Azo Polymers for Reversible Optical Storage. 1. Poly[4′-[[2-(acryloyloxy)ethyl]ethylamino]-4-nitroazobenzene]

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ABSTRACT: Poly[4′-[[2-(acryloyloxy)ethyl]ethylamino]-4-nitroazobenzene] (pDR1A) is used as an example to demonstrate the ability of amorphous high-T_g azoaromatic-containing polymers to reversibly store optical information. Writing, reading, erasing, and rewriting processes are performed using laser beams on a pDR1A film. This ability is based on the well-known trans–cis–trans isomerization process which was previously studied on liquid-crystalline polymers containing azoaromatic groups. Liquid crystallinity is not a necessary condition for optical storage. As well, erasing can be performed optically, eliminating the need to heat the polymer sample. The writing and erasing are statistical processes, and the level of optical anisotropy induced depends on the photon flux directed at the sample. The time evolution of the writing process is investigated. A computer simulation of these processes is performed taking into account a relaxation process in which some of the reoriented trans molecules are randomized by thermal motion. The computer model replicates the general features of the optical storage processes. Possible applications and future work on this class of polymers are also discussed.

Introduction

It was demonstrated in 1972 that the isomerization of various azobenzenes bound on the side chain or within the main chain of poly(methyl methacrylate), poly(ethyl methacrylate), polystyrene, a polyamide, and a polyester can be studied in the solid state.[3] There are three processes: a trans–cis photochemical isomerization, a cis–trans photochemical isomerization, and a cis–trans thermal isomerization, which occurs due to the higher stability of the trans configuration. Since that pioneering study, two main directions of research developed and are very active in the current literature. This survey of the literature will omit the more recent development of using azoaromatics as active groups for nonlinear optical properties. Some comments on this application will be presented in the Results and Discussion section of this paper.

The first direction is pursued by two research groups. Sung et al. use azobenzenes as probes for investigating the overall mobility of the host polymer. A few studies were dedicated to molecular motion and physical aging in a polyurethane with the azobenzene moiety bound in the main chain.[4-6] Another publication studies the behavior of the azo probe as a side chain, in the main chain, and at the chain ends of a polystyrene.[7] Victor and Torkelson use azoaromatics as probes in polystyrene and poly(methyl methacrylate).[8-10]

The second direction of research is concerned with the kinetics of isomerization itself when the azoaromatic moiety is mixed or incorporated into a polymer matrix. This direction of research is a direct continuation of Morawetz's work. Eisenbach[11] used an azobenzene-based comonomer for ethyl methacrylate and studied the isomerization kinetics in the copolymer. Sung[12] investigated the above-mentioned polystyrene-based compounds. Poly(ethylene terephthalate) doped with a few azo dyes was the subject of investigation by Dubini-Paglia et al.,[13] who are the only ones to mention a photofading effect noticeable after a few hundred hours of exposure to light. Azobenzene,[14] substituted azobenzene,[15] azonaphthalene,[16] and azophenanthrene[17] embedded in a polycarbonate film were investigated by Mita et al. and Naito et al. Isomerization of azobenzene in an oriented polyethylene matrix was studied by Kryszewski et al.[18] When the matrix was a copolymer of vinylidene fluoride and trifluoroethylene,[19] the shift of electronic absorbances of 4-amino-4′-nitroazobenzene and a stilbene derivative upon illumination or poling was assigned to a protonation of the dye. Probably the most significant papers in relation to the subject of the present research are those published by Spiess et al.[20,21] A combination of backbone relaxation, dye reorientation, and cis–trans isomerization processes is postulated for some liquid-crystalline polymers used in reversible holographic storage. The mechanism of isomerization involves rotation or inversion, as demonstrated by Rau[22] in a poly(methyl methacrylate) matrix. Ion binding, hence, the metal extraction ability of the materials containing azobenzene, is directly dependent on the cis or trans configuration.[23]

The possibility of using a polymer for reversible optical storage, holographic or digital, was first suggested in 1984,[24] using an azo dye (methyl orange) dispersed into poly(vinyl alcohol). The real interest in the subject, accompanied by an increasing number of papers, started in 1987, when Wendorff demonstrated reversible optical storage properties on some liquid-crystalline polymer films.[25,26] One was a homopolymer[25] containing a *p*-nitroazobenzene bonded as a side chain in a polycarbonate through an oxygen atom and a spacer of six methylene groups. The spacer allowed the mesogenic azobenzene moiety to move about and organize into a liquid-crystalline phase. The other film was an acrylic copolymer[26] containing two types of mesogenic units: a *p*-cyanoazobenzene bonded through an oxygen and a spacer of six methylene groups and a *p*-cyanophenylbenzoate bonded in a similar way. The azobenzene moiety was ca. 30% of the structural units. When exposed to laser beams, these films stored the information written on them. The writing was done in the nematic or in the glassy phase (T_g is about 30 °C), and erasure could be achieved by heating the film above the clearing temperature. The mechanism postulated for the phenomenon was obviously related to the well-known trans–cis isomerization and was believed to involve a reorientation of the side groups brought about by the movement of the trans–cis isomerization. This explanation is plausible when one considers that, if a rotation mechanism is the main one in isomerization, a volume of 0.25 nm^3 is required to accommodate the change.[17] A more

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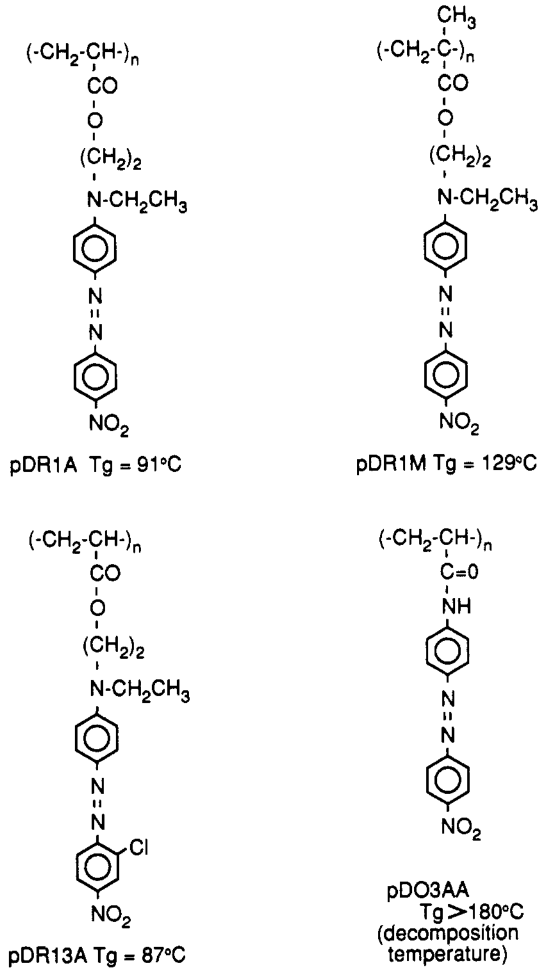
detailed investigation on the above copolymer, published in 1989,[27] showed that the polarized laser light is turning the optical axis of the liquid-crystalline polymer perpendicular to the polarization plane. The same writing phenomenon was observed in an amorphous copolymer (methyl acrylate with 25 mol % azo component), except that in this case the writing beam was *inducing* the alignment.[27] The azo side chain was designed to include a long enough spacer in order to allow for reorientation. Probably the most important conclusion of this paper was to propose that the laser light induced a trans–cis isomerization accompanied by reorientation and that the reorientation was being maintained even after all the cis isomers reverted to the more stable trans form. A more detailed study of the writing phenomenon was published in 1990 on one of the liquid-crystalline copolymers.[28] The same anisotropy could be induced by laser writing onto gelatin films doped with azo dyes.[29]

Recently, Ikeda et al. published two studies on similar copolymers, where the azo component is either a dopant in a liquid-crystalline copolymer or a side-chain comonomer.[30,31] All polymers were liquid crystalline, but the spacers introduced to allow for liquid crystallinity were sometimes shorter (as low as two methylene groups). This produced polymers with higher glass transition temperatures, and the laser writing was performed in the nematic phase[30] or in the glassy state.[31]

The most significant developments in the field, in our opinion, appeared very recently in the literature. Gibbons et al. demonstrated that induction of orientation can be obtained or can be changed with a polarized laser.[32] This orientation can be transmitted to a liquid-crystalline material adjacent to the oriented film. The film employed in that publication was a polyimide doped with a diazo dye. At about the same time, a paper by Stumpe et al.[33] synthesized a liquid-crystalline methacrylate copolymer with 14 mol % azobenzene side chains and with a T_g of 60 °C, significantly higher than any of the previous polymers. They demonstrated that writing can be performed in the glassy state and that the reorientation of the azobenzene moieties actually affects the neighboring mesogenic groups, probably by the same mechanism as described in the *Nature* paper. To erase the writing on their copolymer, heating above the clearing temperature (84 °C) was necessary.

The conclusions that can be drawn from all these studies are that writing with a polarized laser onto a polymer film is being performed by a trans–cis isomerization accompanied by reorientation and that the reorientation perpendicular to the laser polarization is being maintained even after the cis–trans isomerization, which occurs spontaneously with a time constant of ca. 4 h[20] at room temperature. This reorientation is being transmitted to the neighboring mesogenic units which are not photosensitive. Anderle et al.[34] recently observed that an overall orientation is obtained only when writing is performed above the glass transition temperature of the polymer, in the liquid-crystalline state. Below T_g, only the azoaromatic groups are being reoriented by the beam. A discussion of the state of the polymer (glassy or liquid crystalline) and its effect on the reorientation is also presented by Spiess et al.[21] The writing is permanent (a 2-year stability was reported for a hologram at room temperature[28]) unless heating above the glass transition temperature, or above the clearing temperature, is performed. The liquid-crystalline nature of the polymers involved helps in allowing enough flexibility for the azo side group to reorient after the isomerization. The writing procedure itself requires a first step of orientation of the liquid-crystalline film, usually in an electric field, followed by writing in the liquid-crystalline state or in the glassy state obtained by slowly cooling the oriented film in the electric field (i.e., maintaining the preorientation in the glassy state). One drawback is that spacers long enough to allow movement decrease the glass transition temperature of the film and probably increase the rate of relaxation at room temperature.[20] In principle, the higher the T_g of the polymer, the greater the stability of the writing at room temperature (well below T_g).

Chart I



pDR1A Tg = 91°C

pDR1M Tg = 129°C

pDR13A Tg = 87°C

pDO3AA Tg>180°C (decomposition temperature)

We will show in this paper that liquid crystallinity is not a necessary condition for a material to exhibit the reversible optical storage properties. The synthetic procedure is then much simpler and cheaper. By synthesizing amorphous polymers containing azo side groups and very short spacers, the glass transition temperatures can be designed to be relatively high. This results in a significant increase in the stability of the written material. Also, erasing can be done by optical means, not necessarily by heating the sample above a certain temperature. Poly[4′-[[2-(acryloyloxy)ethyl]ethylamino]-4-nitroazobenzene] (pDR1A) was the first polymer we tested. Its synthesis, physical measurements, and a model of the physical phenomena occurring during writing will be presented in this paper. A few other polymers, with even shorter spacers, were synthesized and tested with very good results. This work will be described in forthcoming publications. Chart I shows the chemical formulas of the polymers tested to date.

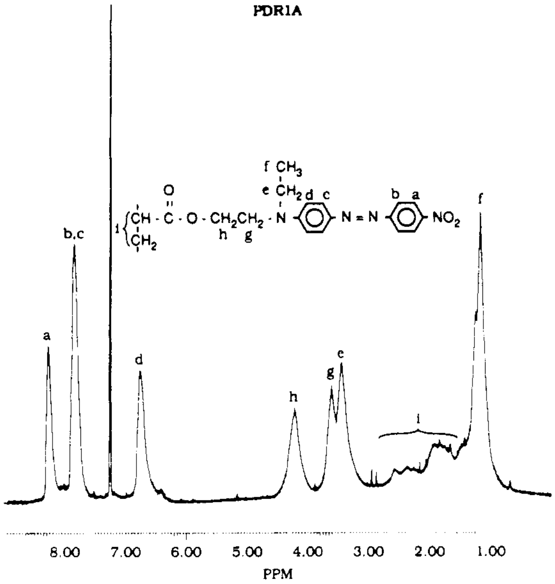


Figure 1. ^{1}H NMR spectrum of pDR1A in $CDCl_3$. The assignments are given on the spectrum.

Experimental Section

The monomer was synthesized by reacting Disperse Red 1 (Aldrich) with acryloyl chloride in THF in the presence of triethylamine as HCl acceptor at ca. 0 °C for 1 h followed by stirring at room temperature for 6 h more. The acryloyl chloride solution in THF was added dropwise to the cooled mixture of THF, Disperse Red 1, and triethylamine. The resulting salt was filtered, and the resulting solution was concentrated on a rotovap and then poured into water. The precipitated monomer (yield 60%) was then filtered, dried, and recrystallized from ethanol. Proton NMR ($CDCl_3$): δ 1.30 ($-CH_3$), 3.56 ($-CH_2$ ethyl), 3.75 ($-NCH_2-$), 4.40 ($-CH_2O-$), around 6.15 ($-CH{=}CH_2$), 6.82 (2 aromatic H, ortho to N), 7.91 (4 aromatic H, ortho to N=N), 8.33 (2 aromatic H, ortho to NO_2). The monomer melting point was 82–84 °C.

Polymerization was performed in dry toluene with 10% AIBN as initiator (this concentration of initiator was found to produce the highest yield (50%) without adversely affecting the average molecular weight) at 60 °C for 4 days. The polymers were precipitated in methanol and reprecipitated from a THF/methanol system. A proton NMR spectrum of pDR1A is presented in Figure 1. The GPC indicated an equivalent molecular weight of 4000.

The measure induced optical birefringence and dichroism, thin films of pDR1A were obtained by dissolving the polymer in THF and casting onto a clean glass slide which acts as a substrate. The films were allowed to dry and subsequently heated above the T_g of the polymer. Relatively homogeneous thin films of approximately 500-nm thickness were obtained by this procedure.

The optically induced anisotropy was measured by placing the sample between two crossed linear polarizers. A low-power He–Ne laser at 632.8 nm was used as a light probe to measure the power which is transmitted through this optical setup. Optical anisotropy was induced in the polymer film using a polarized argon beam at 514.5 nm to write on the sample at a polarization angle of 45° with respect to the polarizer orientation. The transmittance was measured using a fast photomultiplier and was recorded for further analysis. The polarization state of the argon laser beam was controlled using an electronically driven Pockels cell which allowed rapid switching from linearly to circularly polarized states. All measurements were performed at room temperature.

Results and Discussion

The DSC curve of pDR1A shows a glass transition at 91 °C and no other enthalpy changes before decomposition. Observation of a polymer film on a microscope under polarized light shows no birefringence below or above T_g, indicating that pDR1A is an amorphous polymer.

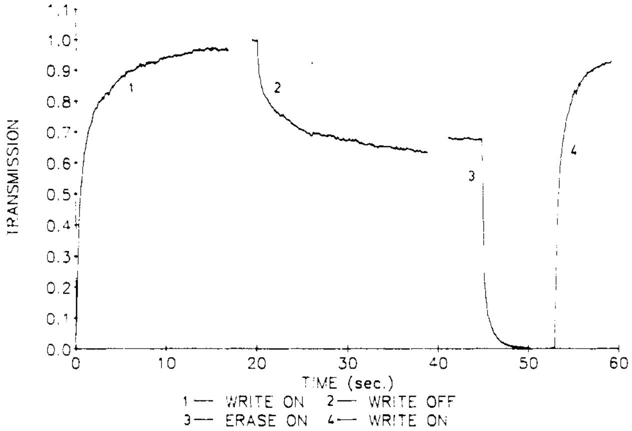


Figure 2. Writing and erasing test on a pDR1A film: (1) The writing beam is turned on. (2) The writing beam is turned off. (3) The erasing beam in turned on. (4) The writing beam is turned on again on the same spot of the film.

A typical writing sequence is presented in Figure 2. The sample is initially homogeneous and optically isotropic, and no transmission of the probe beam through the crossed polarizers is observed. Optical anisotropy is induced by switching on the linearly polarized argon beam. The writing beam is polarized at 45° with respect to the polarizer axes. As optical anisotropy is induced in the polymer film, the probe is partially transmitted through the optical setup. The transmission is seen to reach 60% of saturation in about 1 s and 90% in about 7 s. In this sample the saturation corresponds to a transmission of 0.5% of the input. This corresponds to an induced birefringence of about 10^{-2}.

At a second stage, the writing beam is switched off and the transmitted signal is observed to decrease to about 60% of the saturation value in about 10 s. This shows that the induced optical anisotropy is not completely preserved after writing with linear polarized light, but a significant long-term effect is nevertheless seen. The induced anisotropy has been observed to be stable for several months, from the time of the first test to the time of writing this paper.

At a third stage in the writing sequence, the optically induced anisotropy is optically "erased" by overwriting the test spot with a circularly polarized argon beam. This mode of writing effectively returns the film to an optically isotropic state, thereby erasing the previously encoded information. As seen in Figure 2, the erasing time for this sample is about 0.5 s. Finally, in a fourth stage of the writing sequence, information is rewritten onto the test spot by writing once again with linearly polarized light. The writing time is again about 1 s.

As indicated in the Introduction, the optical anisotropy is an induced birefringence and dichroism in the polymer film resulting from a reorientation of the azo moieties. Linearly polarized light is used to cause a trans–cis isomerization followed by a molecular reorientation and a cis–trans isomerization. The absorption and reorientation sequence will be repeated until the molecule's dipole moment lies in a direction which is perpendicular to the polarization direction of the writing beam. In this way a net macroscopic optical anisotropy can be induced in the film. The writing times will thus be controlled by the photon flux, the trans–cis isomerization rate, and the degree of molecular reorientation attainable in a given sequence. The erasing procedure using circularly polarized light is interpreted in a similar fashion except that in this case light is absorbed for any molecular orientation and

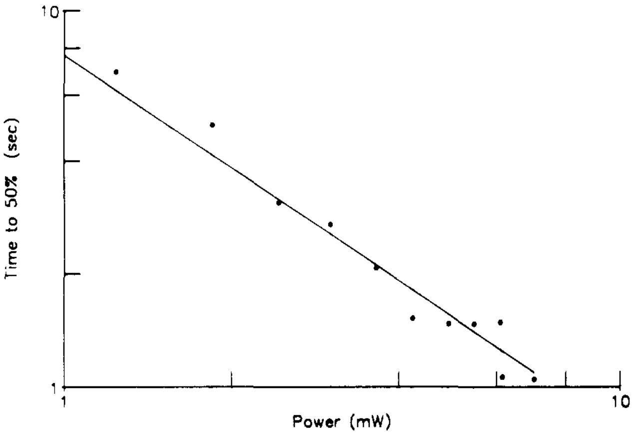


Figure 3. log–log plot of the time to achieve 50% erasure (curve 3 in Figure 2) as a function of the erasing beam power.

no particular reorientation is favored; the result is a removal of the optical anisotropy of the film. The processes invoked to explain these observations are, to first order, statistical in nature, and this aspect is reflected in the observation that the writing times are inversely proportional to the power of the writing beam as illustrated in Figure 3. In this case, the time required to achieve 50% of erasure from saturation is plotted as a function of the power of the circularly polarized argon beam. The level of optical anisotropy is seen to be directly proportional to the number of photons involved in the writing process, confirming the statistical nature of the process. Thermal effects are expected to be reflected in deviations from this observation as well as in affecting the level of saturation attainable.

In a previous publication[35] we have reported the electronic absorption spectra of the written polymer film. The absorbance in the direction of the polarization of the laser is smaller than that in the direction perpendicular to the polarization of the laser. This dichroism can be translated into an "order parameter" (as defined in ref 27) of ca. 0.05.

Model for the Photokinetics. In this section we propose a preliminary model to describe the kinetics of the signal observed in the optical anisotropy experiments illustrated in Figure 2. The signal observed can be interpreted as follows. Consider a molecule in the trans configuration whose dipole moment is at an angle with respect to the polarization direction of the incoming probe beam. The signal which is transmitted to the detector behind the analyzing polarizer is then proportional to sin (2θ). Given a distribution of molecular directions, the net signal received is then given by

$$S(t) = K\sum [\mathrm{T}]_i \sin (2\theta_i) \qquad (1)$$

where K is a constant incorporating geometrical factors, $[\mathrm{T}]_i$ is the concentration of trans molecules oriented at the angle θ_i, and the sum is performed over the entire angular distribution. For a homogeneous distribution the signal is zero, and it goes to a maximum if the molecules are oriented at 45°. The time dependence of the signal then reflects the time dependence of the distribution of dipole moments in the sample. In the present model we will assume that the cis configuration does not contribute to the net orientation of the dipole moment of the sample.

The distribution of molecular orientations is changed when light is absorbed by the trans molecule which undergoes photoisomerization to the cis configuration and then reverts back to the trans configuration in a new direction via an optical or thermal isomerization process.

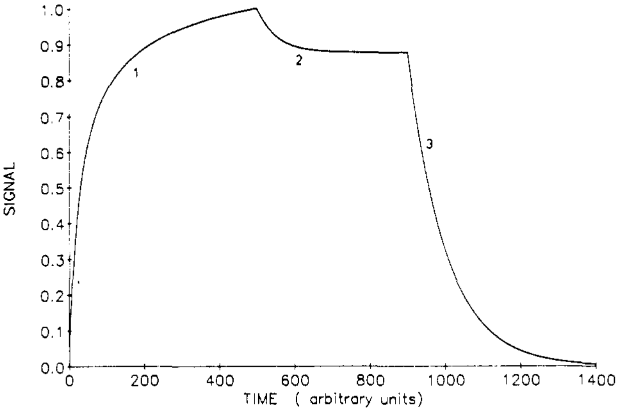


Figure 4. Computer simulation of the write–erase process obtained using parameters discussed in the text: (1) writing simulation; (2) simulation of process no. 2 in Figure 2 (writing beam turned off); (3) erasing simulation.

The reaction kinetics is described by

$$\mathrm{d}[\mathrm{C}]/\mathrm{d}t = \sum_i w_{ic}[\mathrm{T}]_i - \sum_i w_{ci}[\mathrm{C}] \qquad (2)$$

$$\mathrm{d}[\mathrm{T}]_i/\mathrm{d}t = -w_{ic}[\mathrm{T}]_i + w_{ci}[\mathrm{C}] + \sum_j w_{ji}[\mathrm{T}]_j - \sum_j w_{ij}[\mathrm{T}]_i \qquad (3)$$

where w_{ic} is the transition rate from trans to cis for the molecule in the ith orientation, w_{ci} is the transition rate from cis to trans, w_{ij} is a thermal reorientation rate for molecules in the trans configuration (a thermal relaxation process), and [C] is the concentration of cis molecules. These equations are numerically solved, resulting in a model for the writing–erasing experiment illustrated in Figure 2. An example is presented in Figure 4, with the following conditions on the model parameters.

The parameters are defined in terms of the clock units. Equations 1 and 2 are calculated with differential times of $\mathrm{d}t = 0.1$.

(A) $w_{ci} = 1/5$. The transition rate from cis to trans is assumed to be random and equally probable for all trans orientations.

(B) $w_{ij} = 1/5$, $j = i \pm 1$. A 30% fraction of the trans molecules is allowed to reorient at this transition rate. We assume that the reorientation is only onto the neighboring orientation position.

(C) For w_{ic}, the transition rate from trans to cis takes on three values here:

$w_{ic} = I \cos^2 \phi$ where I is the transition rate proportional to the writing intensity and ϕ is the angle between the linearly polarized writing beam and the molecular orientation. This value of w_{ic} is used in the first part of the writing process with $I = 0.1$. The term $\cos^2 \phi$ clearly implies that only the molecules oriented perpendicular to the polarization of the laser beam are inactive in the trans–cis isomerization process. The consequence is that this orientation will be the preferred one while the "writing" process is taking place.

$w_{ic} = 0$. During the second part of the writing process the writing beam is off.

$w_{ic} = 0.1$. For the erasing part with circularly polarized light we assume the transition rate is equally probable for all orientations.

The simulation presented in Figure 4 is seen to replicate the general features of the experimental results. As in the experimental case illustrated in Figure 2, the time constant for the erasing segment of the simulation was found to be inversely proportional to the writing intensity. This indicates that the erasing phenomenon is mostly limited by the photon flux rather than by the intrinsic time constants for the photon flux we have used. The simulation also indicates that the signal decreases after the writing beam is switched off. This reflects the fact that not all the optically oriented molecules maintain their new alignments over the long term but that a significant fraction of the molecules which can be reoriented may not be frozen into position. This thermal relaxation factor was introduced to account for the signal decay when the writing beam is switched off. Even if the polymer is well below its T_g, some azo groups (especially the ones attached to the chain ends) have a rather high freedom of motion. The molecular weight of this first polymer analyzed is low, having a high proportion of terminal structural units. This is probably at least part of the explanation for the ca. 40% decay of the signal observed in Figure 2. The initial part of the writing simulation is controlled by time constants that reflect both the photon flux and the relaxation phenomenon.

We also note that the simple model presented here only considers molecular reorientations in two dimensions. A more realistic model will allow for molecules to align also in the propagation direction of the writing beam. This is expected to change the specific kinetics of the writing process and, in particular, will allow for the photobleaching of the sample. This photobleaching effect is interpreted as resulting from the alignment in the direction of the beam, which can happen especially with circularly polarized light. The dipolar moment of these molecules would now point in or out of the film, and they would no longer participate in the absorption of the light which traverses the film. This bleaching can be removed by heating the sample above its T_g.

From the data given in the literature on the kinetics of the three processes taking place during the laser writing it appears that the cis–trans thermal isomerization is the rate-determining step. One of the parameters that affects this rate is temperature, and we are presently investigating writing at various temperatures. The wavelength of the laser employed for writing is important only in the efficiency of one of the photochemical processes. When the wavelength of the excitation is close to the absorbance of the trans (or cis) isomer, the efficiency of the trans–cis (or cis–trans) photochemical isomerization will increase. Hence, working with yellow–orange dyes and a 514.5-nm laser might result in a better cis–trans isomerization, while working with a red dye and the same laser might increase the efficiency of the trans–cis isomerization. None of these processes is rate-determining, which means that even UV-absorbing azoaromatics could be activated without the need of higher energies or longer times.

It is reasonable to believe that the same writing phenomenon would be present for azoaromatic moieties within the main chain of the polymer, at least for those which have a reasonable rate of thermal cis–trans isomerization. As well, "diluting" the concentration of the active group by obtaining copolymers with nonactive nonmesogenic units will presumably still generate the same properties. In this case it is reasonable to assume that a minimum amount of active groups would be necessary. The writing phenomenon has been reported for contents as low as 1 mol %,[27] but the rest of the comonomer in that case had mesogenic groups which were being oriented by the neighboring azoaromatics. It would be interesting to find out what the lowest limit of sensitivity is when the comonomer has no mesogenic groups. These two directions of research, polymers with azo moieties within the main-chain and side-chain copolymers, are under investigation in our laboratory. We are also pursuing another method of diluting the active groups: blending pDR1A and the other azo polymers with "neutral" polymers, such as poly(methyl methacrylate).[35] Blend compatibility is an important issue, because the films obtained have to be homogeneous and transparent in order to produce writing of good quality.

Possible applications of these azoaromatic-containing amorphous high-T_g polymers include erasable optical memory disks and tape (here the rate of the writing process is very important), erasable holographic storage materials (with no developing necessary), and optical sensors usable over a wide range of temperatures.

Finally, it is worth mentioning that there is a renewed interest in polymers containing substituted azobenzene units, due to their potential nonlinear optical properties.[36] One of the conditions for second harmonic generation is alignment of the chromophores, and this is usually done by poling the material in strong electric fields above the glass transition temperature and then cooling with the field on. The phenomenon of perpendicular orientation of the azoaromatic groups to the polarized light of the laser beam is in fact another poling procedure, much "milder" than the usual one. A recent paper[37] tested the waveguide properties of a polyester containing disperse red 19 bound on the side chain.[38] The waveguides were obtained by photochemically changing the refractive index of the film *and* poling. We are also investigating the nonlinear optical properties of the "written" materials and the possibility of designing optical "printed" circuits drawn with a laser beam on a polymer film.

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Registry No. pDRIA, 13695-46-0; pDRIA (homopolymer), 139427-10-4; disperse Red 1, 2872-52-8; acryloyl chloride, 814-68-6.