tapping mode using a scan rate of 1 line s^{-1} (Agilent Technologies, 5500 scanning probe microscope), was used to analyze the efficiency of the inscription and to determine each valley depth and spacing between peaks.

Photodegradation during irradiation was analyzed in the resulting SRGs by Raman spectroscopy (RS). Raman spectra were recorded with a Renishaw in a via reflex spectrometer system equipped with a charge-coupled device (CCD) detector of 1040 \times 256 pixels and coupled to a Leica microscope with a computer-controlled x-y-z stage. An Ar laser line (514 nm, 50 mW) was used as an excitation source in combination with a grating of 2400 grooves mm^{-1} . The laser power was kept below 10% to avoid sample damage while keeping good spectra quality.

RESULTS AND DISCUSSION

Chemical Characterization

Synthesis of Azo-Urethane Polymer Films (Noncrosslinked Azo Polymer, L-PUazo)

An azo-urethane polymer (L-PUazo) was synthesized by reaction between DR19 and DI in a stoichiometric ratio $r = 1$ ($T_g = 126$ °C). The efficiency of the reaction was monitored using FTIR, following the decrease of the peak corresponding to the NCO group (about 2275 cm^{-1}). Figure 4 shows the FTIR spectrum taken after 1-day reaction at 55 °C. The peaks at 1515 and 1335 cm^{-1} were attributed to the asymmetric and symmetric vibrations of $-\text{NO}_2$ groups, respectively, and the band at 1404 cm^{-1} to the tension vibration of the N=N linkage of the azo chromophore. The isocyanate peak disappeared due to the reaction with the hydroxyl groups of the DR19. A new peak appeared approximately at 1700 cm^{-1} due to urethane bond formation.

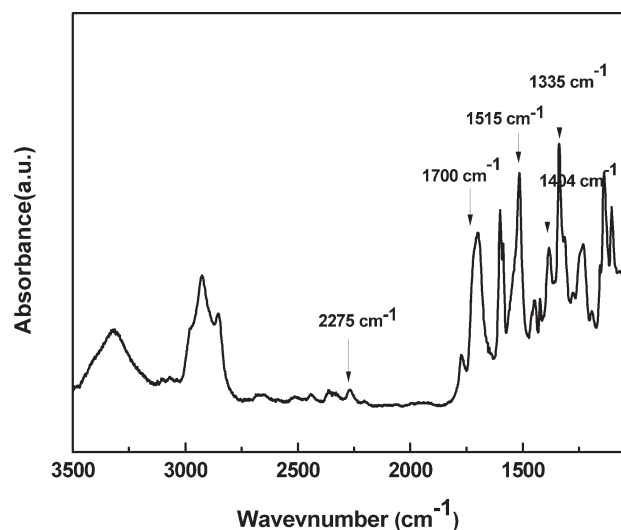


FIGURE 4 FTIR spectrum of L-PUazo after 1-day reaction at 55 °C.

Synthesis of Epoxy-Isocyanate Films (Crosslinked Azo Polymer, DGEBA-PUazo)

An azo-urethane prepolymer (PUazo) was synthesized by reaction between DR19 and DI. The sample was prepared in a stoichiometric ratio $r = \text{eq DR19}/\text{eq DI} = 0.5$ to generate reaction products with isocyanate groups in the extreme of chains.

In the following step, the reaction between the diepoxide (DGEBA) and the diisocyanate provided by PUazo resulted in polymer networks characterized by the presence of isocyanurate and oxazolidone rings in their chemical structure ($T_g = 130$ °C, Figs. 5 and 6). These networks were characterized in detail in a previous publication.²⁶

Generation of Surface Relief Grating (SRG) Azo-Urethane Polymer Films (Noncrosslinked Azo Polymer, L-PUazo)

The SRG forming rates were influenced by several factors, such as light intensity, the angle between the two interfering beams, film thickness, time, etc.^{2,13,14,27,28}

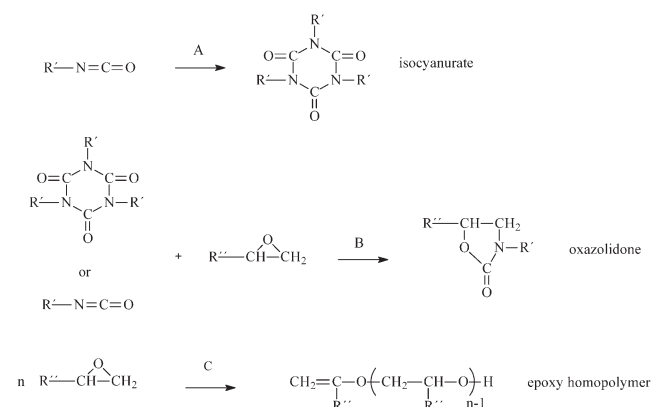


FIGURE 5 Main reactions taking place in an epoxy-isocyanate-tertiary amine system.

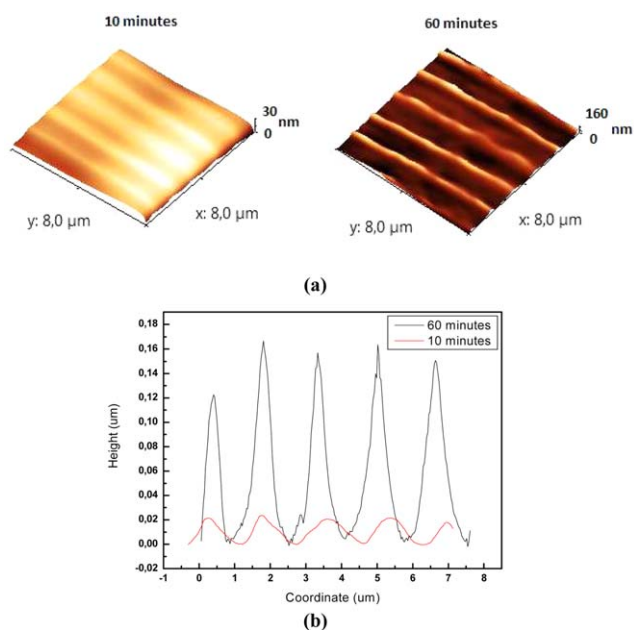


FIGURE 6 (a) Comparison of the topographic images obtained by AFM for two different irradiation times (10 and 60 min) for L-PUazo films. (b) Cross section of the AFM images obtained at these recording times.

In order to correlate these rates with the polymers structure, all the experiments were conducted under the same, controlled conditions. The films used for each comparison had approximately the same thickness (200 nm).

The exposure time was varied between 10 and 60 min, while keeping other conditions fixed (light intensity = 28 mW cm⁻², $\theta = 9^\circ$).

The gratings on the noncrosslinked polymer films were observed by AFM and are displayed in Figure 7. A very regular spaced sinusoidal surface structure with a grating periodicity of 1.49 μm was obtained after 1 h of irradiation using a very weak laser intensity of 28 mW cm⁻². Grating spacing was consistent with the one theoretically calculated for $\theta = 9^\circ$ (1.559 μm).^{2,13}

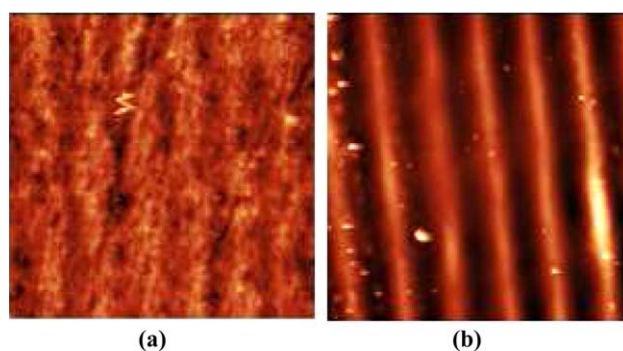


FIGURE 7 Comparison of the AFM topography images of SRGs generated for L-PUazo films under different polarization of the writing beams: (a) s-s and (b) +45°:-45°.

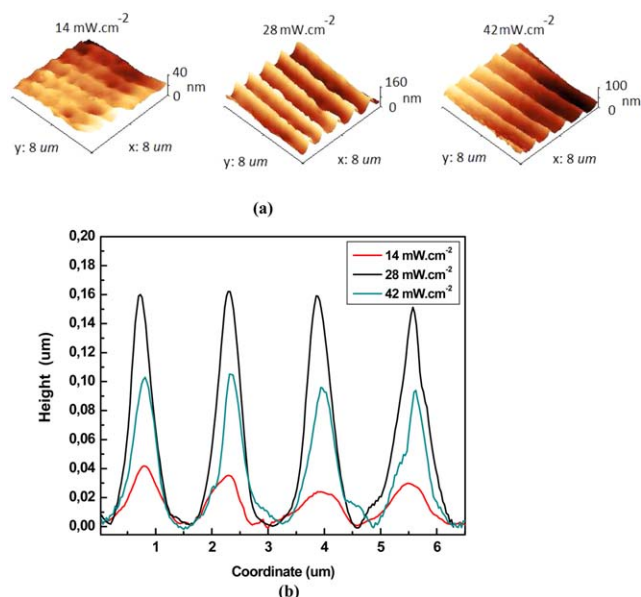


FIGURE 8 (a) Topographic images obtained by AFM for different light intensities (14, 28, 42 mW cm⁻²) for L-PUazo and (b) cross-section of AFM images.

A larger surface modulation depth of about 160 nm was obtained when exposed to +45°:-45° polarization. This substantiates the fact that the polarization of the writing beam played a significant role on the surface modulation process.^{5,29,30} Figure 7 illustrates the AFM images of SRGs surface modulation recorded on the L-PUazo films under the different polarizations of the writing beams.

The gratings efficiency induced by two laser beams under intensity recording condition (s-s polarization) yielded the highest light intensity variation. However, no spatial variation was observed in the direction of the resultant electric field nor a component of the resultant electric field along the grating vector direction.⁵ As shown in Figure 7(a), this configuration only produces a very low diffraction efficiency and small surface modulation for SRG. Similar results were expected when the two writing beams featured orthogonal polarization (s-p polarization, pure polarization recording condition). The resultant electric field on the film surface yielded the largest variation, though light intensity was uniform over the entire irradiated area.

Nonetheless, when variations of both intensity and the resultant electric field polarization occurred on a simultaneous basis (+45°:-45°), the SRGs formed yielded much higher values for surface modulation and diffraction efficiency [Fig. 7(b)]. This indicates that light intensity and the resultant electric field variations are essential for SRG formation on the azo functionalized polymer films.⁵

In general terms, it has been observed that when the intensity of the excitation laser is increased, the formation of surface reliefs turns easier, to such an extent that they reach saturation, and the degradation and photobleaching phenomena appear.^{14,28}

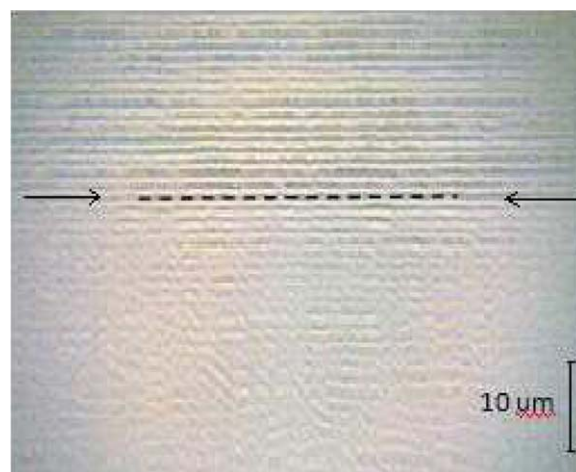


FIGURE 9 Image from optical microscopy (magnification 100×) taken in the limit of the SRG region for L-PUazo film.

In this particular case, regarding thermoplastic polymer films (L-PUazo), after reaching a certain value of light intensity recording, the depth of the relief decreased with intensity [Fig. 8(a,b)]. The maximum depth found after 1 h of irradiation was 160 nm for an intensity of 28 mW cm⁻².

Raman spectroscopy was used to evaluate films photodegradation presence after SRG generation. Raman spectra were analyzed in two distinct film regions that are illustrated in Figure 9: outside the SRG area, and on SRG. Figure 9 shows an optical image taken by Raman microscopy on a SRG (magnification of 100×). A uniform pattern of bright and dark parallel lines was observed in the zone where the SRG was generated.

The intensity of the bands associated with the N=N and phenyl-N stretching were followed (Fig. 10). The peaks were assigned as follows: the band at 1589 cm⁻¹ corresponds to the phenyl mode; the bands at 1445 and 1392 cm⁻¹

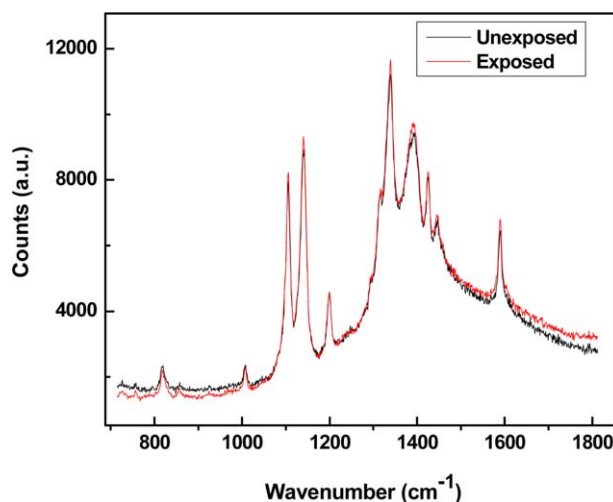


FIGURE 10 Raman spectra outside and on SRG area for L-PUazo film inscribed with a recording intensity of 28 mW cm⁻².

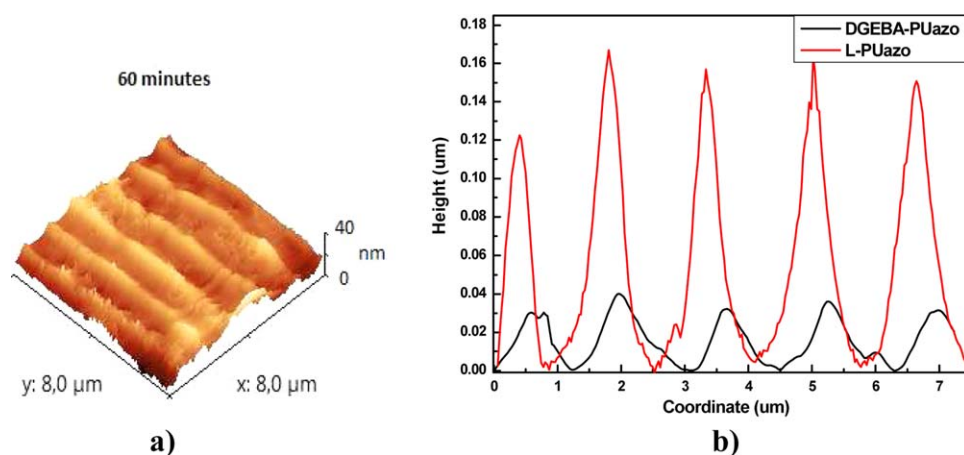


FIGURE 11 (a) Topographic image obtained by AFM for DGEBA-PUazo using an intensity of 28 mW cm^{-2} during 60 min. (b) Comparison of the cross-section of the AFM images obtained for LPUazo and DGEBA-PUazo under the same experimental conditions (recording intensities of 28 mW cm^{-2} , grating period of $1.5 \mu\text{m}$, $+45\text{:-}45$ polarization light, 60-min irradiation time).

correspond to the $\text{N}=\text{N}$ stretching and the peak at 1142 cm^{-1} to the phenyl- N stretching band.^{30,31} A reduction of these bands intensity should be observed if photodegradation took place. As far as L-PUazo films are concerned, the intensity of the bands remained constant, thus indicating that no photodegradation occurred during SRG inscription.

To investigate the crosslinking effect on SRGs fabrication, we evaluated the same experimental conditions used for L-PUazo (noncrosslinked azopolymer).

Epoxy-Isocyanate Films (Crosslinked Azo Polymer, DGEBA-PUazo)

A satisfactory finding was that surface gratings were also obtained on crosslinked film. SRGs of about 30 nm depth were inscribed under the same irradiation conditions (recording intensities of 28 mW cm^{-2} , grating period of 1.5

μm , $+45\text{:-}45$ polarization light, 60-min irradiation time) [Fig. 11(a)]. In spite of the difference in process efficiency regarding these polymers as compared to noncrosslinked samples [Fig. 11(b)], the possibility of generating SRG on previously crosslinked polymers in which the large-scale polymer chain migration is restricted by the rigid backbone was notable, and it has scarcely been accounted for in the literature.²⁰

In order to improve the inscription efficiency, the light intensity was increased keeping all the other parameters constant. SRGs were satisfactorily generated. Figure 12(a) depicts the topography image obtained by AFM after 1 h of irradiation. From the cross-sections of the AFM images of the gratings [Fig. 12(b)], it can be noticed that the grating depth increases from 30 to 85 nm when a greater light intensity is used (244 mW cm^{-2}). As a consequence, it is worth

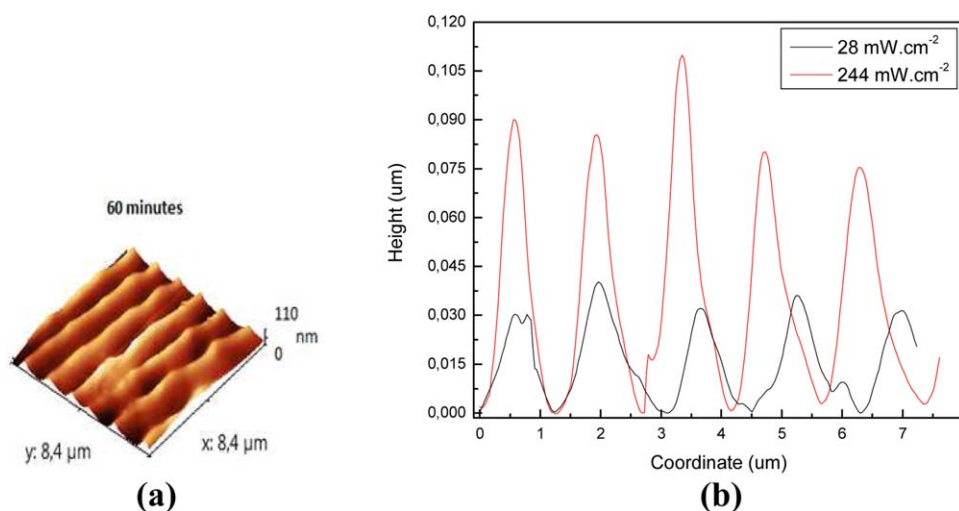


FIGURE 12 (a) Topographic image obtained by AFM for DGEBA-PUazo and (b) cross section of the AFM images of the gratings for DGEBA-PUazo during 60 min of irradiation (recording intensities of 28 and 244 mW cm^{-2}).

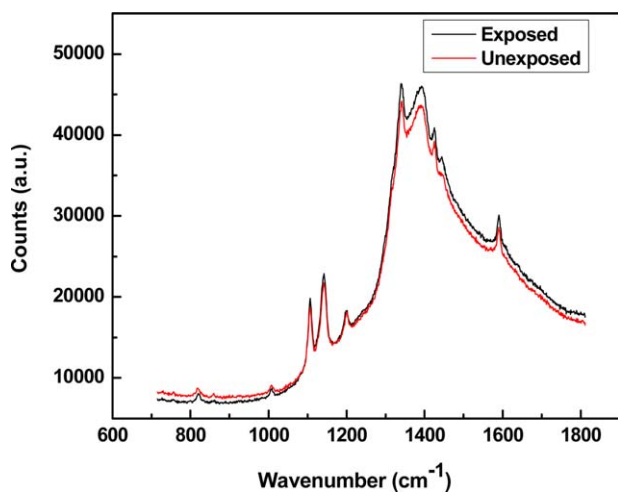


FIGURE 13 Raman spectra outside and on the SRG area for DGEBA-PUazo films (recording intensity of 244 mW cm^{-2}).

underlining that considering the crosslinked structure of these polymers, this surface modulation is quite remarkable and unique.

In addition, Raman spectra (Fig. 13) indicated that, despite the high light intensity employed in DGEBA-PUazo films, no photodegradation effects were observed.

Comparison of the Thermal Stability of SRG

Another important requirement of SRG is shape stability in terms of long-term storage and durability at high temperatures. In order to investigate the thermal stability of SRG in the crosslinked and noncrosslinked samples, the films with gratings were heated at several temperatures, and their diffraction efficiency was measured. The actual diffraction efficiency was in the order of 0.40% for PUazo and of 0.35% for the crosslinked sample.

Figure 14 shows the variation of the normalized diffraction efficiency with temperature. As temperature increased, the

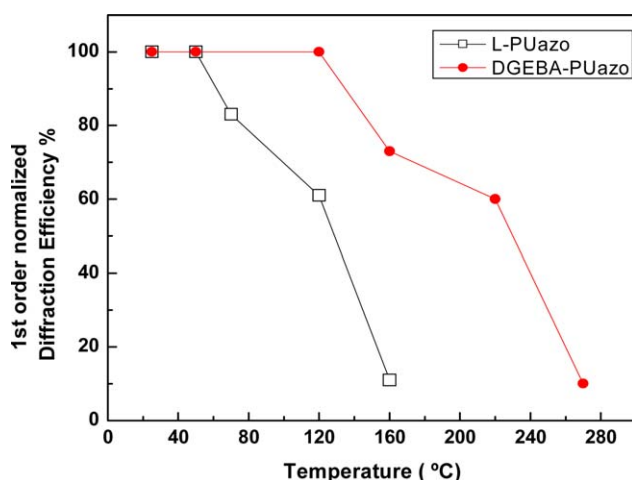


FIGURE 14 Comparison of gratings thermal stability in crosslinked and noncrosslinked samples.

efficiency was kept relatively stable for the crosslinked sample (DGEBA-PUazo) even upon heating up to $140 \text{ }^\circ\text{C}$ ($T_g = 130 \text{ }^\circ\text{C}$, for bulk sample), while it decreased to 40% for L-PUazo ($T_g = 126 \text{ }^\circ\text{C}$). Then, when the samples were heated to $160 \text{ }^\circ\text{C}$, the grating of the noncrosslinked samples disappeared altogether, while for the crosslinked samples, 70% of the initial diffraction efficiency remained. Thus, it becomes clear that crosslinking reactions significantly improved thermal stability of SRGs even when no evident differences in T_g existed between the samples.

CONCLUSIONS

Crosslinked azobenzene-containing epoxy-isocyanate polymers were prepared; and surface relief gratings were successfully inscribed on them. The inscription efficiency was compared with a noncrosslinked azo-polyurethane. Indeed, even though the mobility of the azo chromophores was restrained in the crosslinked network, certain fractions of the azo chromophores maintained high mobility, enough to generate surface reliefs of remarkable depth.

In addition, crosslinked films exhibited good grating stability, even at high temperatures. The shape of the gratings was retained and significant diffraction was still observed even well above the T_g of the bulk sample. On the other hand, for noncrosslinked samples, gratings and diffraction rapidly decreased upon heating near the T_g of the bulk sample.

ACKNOWLEDGMENTS

The authors acknowledge the financial support of the National Research Council (CONICET, Argentina), the National Agency for the Promotion of Science and Technology (ANPCyT, Argentina) and the Universidad de Mar del Plata (Argentina).

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