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Fast and stable recording of birefringence and holographic gratings in an azo-polymethacrylate using a single nanosecond light pulse

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Pulsed light-induced recording in azobenzene polymers has recently been studied due to its potential use in optical storage applications. In this paper we study the photoinduced birefringence (Δn) and holographic grating recording in an azobenzene side chain liquid-crystalline polymethacrylate irradiating with a single 4 ns light pulse at 532 nm. For some irradiation conditions, Δn grows in less than 50 ns reaching an essentially stable value of about 10^{-2}. Holographic gratings have been registered using intensity and polarization patterns. Fast response and stability, similar to those of Δn, was observed in the holographic recording process. Both light-induced anisotropy and relief contributions have been found in the case of gratings recorded using intensity patterns, relief being the dominant contribution at high recording energies. Polarization gratings have been recorded using two orthogonally circularly polarized beams. The resultant gratings showed stable efficiencies up to 0.8% (measured at 633 nm in 1-μm-thick films) and no measurable relief was observed. © *2005 American Institute of Physics*. [DOI: 10.1063/1.2124647]

I. INTRODUCTION

Polymer films containing azobenzene units have been intensively studied because they are promising systems for optical applications such as holographic and digital storage, liquid-crystal (LC) command surfaces, and nonlinear optical devices.[1–8] Molecular reorientations can be induced in these materials through *trans-cis-trans* isomerization processes. Usually, polarized light from a cw Ar^+ laser in the blue-green region (488 or 514 nm), in which there are optical absorptions associated with both *trans* and *cis* isomers, is used to induce those isomerizations. Due to the selection rules of the transitions involved in the absorption processes, a preferential orientation of the azo molecules perpendicular to the polarization vector of the irradiating light is achieved. High diffraction efficiency holographic gratings associated with changes in the refractive index (intensity and polarization gratings) as well as with a relief modulation in the film surface (relief gratings) have been reported.[9–11] The basic mechanism involved in grating generation is the photoinduced preferential orientation (perpendicular to the blue light polarization direction) of the azo moieties trough *trans-cis-trans* isomerizations.

Most of the experiments dealing with holographic storage in azobenzene polymers have been performed using cw lasers. Although *trans-cis-trans* photoisomerizations take place in a few picoseconds,[12] it can be expected that many isomerization cycles will be needed to induce molecular reorientations. However, both birefringence (Δn) and holographic diffraction gratings, induced by short laser pulses (in the nanosecond to femtosecond ranges) have recently been reported.[13–21] In particular several papers have appeared dealing with photoinduced effects in azobenzene polymers by a single 532 nm pulse of a few nanoseconds.[16–21]

Using an azobenzene polyester Hildebrandt *et al.*[16] have found that Δn can be induced with a single 532 nm pulse. Δn first increases after the pulse and later on decreases by at least one order of magnitude. The evolution time ranges from microseconds to seconds depending on the pulse energy. The final Δn values are about 10^{-3}. Borshch *et al.*[21] have obtained similar results with a bisphenol-A diglycydil ether with 4-aminoazobenzene units in the side chain. In this case the anisotropy continues growing for 50–70 μs after the pulse. Later on, Δn shows a strong decrease in times ranging from seconds to hours. A residual Δn value remains stable for a long time.

Holographic intensity gratings induced in cross-linkable azobenzene polymers with pulsed 532 nm light were reported for the first time by Schmitt *et al.*[17] These gratings are induced by a periodically intensity-modulated interference pattern. The authors associated the grating formation to thermal effects. No anisotropy effects were reported.

Ramanujam *et al.*[18] were able to induce polarization gratings in an amorphous azo-polyester. A polarization grating is induced by the interference of two circularly polarized beams with orthogonal polarizations. The light intensity is uniform along the interference pattern while the polarization direction of the light is periodically modulated. Both surface relief and anisotropy gratings were produced by a pulse excitation of a few nanoseconds, but the dominant contribution

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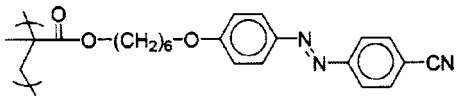

FIG. 1. Chemical structure of PC6 polymer.

to the grating efficiency seems to be associated with surface relief. Besides, the efficiency shows a strong time evolution reaching a maximum at several seconds after the pulse.

Leopold *et al.*[19] have also reported the production of holographic intensity gratings in several azo copolymers under nanosecond pulses of 532 nm light. For low pulse energies diffraction is mainly due to a *cis-trans* population grating that decays in a millisecond time scale. The remaining orientational grating is very small. For pulse energies above a certain threshold a stable surface grating appears. It has been associated to thermal effects. The authors were not able to induce polarization gratings in the azo-polymers.

Baldus *et al.*[20] described the induction of holographic gratings in different polymers (some of them containing azo units). In intensity gratings induced with low-energy pulses (10 mJ/cm^2), the grating efficiency first increases and then strongly decreases in about 2 μs after the laser pulse. Some efficiency remains, which has been associated to surface relief gratings. Also in this case, no polarization gratings could be induced in the films and the relief gratings were associated with thermal effects.

Finally, Borshch *et al.*[21] have recently reported the formation of holographic polarization gratings using 532 nm pulses in some epoxy polymers containing azobenzene units in the side chain. The dynamics of polarization grating buildup is similar to that of birefringence. The diffraction efficiency grows during the pulse and continues growing for 50–70 μs. After reaching a maximum the efficiency shows a strong decrease in a few seconds. Some diffraction efficiency (about 0.5% in a 140-μm-thick film) seems to remain after 20 s although it has not been checked whether it is due to a phase grating or to a surface relief one.

The fast induction of stable anisotropy and/or polarization gratings is important for optical storage applications. The results summarized above show that although birefringence as well as anisotropy and polarization gratings have been induced with the interference pattern of two coherent nanosecond pulses of 532 nm light, the most important contribution to the stable diffraction efficiency (for the materials and experimental conditions used) seems to come from relief gratings (but perhaps in the work of Borshch *et al.*[21] in which the contribution of surface relief gratings to the diffraction efficiency has not been analyzed). On the other hand, the induced birefringence as well as the anisotropy and polarization gratings show a time evolution after the laser pulse, in such a way that stable values are reached in times ranging from tens of microseconds to seconds or even hours.

Trying to get a faster response to pulsed excitation, associated with the photoorientation of the azo units, we have undertaken a study of photoinduced Δn and holographic gratings in several azobenzene polymers using a single pulse of 532 nm light and different irradiation conditions. In this paper we present the results corresponding to an azobenzene containing polymethacrylate. Both Δn and holographic gratings have been produced and analyzed. Stable values of Δn and diffraction efficiency have been reached in times of about 50 ns, which is close to the time resolution limit of our experimental setup. Holographic gratings recorded using intensity patterns showed anisotropy and relief contributions. Polarization gratings with efficiencies up to 0.8% (measured at 633 nm) have been obtained with film thickness of about 1 μm and no measurable relief associated.

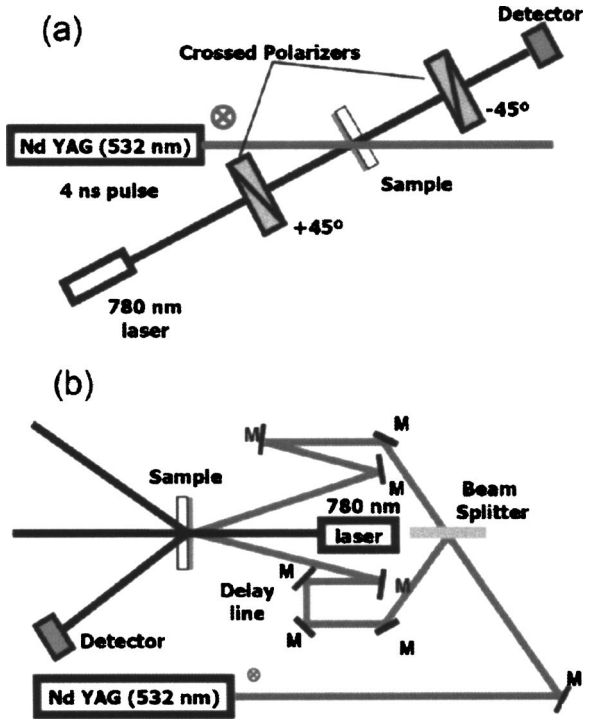

FIG. 2. Experimental setup for (a) photoinduced birefringence measurements and (b) holographic recording and diffraction efficiency measurements.

II. EXPERIMENTAL SECTION

The chemical structure of the polymer chosen for this study (PC6) is shown in Fig. 1. The polymer was synthesized in dimethylformamide (DMF) using azobisisobutyronitrile (AIBN) as thermal initiator. This polymer is liquid crystalline showing a broad smectic A mesophase determined by polarization microscopy. A glass transition (T_g) was detected at 60 °C and the isotropization transition (T_i) at 160 °C on the second heating scan of the differential scanning calorimetry (DSC) study (scan rate: 10 °C/min). A Perkin Elmer DSC-7 apparatus was used and T_g was determined at the midpoint of the base line jump and T_i at the maximum of the peak. Molecular weights were characterized by gel permeation chromatography (GPC) using polystyrene standards and the values obtained were 24 000 for M_n and 37 000 for M_w (polydispersity index 1.5).

Films were produced by casting from a solution of the polymer in dichloromethane onto clean glass substrates. The thickness was measured using a DEKTAK profilometer obtaining values in the range of 0.4–1 μm thick. Before performing any experiment, films were heated up to 180 °C (above the isotropization temperature) in order to erase any

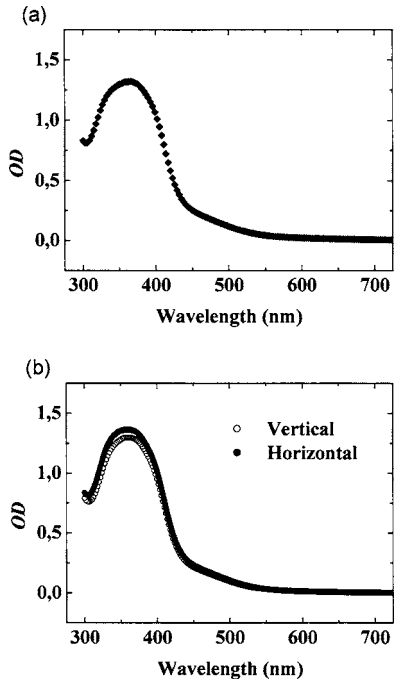

FIG. 3. (a) Optical absorption and (b) dichroism of a film of PC6 after one single pulse.

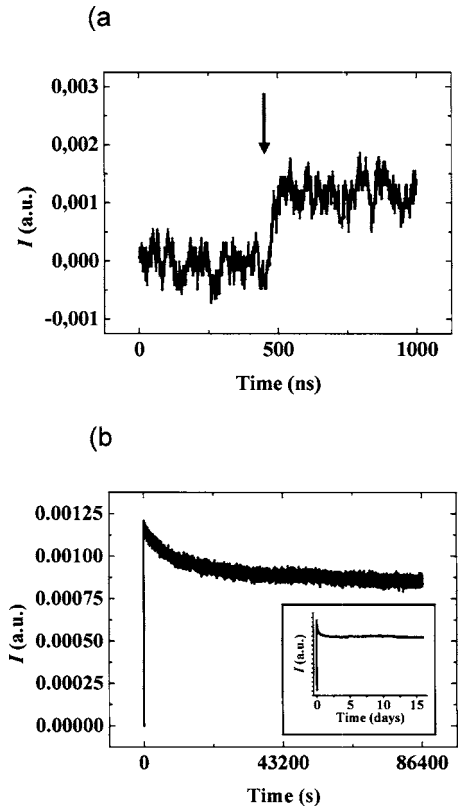

FIG. 4. Intensity transmitted by a polymer film placed between crossed polarizers as a function of time after irradiation with a laser pulse (100 mJ/cm^2) (a) in the range of nanoseconds, (b) in the range of seconds, and in the range of days (inset). The arrow indicates the time at which the pump beam is triggered.

dependence due to the morphology induced either during the preparation process or in previous experiments. Films treated in this way showed reproducible behavior with respect to Δn and holographic recording. Optical absorption was measured using a Varian Cary 500 UV-visible-IR spectrophotometer.

Δn measurements were performed using the setup shown in Fig. 2(a). The sample was placed between crossed polarizers with their polarization directions at ±45° with the vertical axis. The light from a 780 nm diode laser (30 mW) transmitted through the polarizer-sample-polarizer system was measured with a Si *p-i-n* photodetector. The response time of our system was about 50 ns. It has been checked that the 780 nm light does not introduce any changes in the Δn values. The transmitted intensity I is given by the equation

$$I = I_0 \sin^2\left(\frac{\pi|\Delta n|d}{\lambda}\right), \tag{1}$$

where I_0 is the intensity transmitted by the as-quenched films between parallel polarizers, d the film thickness, and λ the wavelength of the measuring light (780 nm).

The setup used for holographic recording and diffraction efficiency measurements is shown in Fig. 2(b). The 532 nm light from the second harmonic of a pulsed (4 ns pulses) Nd:YAG (yttrium aluminum garnet) laser was divided into two equal intensity beams which were made to interfere on the film. The angle between the two interfering beams was 6° giving a pattern with a spacing of approximately 5 μm between lines. In some of the experiments the 532 nm beams were *s* polarized and an intensity modulation was generated on the surface of the film. In other experiments the two 532 nm beams were left- and right-circularly polarized (obtained by inserting properly oriented quarter-wave plates). In this way the light intensity is constant along the film and a polarization holographic grating was obtained.

As for Δn measurements, the time evolution of the diffraction efficiency was measured using a linearly polarized 780 nm diode laser and a Si *p-i-n* photodiode. The light diffracted in first-order maximum was measured. For polarization gratings, the selectivity of the grating for circularly polarized light characteristic of this type of gratings was checked by using a circularly polarized beam from a He-Ne laser at 633 nm. During the measurements none of these lights induced changes in the film properties.

III. RESULTS AND DISCUSSION

The optical-absorption spectrum of a PC6 film (0.4 μm thick) measured after heating it up to 180 °C and quenching to RT, is shown in Fig. 3(a). The main band at 370 nm and the shoulder at about 450 nm correspond to the π-π^* and n -π^* electronic transitions of the *trans* azo units, respectively. The optical density (OD) at 532 nm (the tail of the 450 nm band) is less than 0.1. Thus the 532 nm light will penetrate the film with a small attenuation.

The film has been irradiated with a single 4 ns pulse (130 mJ/cm^2) of vertically polarized 532 nm light. The absorption spectrum measured with both vertically and horizontally polarized light (optical dichroism) are shown in Fig. 3(b). It can be seen that the absorption corresponding to the horizontal polarization is larger than that for vertical polarization. Taking into account that the transition dipole of the π-π^* transition is parallel to the long axis of the *trans* iso-

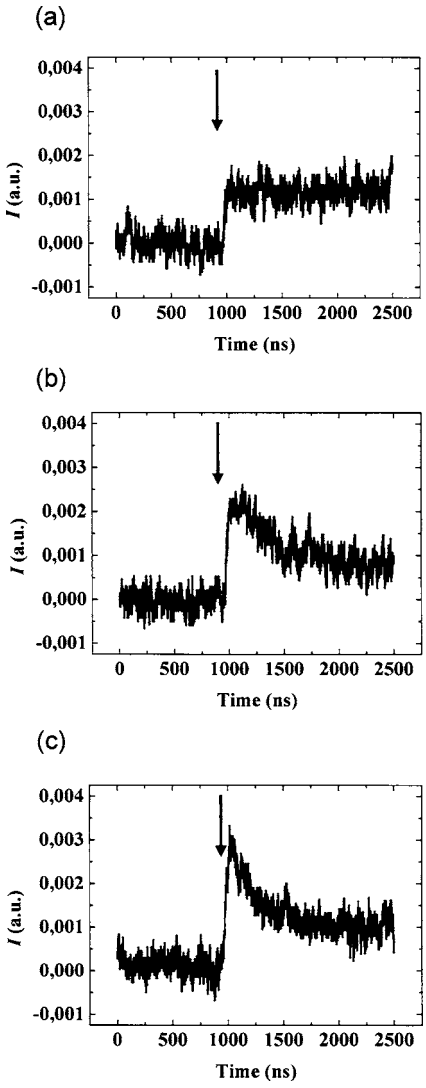

FIG. 5. Intensity transmitted by a polymer film placed between crossed polarizers as a function of time after irradiation with a laser pulse for three different energies: (a) 100, (b) 125, and (c) 140 mJ/cm^2. The arrow indicates the time at which the pump beam is triggered.

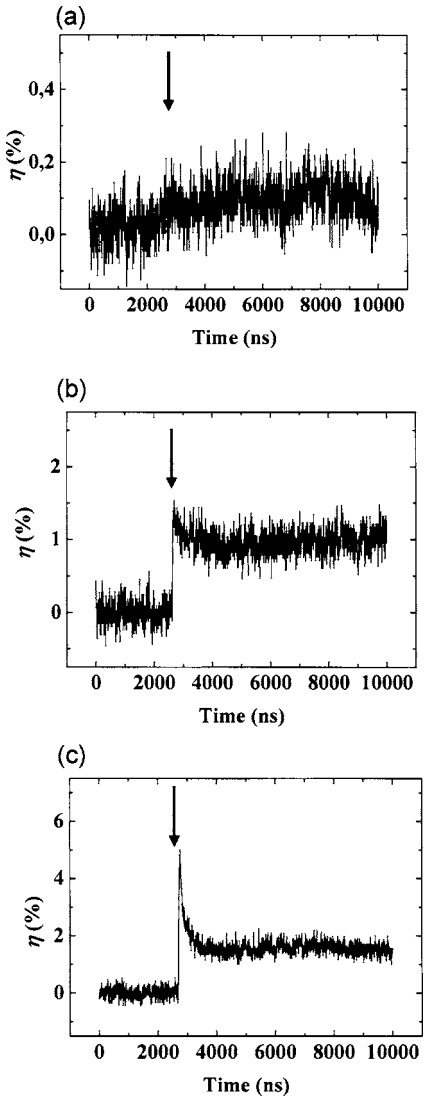

FIG. 6. Diffraction efficiency as a function of time (nanosecond range) of a film irradiated with an intensity pattern for three different energies: (a) 70, (b) 150, and (c) 240 mJ/cm^2. A *p*-polarized 780 nm laser beam was used as a probe. The arrow indicates the time at which the recording beam is triggered.

mer, we conclude that the 532 nm light pulse has induced a preferential orientation of the *trans* units perpendicular to the polarization of the exciting light. This orientation is stable and is of the same type as the one induced with cw light of 488 or 514 nm.

No detectable changes have been found in the optical-absorption region around 450 nm. Since this is one of the regions where the *cis* isomers absorb we have to conclude that the *cis* concentration in the irradiated film is rather small. A similar conclusion can be derived from the small changes in the 370 nm absorption associated with the *trans* isomers.

The time evolution of light intensity transmitted through the polarizer-film-polarizer system after irradiation with a single pulse (4 ns, 100 mJ/cm^2) of linearly polarized 532 nm light is shown in Fig. 4. Figure 4(a) shows this evolution in the nanoseconds range while Fig. 4(b) shows the evolution for times up to 1 day. It can be seen that the transmitted intensity that is proportional to $|\Delta n|^2$ for low $|\Delta n|$ values [see Eq. (1)] shows a fast increase after pulse excitation reaching a maximum in about 50 ns. Since this is the time resolution of our setup we can only say that the induction time for birefringence is at most 50 ns. Later on Δn remains essentially stable with a decrease of about 15% in 24 h. Then birefringence remains stable within ±1% at least over a period of 2 weeks [see inset Fig. 4(b)].

Similar evolutions have been obtained with different energy pulses. The results are shown in Fig. 5. For low energies the transmitted intensity is low and increases with the incident energy of the pulse. For pulse energy values bigger than 100 mJ/cm^2 a strong decrease is observed in times close to 1 μs after the pulse. Later on birefringence remains essentially stable. The decrease is bigger as the pulse energy increases but the stable value of $|\Delta n|$ is similar in all the cases (about 10^{-2}).

Holographic gratings have been induced in as-quenched films (1 μm thick) with the interference pattern produced by two *s*-polarized coherent beams of 532 nm light. This pattern consists of periodically modulated intensity regions of

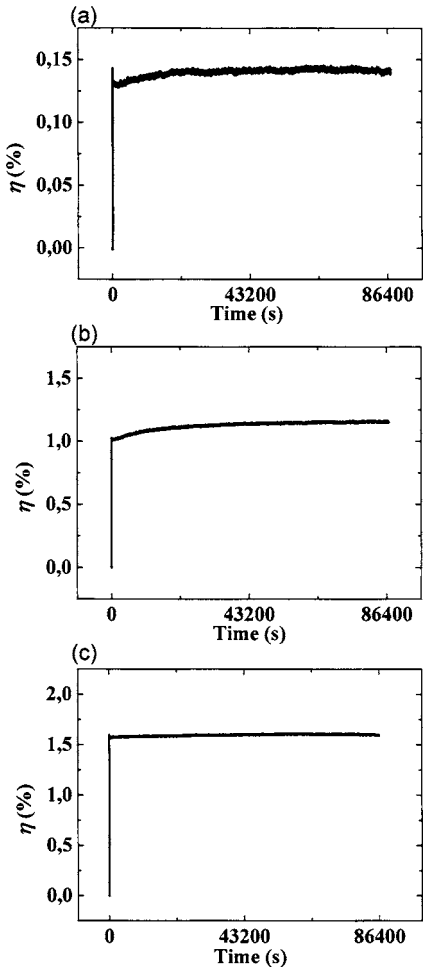

FIG. 7. Diffraction efficiency as a function of time (in the second range) of a sample irradiated with an intensity pattern for three different energies: (a) 70, (b) 150, and (c) 240 mJ/cm^2. A *p*-polarized 780 nm laser beam was used as a probe. The pulse is triggered at $t=0$ s.

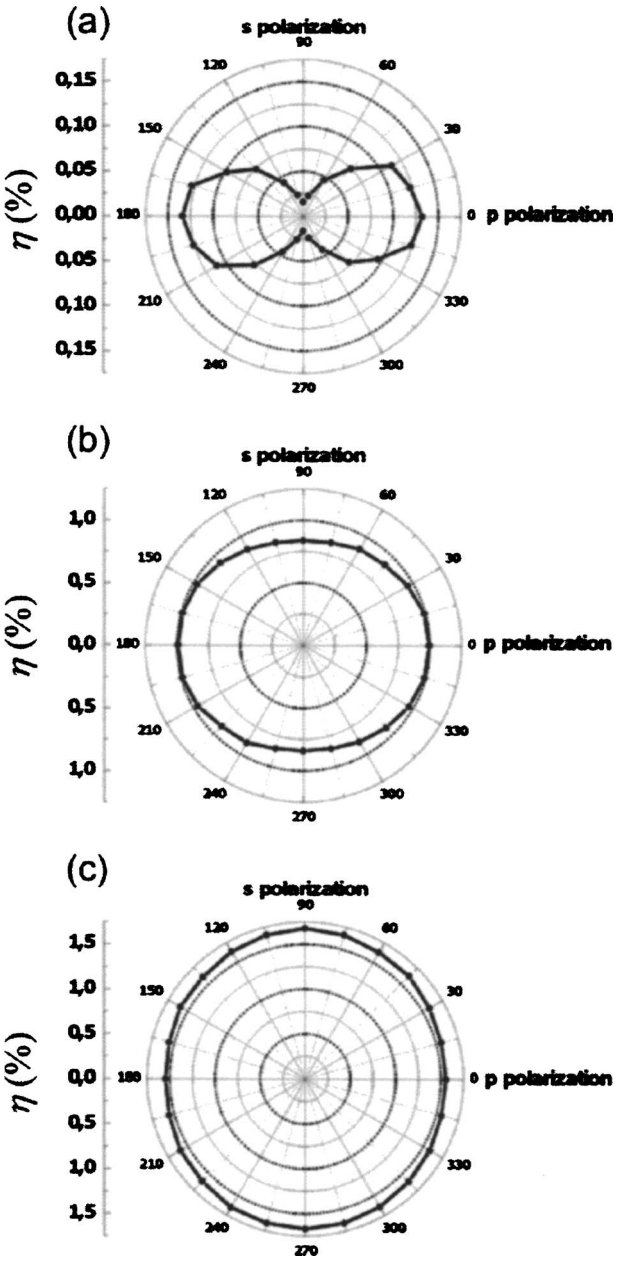

FIG. 8. Diffraction efficiency as a function of polarization direction (linearly polarized light from a 780 nm laser) of a sample irradiated with an intensity pattern for three different energies: (a) 70, (b) 150, and (c) 240 mJ/cm^2.

s-polarized light. The grating efficiency has been measured with *p*-polarized 780 nm light. The time evolution (in the nanosecond range) of the grating efficiency is shown in Fig. 6 for different pulse energies. The behavior is similar to that of birefringence. Thus, we conclude that we need at most 50 ns to induce the gratings. The stability of the intensity gratings has been followed up to 1 day. The results for different powers are given in Fig. 7. It can be seen that the induced gratings are stable reaching values up to 1.6%.

As it has been said in the Introduction, both anisotropy and relief gratings have been observed in different azo polymers after nanosecond pulsed irradiation with 532-nm light. The relief contribution seemed to be the dominant one in all the cases. To check for the presence of both contributions in our intensity grating experiments, we have measured the diffraction efficiency as a function of the 780 nm light polarization direction. The results are given in Fig. 8. Gratings induced with low pulse energy show a strong dependence of the grating efficiency with the polarization direction of the reading light while the gratings induced with higher-energy pulses show a small dependence. Since relief gratings are not sensitive to the polarization direction of the reading beam, our results indicate that both anisotropy and relief gratings contribute to the diffraction efficiency and that relief contribution increases with the energy of the exciting pulse.

Surface relief has also been checked with a profilometer. The relief observed for different pulse energies is shown in Fig. 9. In agreement with the results of Fig. 8 surface relief and consequently its contribution to the grating diffraction efficiency increases with the recording pulse energy.

The results reported up to now show that stable birefringence as well as anisotropy gratings can be induced with an induction time shorter than 50 ns. In addition their time evolution after reaching the maximum value is small if pulse energies around 100 mJ/cm^2 for birefringence and 70 mJ/cm^2 (35 mJ/cm^2 per beam) for intensity gratings are used. Relief gratings have also been observed.

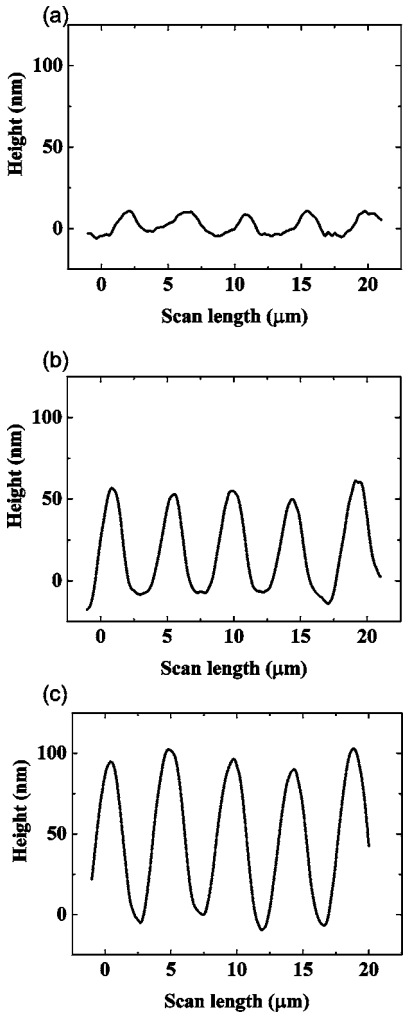

FIG. 9. Surface relief profiles of a sample irradiated with an intensity pattern for three different energies: (a) 70, (b) 150, and (c) 240 mJ/cm^2.

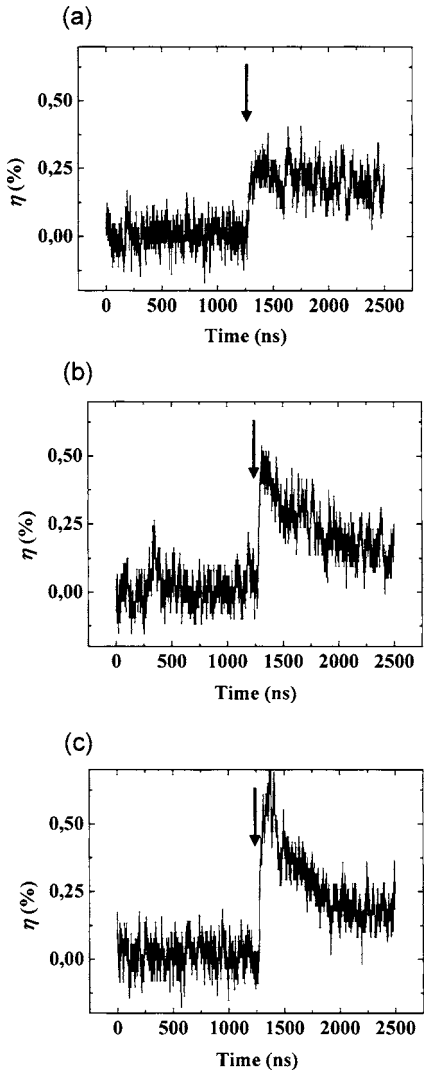

FIG. 10. Diffraction efficiency as a function of time (nanosecond range) of a sample irradiated with a polarization pattern for three different energies: (a) 100, (b) 130, and (c) 150 mJ/cm^2. A *p*-polarized 780 nm laser beam was used as a probe. The arrow indicates the time at which the recording beam is triggered.

Polarization gratings induced in our films by the interference of two circularly polarized light pulses with orthogonal polarizations have also been studied. The time evolution of the diffraction efficiency for these polarization gratings induced with different pulse energies and measured with *p*-polarized light is shown in Fig. 10. As for intensity gratings the measured time for building up polarization gratings is about 50 ns and is likely limited by the time resolution of our setup. Also the grating shows long term stability (Fig. 11). No surface relief associated to these gratings has been detected in profilometer measurements. Without a relief contribution the efficiency of polarization gratings should have the same dependence on Δn as the light transmitted between crossed polarizers in Δn measurements.[22] This has been found in our case as can be seen by comparison of Figs. 4 and 5 and Figs. 10 and 11.

Finally when the grating efficiency is read with circularly polarized 633 nm light the polarization selectivity typical of polarization gratings has been observed. Thus only the +1 order is visible while the −1 one is not (order +1 is 100 times more intense than order −1). This also indicates that relief gratings do not appear together with polarization gratings. Thus, the efficiency of these gratings is only due to an anisotropy contribution. Values of diffraction efficiency up to 0.8% have been reached for a film of about 1 μm thick.

IV. CONCLUSIONS

We report in this paper a study on the recording of Δn and holographic gratings in films of a side chain liquid-

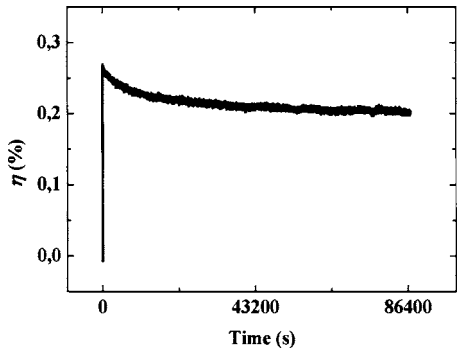

FIG. 11. Diffraction efficiency as a function of time (second range) of a sample irradiated with a polarization pattern (100 mJ/cm^2). A *p*-polarized 780 nm laser beam was used as a probe. The pulse is triggered at $t=0$ s.

crystalline polymethacrylate, using one single 4 ns laser pulse at 532 nm. For some irradiation conditions Δn grows in 50 ns reaching a value of about 10^{-2}. This value is essentially stable after 15 days. Holographic gratings have also been recorded using the same light source. Both intensity and polarization patterns were employed. A stable diffracted intensity was induced in 50 ns. In the case of intensity gratings we found anisotropy and relief contributions to the diffraction efficiency. At low energies bulk birefringence plays a relevant role as it is evidenced by the different efficiencies when gratings are read with *p* and *s* polarizations. On the other hand, relief gratings seem to be dominant at high energies. Diffraction efficiency values as high as 1.5% (measured at 780 nm) were obtained in one single pulse. Polarization gratings were also registered using two orthogonally circularly polarized beams. No measurable relief was observed associated to this kind of recording. In addition the formed grating showed the typical polarization properties present in polarization gratings. Only one diffracted order was detected when circularly polarized light was used as a probe beam. Stable values of diffraction efficiency up to 0.8% were measured in these gratings when read with a circularly polarized beam at 633 nm.

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