

## Azo Polymers for Reversible Optical Storage. 6. Poly[4-[2-(methacryloyloxy)ethyl]azobenzene]

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**ABSTRACT:** Poly[4-[2-(methacryloyloxy)ethyl]azobenzene] (pMEA) has been synthesized and its reversible optical storage properties tested in comparison with previously reported electron-donor–electron-acceptor substituted azobenzene-containing polymers. The cis–trans thermal isomerization rate is fairly slow in pMEA, and while it is possible to induce birefringence using UV-polarized light, the levels and rates are not reproducible, due to the persistent cis population. Birefringence can, however, be induced with polarized visible light (514.5 nm), but at lower levels than in the previous polymers, due to the lower absorbance levels at this wavelength. The efficiency of the inducing birefringence process is about  $4.3 \times 10^{-6} \text{ cm}^3/\text{J}$  and is comparable to the efficiency of the same processes in the previous polymers only if the differences in absorbances are considered. pMEA is also a good substrate for high efficiency diffraction gratings inscription on the film surface. A 90-nm grating (4% efficiency) can be obtained in only 35 min of irradiation with 22 mW/cm<sup>2</sup> at 514.4 nm.

### Introduction

In a previous series of papers<sup>1–6</sup> we have demonstrated how the trans–cis–trans isomerization cycles of azobenzenes bound in high glass transition temperature polymers could be used to induce birefringence in the polymer film. Linearly polarized light orients an excess of the azobenzene groups perpendicularly to the polarization direction, while circularly polarized light restores the original disorder of orientations, thus “erasing” the induced birefringence. Most of the experiments were performed on donor–acceptor substituted azobenzenes, typically amino–nitro substituted. It is well-known that such groups absorb strongly in the visible region of the electronic spectrum. For example, poly{4'-[[2-(acryloyloxy)ethyl]ethyl]amino]-4-nitroazobenzene} (pDR1A); the abbreviation comes from the precursor: Disperse Red 1) has a maximum absorbance at 490 nm. The azobenzene groups are normally in their trans configuration, but the cis isomers absorb at the same wavelength.<sup>7</sup> This means that irradiation with an argon laser at 514 or 488 nm will photochemically activate both the trans–cis and cis–trans isomerization processes. The cis isomers are relatively short lived even in the absence of irradiation;<sup>7,8</sup> thus—after the laser has been switched off—only trans isomers are present in the film.

If the azobenzene groups have no electron-donor–electron-acceptor substituents or no amino substituents, the thermal cis–trans isomerization is relatively slow.<sup>9</sup> No electron-donor–electron-acceptor substituents also means that the maximum absorbance will be shifted toward higher energy (shorter wavelength) for the trans isomer. The cis isomer still has a longer wavelength absorbance due to the steric hindrance present in the molecule. How would birefringence be photochemically induced in such a system, where repetitive trans–cis–trans isomerization cycles are less probable? This paper presents the synthesis and optical storage properties of a polymer containing an azobenzene group without

electron-donor and electron-acceptor substituents: poly[4-[2-(methacryloyloxy)ethyl]azobenzene].

### Experimental Section

**Materials. 4-(Phenylazo)phenethyl Alcohol.** To obtain 4-(phenylazo)phenethyl alcohol, a mixture of aminophenethyl alcohol (15.0 g, 0.11 mol) and nitrosobenzene (10.0 g, 0.094 mol) was dissolved in absolute ethanol (100 mL). The mixture was stirred, and glacial acetic acid (10 mL) was added slowly. The mixture was then heated in a water bath at about 70 °C for 2 h. After cooling down to room temperature, the solution was poured into distilled water (1 L). The solid was filtered and air dried. The solid was recrystallized from an ethanol/water mixture (3/2 by volume). Yield: 18.2 g of orange–yellow crystals (85%). <sup>1</sup>H-NMR (CDCl<sub>3</sub>):  $\delta$  1.52 (–OH), 2.95 (ArCH<sub>2</sub>–), 3.93 (–OCH<sub>2</sub>–), 7.38 (aromatic, ortho to –CH<sub>2</sub>–), 7.45 (aromatic, meta and para to –N=N–), 7.88 (aromatic, ortho to –N=N–).

**4-[2-(Methacryloyloxy)ethyl]azobenzene (MEA).** A solution of 4-(phenylazo)phenethyl alcohol (13.5 g, 0.06 mol) and triethylamine (9.0 mL) was dissolved in THF (200 mL). The solution was kept in an ice bath for 10 min. A solution of distilled methacryloyl chloride (6.0 mL, 0.06 mol) was added slowly to the above mixture. After the addition of methacryloyl chloride, the resulting mixture was stirred at room temperature overnight. The solvent was removed by rotovap, and the residue was washed with a solution of sodium carbonate (3.2 g) in water (100 mL). The solid was filtered, washed with water, and air dried. The solid was recrystallized from ethanol. Yield: 11.1 g of orange–yellow crystals (80%). <sup>1</sup>H-NMR (CDCl<sub>3</sub>):  $\delta$  1.95 (–CH<sub>3</sub>), 3.05 (ArCH<sub>2</sub>–), 4.40 (–OCH<sub>2</sub>–), 5.53 and 6.10 (CH<sub>2</sub>=), 7.42 (aromatic, ortho to –CH<sub>2</sub>–); 7.51 (aromatic, meta and para to –N=N–); 7.90 (aromatic, ortho to –N=N–).

**Poly[4-[2-(methacryloyloxy)ethyl]azobenzene] (pMEA).** Polymerization was performed in dry toluene with 1% by weight benzoyl peroxide as initiator at 90 °C for 2 days. The polymer was precipitated in methanol and purified by reprecipitation in a THF/methanol system. The yield was 40%, and the polymer had a molecular weight of 26 000 (relative to polystyrene) and a *T<sub>g</sub>* of 80 °C. There was no sign of thermal decomposition up to 300 °C.

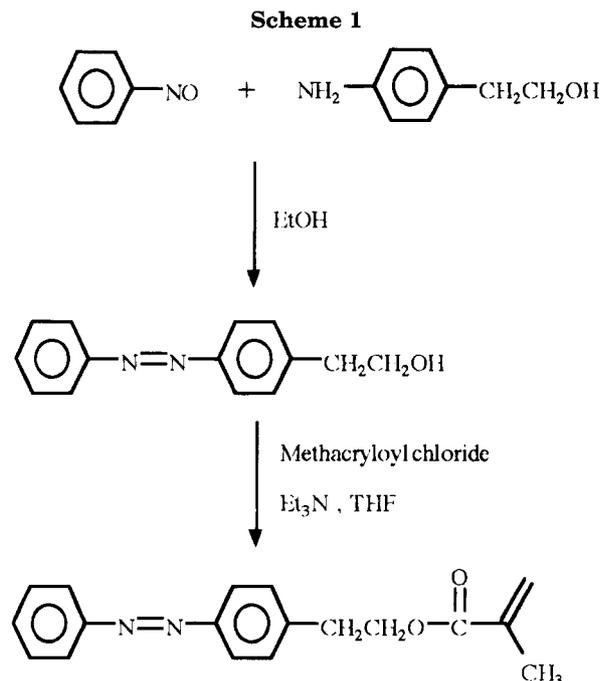
The synthetic scheme for pMEA is presented in Scheme 1.

**Optical storage** was performed in three ways. First, an argon laser operating at 514.5 nm was used as described in our previous publications.<sup>2</sup> The polarization was switched between linear and circular with a Pockels cell in order to

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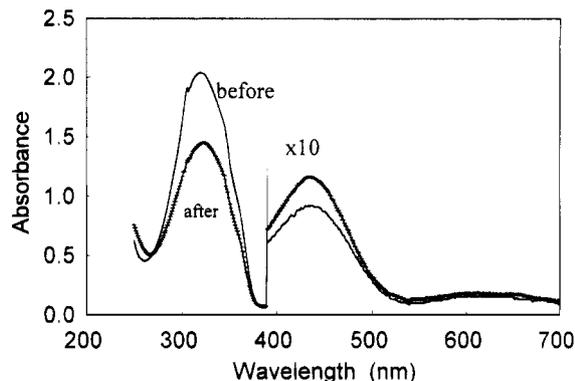
achieve “writing” (induced birefringence) and “erasing”. The birefringence is measured at 633 nm. Second, writing and erasing were performed with a xenon arc lamp where light was filtered with a band-pass filter that transmits only between 350 and 400 nm, to ensure writing with UV light only. The power at the sample is 3 mW/cm<sup>2</sup>, while the argon laser generates 500 mW/cm<sup>2</sup> at the sample. Third, an argon laser operating at 360 nm with a power of 1.5 W/cm<sup>2</sup> was used to perform the writing and erasing.

## Results and Discussion

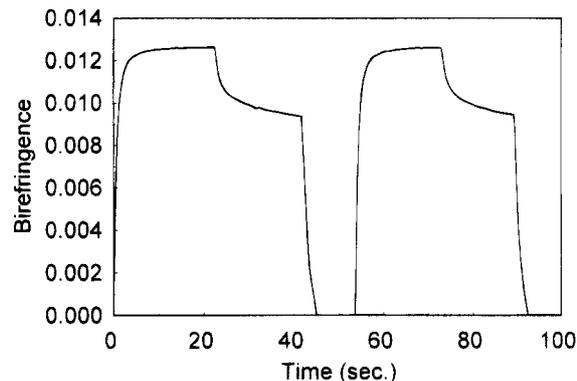
MEA and pMEA have no amino and no donor/acceptor substituents on the azo group; hence, they belong to the “azobenzene-type” in Rau’s classification of trans–cis isomerization processes.<sup>9</sup> A solution of 4-(phenylazo)phenethyl alcohol in chloroform kept in normal room light will isomerize to a photostationary state which has about 80% trans and about 20% cis isomers at room temperature, as obtained by NMR. For a solution of MEA in the same conditions, the cis content in the photostationary state is about 6%. By extrapolating the absorption coefficient of the monomer in solution to the polymer film, about 2% cis isomer is estimated to be present in the polymer film in the photostationary state at room temperature. The absorbance of a film of pMEA in its photostationary state is shown in Figure 1 together with its absorbance immediately after being subjected to illumination from an UV lamp (350–400 nm) for 120 h. The absorbance corresponding to the trans isomers (325 nm) decreases upon UV irradiation and the absorbance corresponding to the cis isomers (440 nm) increases, indicating the UV light induced trans–cis isomerization. The cis fraction at the photostationary state can be estimated at 0.3, using  $\epsilon_{\text{cis}}/\epsilon_{\text{trans}} = 0.05$  at 325 nm.<sup>10</sup> The cis–trans thermal isomerization in the film can be described by two processes: one fast, due to azo groups trapped in strained conformations, and the other one slow, characterized by a rate constant of  $1.9 \times 10^{-4} \pm 3 \times 10^{-5} \text{ s}^{-1}$ , which is, as expected, orders of magnitude slower than the rate for pDR1A films.<sup>11</sup>

### Induced Birefringence with an Argon Laser.

Figure 2 shows a typical sequence of inducing and erasing birefringence using the argon laser. At time zero the linearly polarized laser is turned on, and a level



**Figure 1.** Electronic spectrum of a film of pMEA before (a) and after (b) exposure to UV light for 120 h.



**Figure 2.** Optical storage on a pMEA film using an argon laser: time = zero and time = 53 s, linearly polarized laser ON; time = 20 s and time = 70 s, argon laser OFF; time = 42 s and time = 90 s, circularly polarized laser ON.

of birefringence of about 0.012 is achieved in a few seconds. The dichroic ratio between the absorbances (at 360 nm) parallel and perpendicular to the polarization direction is found to be 0.96, about the same order of magnitude as in pDR1A films.<sup>5</sup> It is interesting that, while the level of alignment is similar, the birefringence is much smaller in pMEA, and this is due to the different distances between the absorbance wavelength and the probe beam at 633 nm. pDR1A shows a birefringence 1 order of magnitude higher, since its absorbance is much closer to the probe wavelength. The induced birefringence level in pMEA is stable while the laser is on, but decays to about 72% of its original value when the laser is switched off at 20 s. The decay is as rapid as the decay experienced by pDR1A,<sup>2</sup> for example. Because the thermal cis–trans isomerization rate is much slower, this change in relaxation level must be attributed mainly to motion arising from heat dissipation. A small part of it may be cis–trans isomerization of groups in stranded conformations.<sup>12</sup> At 40 s, the circularly polarized argon laser is turned on, and the induced order is completely erased. This writing–erasing cycle can be repeated many times on the same spot on the polymer film, achieving the same level of birefringence with the same rate. This behavior is very similar to that of the donor–acceptor substituted azobenzene-containing polymers.<sup>2</sup> The two differences for pMEA are as follows: the level of the birefringence achieved, which is about one-tenth of the level achieved on, say, pDR1A<sup>2</sup> and the time required to achieve it, which is about 10 times longer. The explanation is very simple. The trans–cis isomerization rate is proportional to the energy absorbed by the film at the irradiation wavelength. The absorbance of pMEA films at 514.5 nm is much lower than the absorbance of pDR1A films,

**Table 1. Level of Remnant Birefringence at 633 nm after Writing Cycles**

cycle no.	birefringence	cycle no.	birefringence
1	0.0085	3	0.0040
2	0.0066		

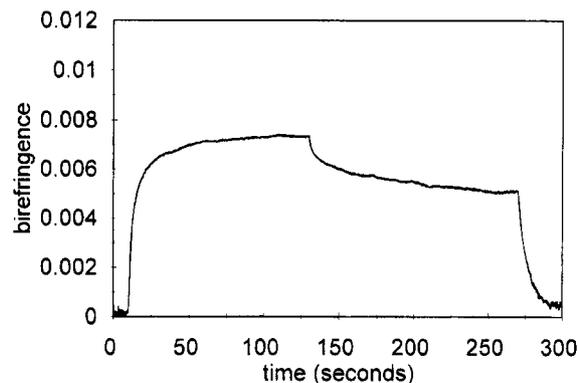
and most of the energy is absorbed by the cis isomers. Hence, the rate and frequency of trans-cis isomerization will be much lower in pMEA than in pDR1A. However, the advantage of using a laser at this wavelength consists of photochemical activation of the cis-trans isomerization. For a polymer such as pMEA, thermal cis-trans isomerization is too slow to produce enough trans-cis-trans isomerization cycles in order to create birefringence. This will become clearer later in the paper, when the results of using UV light will be investigated.

**Induced Birefringence with a UV Lamp.** Using UV light should activate exclusively the trans-cis isomerization, and the cis-trans isomerization would occur thermally (at room temperature the time constant would be 1.5 h). A UV lamp does not generate comparable power at the film; hence, for comparable results, writing was performed for 16 h with linearly polarized light. Then the birefringence was measured, and erasing was performed with circularly polarized light for 16 h. This writing/erasing procedure was repeated a few times. As Table 1 shows, the levels of birefringence measured at the end of a writing cycle decrease after each cycle. The explanation for this phenomenon is related to the presence of a significant and increasing amount of cis isomers. The only photochemically induced process is trans-cis isomerization. The thermal cis-trans isomerization occurs very slowly. Under illumination, linearly or circularly polarized, the trans population is continually excited and the cis population increases steadily. In each subsequent writing cycle, less trans molecules are available to generate the overall orientation that creates birefringence; hence, a lower birefringence level can be attained.

**Induced Birefringence with a UV Laser.** The writing and erasing cycles obtained using the UV laser are shown in Figure 3. The cycles are very similar to those obtained using the 514 nm writing beam, except that the level of saturation is seen to decrease slightly at each cycle. The dichroic ratio obtained with the UV laser is of the same order of magnitude as the dichroic ratio obtained with the argon laser. The decrease in the saturation level upon successive writing is much less than the case of the UV lamp. This is probably due to the temperature rise because of the higher writing intensity, which is sufficient to increase the thermal cis-trans isomerization rate and thus reduce the number of "frozen" cis conformers during a writing cycle.

The level of birefringence achieved in this case is somewhat lower than when using 514 nm for writing. This should be attributed to a temperature rise due to heating by the laser radiation, which is highly absorbed by the sample. Newer results obtained on MEA copolymers indicate that the optimum birefringence would be achieved at a UV laser power somewhat smaller than that used in this experiment.

**Efficiency.** In order to compare polymers of various structures in terms of their ability to be used as materials for optical storage, two kinds of efficiency definitions can be used. The first definition is as birefringence obtained per energy input ( $\epsilon_1$ ), and the second is as birefringence obtained per energy absorbed ( $\epsilon_2$ ). The phase lag at 90% of the saturation level of birefringence is measured, as usual, with the HeNe



**Figure 3.** Optical storage with a UV laser. At time = 10 s the linearly polarized laser is turned ON; at 130 s the laser is turned OFF; at 270 s the circularly polarized laser is turned ON.

**Table 2. Efficiencies of Optical Storage**

polymer	$\Delta\bar{n}$	$\epsilon_1$ ( $10^{-6}$ cm <sup>3</sup> /J)	$\epsilon_2$ ( $10^{-6}$ cm <sup>3</sup> /J)
pMEA	0.012	0.64	4.3
pDR1A	0.07	5.2	6.2
pDR13A	0.08	3.7	4.4
pDR19T	0.21	1.6	2.5

laser. The 90% level is chosen because the actual time of reaching saturation cannot be precisely determined. The phase lag ( $\Phi$ ) is proportional to the birefringence ( $\Delta n$ ) and to the film thickness ( $d$ ):

$$\Phi = k_0 \Delta n d = (2\pi/\lambda_0) \Delta n d \quad (1)$$

Then, the efficiency  $\epsilon_1$  is expressed as:

$$\epsilon_1 = \Phi A / k_0 P t \quad (2)$$

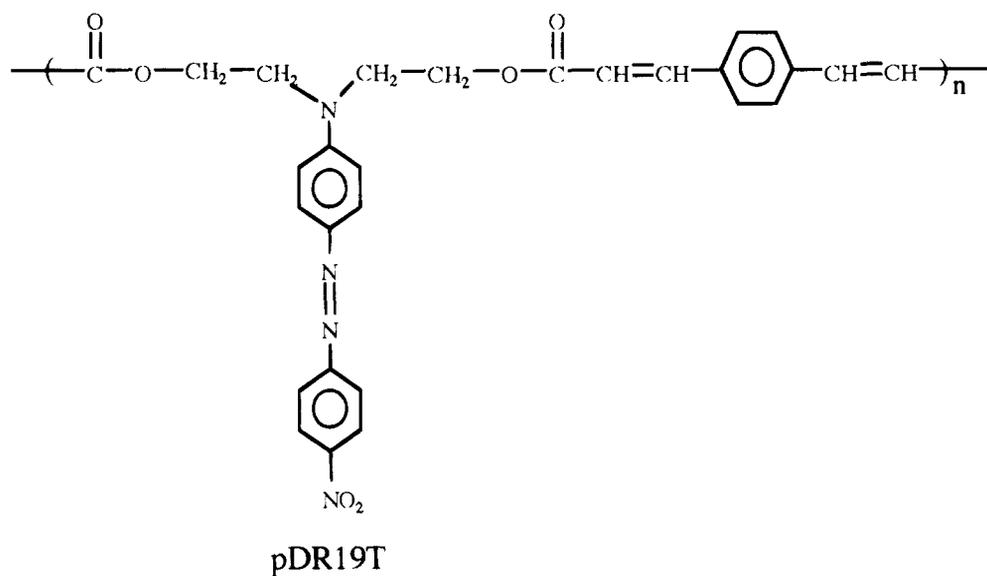
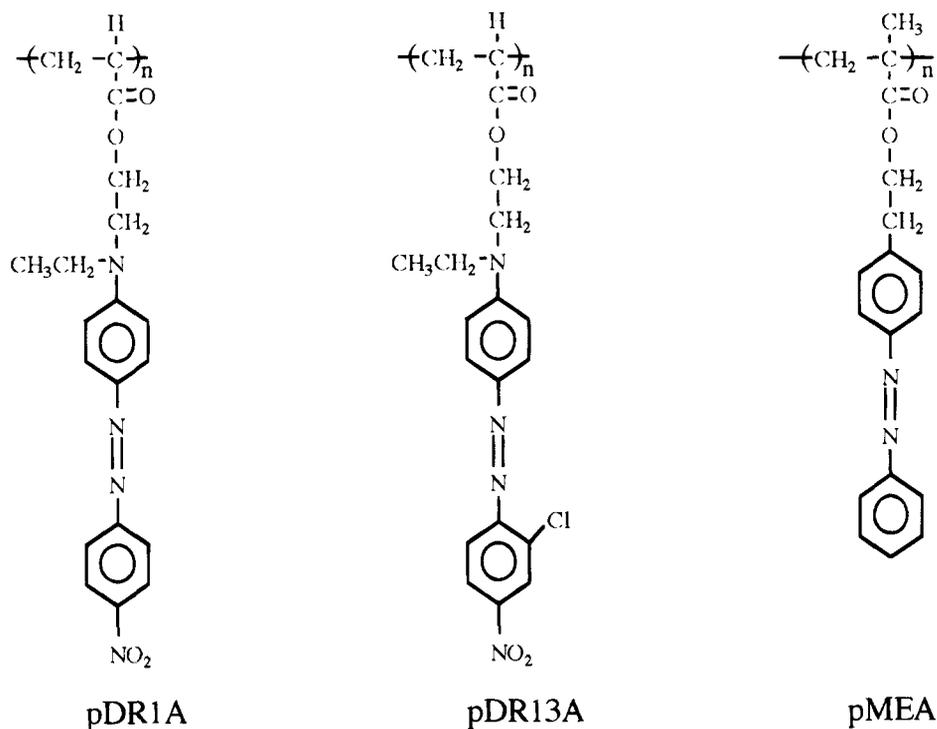
where  $A$  is the area of the film under illumination,  $P$  is the laser power, and  $t$  is the writing time. Assuming that the laser power is uniformly absorbed, the sample thickness does not affect this efficiency. This approximation is valid only for fairly thin samples.<sup>4</sup>

The other type of efficiency is defined as in eq 2, but the power  $P$  in this case is the power absorbed by the film. This is evaluated using the film transmittance.

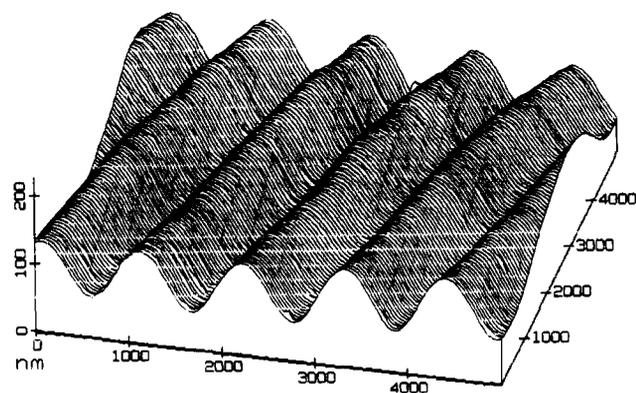
Table 2 shows the efficiency values when writing at 514.5 nm for four polymers: pMEA, pDR1A,<sup>2</sup> pDR13A,<sup>3</sup> and pDR19T.<sup>5</sup> The structures of these polymers are presented in Chart 1. pDR13A has a structure very similar to that of pDR1A, except for one chlorine atom substituted in a meta position relatively to the nitro group. pDR19T has the same azo group as pDR1A but forms crystalline domains together with another rigid group in the polymer structure. Obviously, because of the very low absorbance at 514.5 nm, pMEA is the least efficient material in terms of power used; its efficiency is 1 order of magnitude lower than the efficiency of all other polymers. When one uses the energy input into the sample, however, all the efficiencies are comparable. It is interesting to note that pDR19T, which has a much higher induced birefringence, is not more efficient in terms of optical storage than the other materials, because of the time required to achieve this birefringence.<sup>5</sup>

**Gratings.** For optical storage properties, creation of local holographic gratings is very important, and it is customary to report the diffraction efficiencies achieved on various materials.<sup>13</sup> Very stable surface profile gratings can be induced on azo-containing polymer films,<sup>14,15</sup> by a mechanism which is still under investi-

Chart 1



gation. The depth of the inscribed profiles and the diffraction efficiencies are a function of the length of time of exposure to light.<sup>16</sup> The best procedure of inscribing gratings makes use of a mirror at a right angle to the sample holder. The part of the light beam which strikes the mirror is reflected onto the sample and creates an interference pattern. The grating formed on the film surface can be probed with an atomic force microscope, and the resulting profile is shown in Figure 4. The pMEA film shown in Figure 4 was written with a circularly polarized argon laser at 514.5 nm for 35 min at 22 mW/cm<sup>2</sup>. Circularly polarized light was shown to be more efficient than linearly polarized light in inducing gratings.<sup>16</sup> For this film a typical grating spacing of 1035 nm and a depth of 90 nm are obtained after 35 min. The diffraction efficiency can be calculated from the grating profile using Kogelnick's expression and an approximate refractive index for the polymer of 1.6.<sup>17</sup> The calculated diffraction efficiency is 7%, while



**Figure 4.** Atomic force microscopic profile of a pMEA film on which gratings have been inscribed (see text).

the measured diffraction efficiency using a HeNe probe beam at 633 nm is 4%. The difference is probably due

to losses generated by reflections on film and substrate surfaces. This diffraction efficiency can be increased by increasing the exposure time to levels of about 20%. A more detailed investigation of this process is underway.

### Conclusions

Although of a different spectral type, pMEA behaves in a fairly similar manner with electron-donor–electron-acceptor substituted azobenzene-containing polymers. Birefringence can be photochemically induced through a series of trans–cis–trans isomerizations, but to a lower level than in the previous polymers. This lower level is associated with a fairly low absorptivity in the visible region and with a high temperature associated with absorbance in the UV. Higher temperatures increase the internal motions in the polymer film and destroy the order necessary to produce birefringence. Due to its relatively slow thermal cis–trans isomerization rate, pMEA is not a good material for optical storage with UV light, because the level of induced birefringence cannot be reproduced within a short time interval. Both writing and erasing activate the trans–cis isomerization, while the cis–trans isomerization is slow. Efficiencies of storage are similar to the previously reported polymers when the polymer absorbance is considered. Highly efficient diffraction gratings can be inscribed on the polymer film surface.

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