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REVERSIBLE OPTICAL STORAGE IN AZO POLYMERS

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Abstract: Amorphous high-T_g azobenzene-containing polymers can be used as reversible information storage materials in form of films. The procedure takes advantage of the photochemically activated trans-cis-trans isomerization of the azobenzene groups. The written information is stable below the polymer glass transition temperature. Writing and erasing can be performed up to 10⁵ times on the same spot of the polymer film. The reorientation mechanism depends on the type of substituents bound to the azobenzene group, on the type of the neighboring group on the polymer chain and on the tendency of the polymer to self-organize. The efficiency of the process depends on the maximum absorbance of the azobenzene group and can be tailored to reach unity. This property of azobenzene-containing polymers can be used in optical and holographic memory, waveguides and sensors, and photonic devices.

INTRODUCTION

It is well known that azobenzenes isomerize from trans to cis and from cis to trans when subjected to light of appropriate wavelength (1). This property has been the basis of a series of applications in polymer science, such as the use of azobenzene groups as probes for various types of motion within polymer chains. A review of azobenzene photochemistry and some of its applications in polymer chemistry appeared in 1989 (2). More recently, some novel potential applications involving azobenzene-containing polymers were reviewed (3). They are based on supramolecular orientation of the rigid azobenzene groups. For example, azobenzene mesogens form various liquid crystalline phases and their order can be destroyed by illumination, because the cis form of the azobenzene obtained by photoisomerization has a bent shape and cannot form ordered domains. In another example, the azobenzene mesogens can be aligned by poling in an electric field to give materials with second order nonlinear properties. Photoisomerization can also be exploited in switching the ordering of Langmuir-Blodgett films containing azobenzene groups.

Our research is using high glass transition temperature amorphous polymers in which substituted azobenzenes are bound on the side chain or in the main chain, as thin films. The films are subjected to polarized light, which induces trans-cis-trans isomerization cycles and subsequent rearrangement of the azobenzene groups preferentially perpendicular to the polarization direction. This preferential director of the azobenzene groups creates a dichroism

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which translates into birefringence. Original disorder can be easily restored by switching the polarization of the light from planar to circular (4-6).

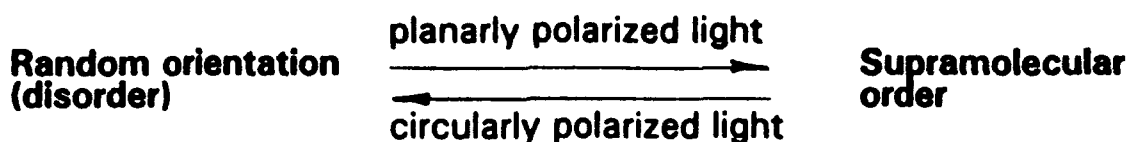
Background And Previous Literature

The reorientation of azobenzene groups subjected to polarized light was first observed in 1983 by Todorov et al (7) using methyl orange dissolved in poly(vinyl alcohol). The phenomenon was very unstable, decaying almost immediately as the laser was switched off. Independently, in 1987, Ringsdorf et al (8) reported a similar phenomenon in liquid crystalline side-chain polymers. The polymer sample was a film which was initially subjected to an electric field to obtain a general director for the nematic or smectic organization of the azobenzene groups. After this preorientation, the film was subjected to light of polarization parallel to that of the director. The azobenzene groups orientation was thus changed at 90° from its initial director. A series of papers followed from Wendorff's laboratory in which the phenomenon was shown to be applicable to a variety of liquid crystalline polymers containing substituted azobenzene groups. Erasing the orientation was performed by heating the polymer film above its T_g or (more efficiently) above its clearing temperature.

Our initial reports (4-6) concentrated on amorphous high- T_g polymers, for a few reasons. First, if an amorphous polymer is used, there is no need (or possibility) to preorient the azobenzene groups in an electric field. Second, the orientation induced by the laser is stable below the polymer glass transition temperature. If no spacers are present between the azo groups and the polymer backbone, the polymer can be designed to have a very high T_g , hence a very good stability of the "written" orientation. A very important point is that azobenzenes which are bound within the polymer will keep their orientation much better than azobenzenes simply dissolved in the polymer. Our oldest sample has kept its "written" birefringence for almost three years now. Probably the most important improvement in our system is the use of circularly polarized light to erase the signal. This allows for local erasure, as opposed to complete erasure of the whole film in the case of the liquid crystalline polymer system.

Brief Description of the Phenomenon

The rate of trans-cis isomerization depends on the angle between the laser polarization and the azobenzene group orientation by a $\cos^2\theta$ factor. Azobenzenes perpendicular to the laser polarization direction are not activated. While undergoing multiple trans-cis-trans isomerization cycles, the azobenzene groups change their orientation. Any group falling perpendicular to the polarization direction will remain in that position, while all others will be reactivated. In the end, there will be a slight increase in the concentration of azobenzene groups perpendicular to the polarization direction, which will give the dichroism and birefringence. When the laser light is turned off, dissipation of energy by heat reduces the birefringence by ca. 20%, but the remainder is frozen in the film for a long time. Circularly polarized light activates all azobenzene groups, restoring the initial disorder of azobenzene orientations. A schematics of the process is presented on the next page:



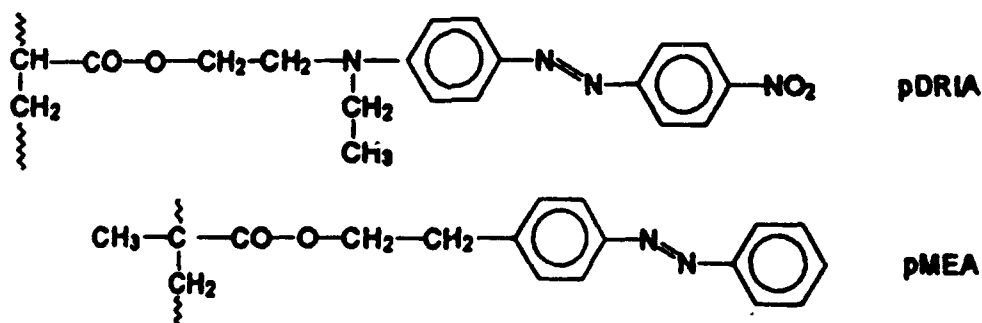
REORIENTATION MECHANISM

Parameters

There are a few important parameters governing the extent and rate of reorientation of the azobenzene groups in an amorphous polymer film.

The nature of the azo group: The most important structural feature of an azobenzene group is the type of substituents it possesses. If there is no amino substituent, or if there are no electron-donor - electron-acceptor substituents to confer a push-pull electron movement, the cis isomer is relatively long lived. If such substituents are present (aminoazobenzenes or stilbene-like azobenzenes), the cis isomer reverts back to trans in a few seconds at room temperature, which means that its absorbance and other characteristics cannot be directly measured. Typically, the maximum absorbances of cis and trans isomers of an aminoazobenzene or of a stilbene-like azobenzene are superimposed, while nonsubstituted cis azobenzenes have absorbances at higher wavelengths than the trans isomers. Thus in the nonsubstituted azobenzenes, the trans-cis and cis-trans isomerization processes can be separately activated.

An example on how the reorientation process is affected by the type of azobenzene used is given below. Poly[4'-[[2-(acryloyloxy)ethyl]ethylamino]4-nitroazobenzene] (pDR1A) (5) and poly[4-(2-methacryloyloxy)ethyl-azobenzene] (pMEA) (9) are subjected to irradiation with a polarized argon laser at 514 nm.



The writing/erasing curve is very similar in both cases, however there are significant differences in the level of birefringence achieved and the time required to achieve it. pDR1A has a maximum absorbance at 490 nm, very close to the laser wavelength. pMEA has a maximum absorbance at 330 nm, while its cis isomer absorbs at 450 nm. pDR1A absorbs the laser light more efficiently, thus the saturation level of birefringence is 0.08 and is achieved, depending on the film thickness, in about 100 ms. pMEA has only a tail of its absorbance at 514 nm. Its maximum level of birefringence is 0.009 and it takes over 10 seconds to

achieve it. This experiment is done with a laser power of 3 mW/cm². pMEA can also be "written" with UV light.

Another example in which the nature of the azobenzene determines different "writing" behavior has been published previously (6).

The polymer structure: This is obviously very important, as it determines the potential mobility of the azobenzene group, the stability of the "writing" (by its glass transition temperature) and the overall thermal stability of the material.

The film thickness: Depending the absorbance of the azo group and on the wavelength of the laser, thicker films may present a nonlinear behavior which was described in another publication (10). There is a maximum workable thickness of the film for a certain wavelength: $4/\alpha$, where α is the absorption coefficient of the film. Obviously, pMEA films will have a greater useful thickness than pDR1A films at 514 nm, due to the great difference in absorption at this wavelength.

The azo group content: Intuitively, the more azo groups are present in a sample, the greater will the achievable birefringence be. This was confirmed in our experiments and in others found in the literature. We have also observed a neighboring group effect associated with increasing azo content, and this effect will be described in a following subheading.

The self-organizing tendency of the polymer: The literature contains examples of semicrystalline polymers (11,12) in which much higher levels of birefringence (0.2-0.3) can be attained. This is achieved because "writing" on such films reinforce the thermodynamic tendency of these polymers to form organized domains. We will show in a following subheading that in the process of reorientation, some other rigid groups present in the polymer are moved by "sympathy", and that this cooperative motion enhances the effect created by the laser.

Efficiency and Stability

Figure 1 illustrates the result of an experiment with a pulsed laser. The aim of the experiment was to determine how many times one can "write" on the same spot of the film before the film is damaged. It is clear from Figure 1 that the determining factor is not the number of times one can "write and erase", but the overall power input into the film. With a power of 5mW, the film is damaged earlier than with a power of 1 mW, even though the number of cycles at 10Hz and at 100 Hz is quite different. For 100 Hz, one can see that 10^5 cycles can be attained (with 1 mW power) which indicates good long term usage of such a material. There probably is a correlation between the overall thermal stability of these films and the resistance under a laser light, but this correlation is still to be established. A typical pDR1A film starts decomposing when heated above 180°C.

The overall thermal stability of the induced reorientation (of the "writing") is illustrated in Figure 2. It is clear that heating of a "written" sample destroys the induced orientation, and as one gets closer to the glass transition temperature, all reorientation is lost.

When trying to "write" at different temperatures, the amount of birefringence remaining after the laser is switched off clearly depends on how far from T_g is the writing temperature. This experiment illustrates how important is to synthesize polymers with high glass transition temperatures to be used in this reversible optical storage process.

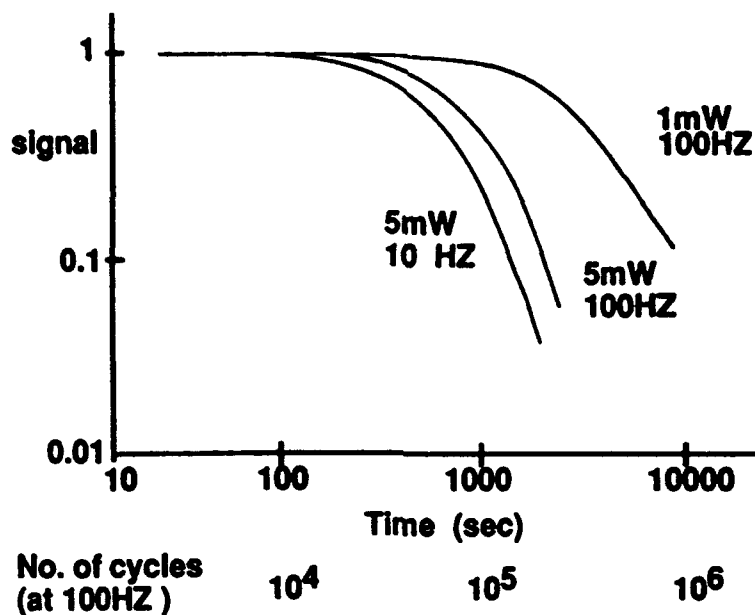


Figure 1. Normalized signal (proportional to the square of the birefringence) as a function of the time the pulsed laser is kept ON on the same spot on a film of pDR1A.

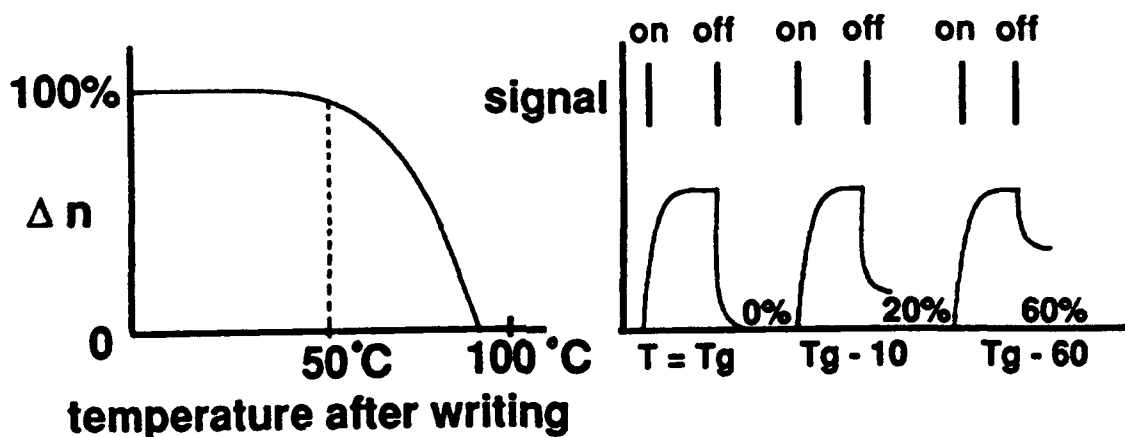


Figure 2. Thermal stability of "writing" in a pDR1A film. a. Birefringence as a function of temperature. b. Normalized signal in a sample written at about T_g , about 10 degrees below T_g and at about 60 degrees below T_g (room temperature for pDR1A).

The efficiency of the process can be best described by the diffraction efficiency obtained when inscribing a phase grating (as in holographic storage). This is defined as the ratio between the

amount of probe light which is diffracted by the grating and the amount of incident light (13). The efficiencies for pDR1A at 514 nm are in the range of 10^{-4} for films of 0.3 nm thickness. This type of efficiency depends on the film thickness (the thicker the film the more efficient the diffraction), and one has to take into account the fact that at this wavelength pDR1A is absorbing, hence its useful thickness is very low. The best photorefractive polymer reported in the literature has an efficiency of 1.2% (14) for a 125μ thick film. When normalizing, the square root of efficiency per cm is 8.8 for the photorefractive polymer and 745 for pDR1A (15).

These results suggest that for holographic storage use, nonabsorbing films may be much better.

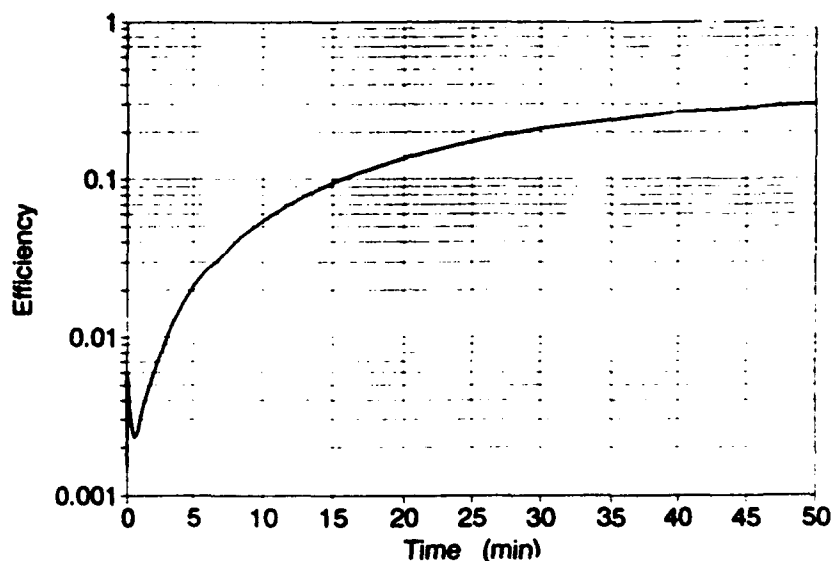


Figure 3. Diffraction efficiency as a function of time for a 12μ film of pMEA irradiated at 514 nm.

Figure 3 shows how the efficiency, expressed as diffracting efficiency, increases with time for a pMEA film (12μ thick) at 514 nm. The process is very slow, because pMEA barely absorbs this wavelength, but the efficiency levels are very high : up to ca. 20%. Thicker films should show even better efficiencies. Thus, if pMEA is not such a good candidate for reversible fast writing as described previously, it may be the best material for holographic storage use.

Neighboring Group Effect

As it was mentioned above, the level of birefringence that can be achieved in a sample depends - among other factors - on the azo group content in the sample. Various references in the literature report induced dichroism and/or birefringence in polymers containing different amounts of azobenzene groups. We have decided to systematically study the effect of composition on the reorientation phenomenon. To this end, we have synthesized and characterized two series of copolymers and one series of blends. The copolymers are poly(DR1A-co-MMA) and poly(DR1M-co-MMA) [DR1M is the methacrylate equivalent of DR1A] and the sequence distribution has been analyzed by solution NMR and found to be

fairly different between the two series (16). This means that for two samples of the same composition, poly(DR1M-co-MMA) will have a different distribution of units than poly(DR1A-co-MMA). The blends were prepared by mixing various amounts of pDR1A and pMMA. With a proper thermal pre-treatment, the two polymers are miscible at the molecular level in any proportion (17).

Figure 4 illustrates the birefringence of all these sample as a function of the azo group content (by weight). It is very clear in the figure that, apart from the overall azo group content, there is some other factor influencing the saturation level of birefringence. All films reported in Figure 4 have similar thicknesses and similar Tgs.

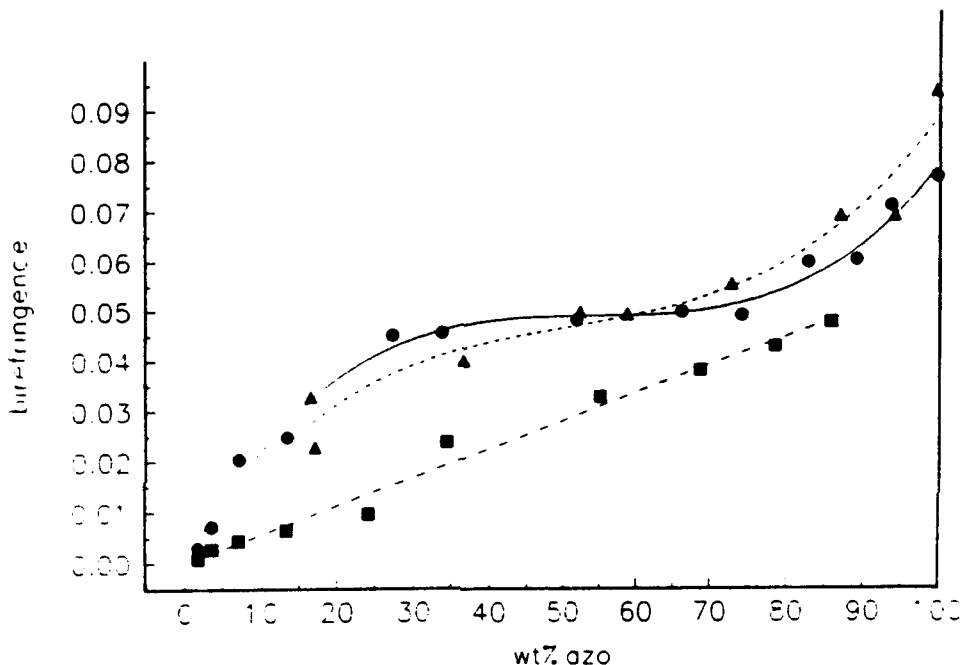


Figure 4. Saturation birefringence level as a function of weight percent azo in the copolymer or blend. (Δ) poly(DR1A-co-MMA); (●) poly(DR1M-co-MMA); (■) blends of pDR1A with pMMA.

For the blends, there is a linear increase in the birefringence level as the azo group content increases. For the copolymers, however, there is a rapid increase at low azo content, followed by a plateau region (between 25 and 75 weight% azo), and then another rapid increase at very high azo content. The two copolymers also behave slightly differently from each other (18). Work is in progress to correlate this behavior with the difference in sequence distribution between the two copolymer series.

More evidence for the influence of the next neighbor on the reorientation of an azo group is provided by the level of relaxation after the "writing" laser is turned off, which depends on composition for the copolymers and has a different shape for each series of copolymers. Copolymers with high azo content retain more of the signal than copolymers with low azo content. This level of relaxation does not depend on composition for the blends (18). Also, the cis-trans thermal relaxation apparent rate constant can be modeled very well using the triad distribution in these two series of copolymers. Again, the cis-trans thermal isomerization is

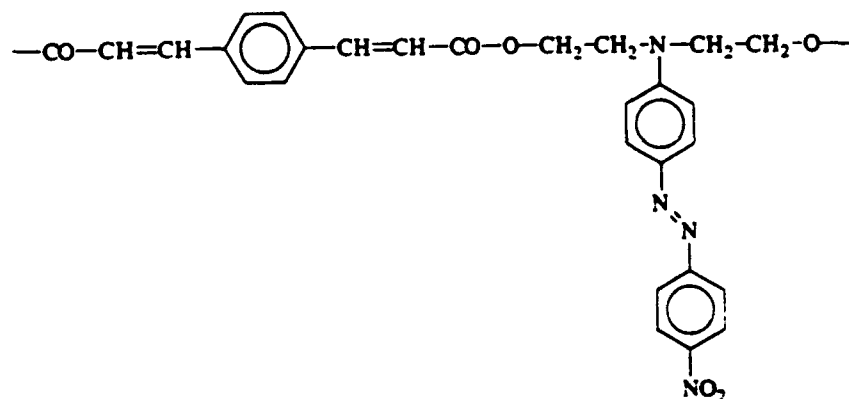
about twice as fast for azo groups with azo neighbors than for azo groups with methyl methacrylate neighbors (19).

Cooperative Motion

From the above described results it is very clear that there is an "amplification" effect in reorientation if two azo groups are next to each other. The term amplification has been used to describe a similar phenomenon of reorientation of liquid crystals triggered by azo-containing Langmuir-Blodgett monolayers (20). For the phenomenon described in Figure 4, an enhancement of about 33% can be calculated for instances where azo groups neighbor other azo groups and tend to reorient together.

This phenomenon is also known for liquid crystalline copolymers containing azo mesogens and mesogens of the same shape and situated at the same site on the copolymers, but containing ester or amide bonds instead of azo. These mesogens are not responding to the laser light, but they do reorient by "sympathy" when the azo mesogens are moved by the laser light (21).

As we mentioned in a previous section, if the polymers are semicrystalline, there may be a three-fold amplification of the induced birefringence. We have synthesized pDR19T:



following the literature procedure (12) and investigated this unexpected increase in birefringence using our "writing" procedure and infrared and UV-Vis dichroism. A typical writing curve for pDR19T is shown in Figure 5.

The "writing" curve in Figure 5 confirms that the level of birefringence achievable in an amorphous pDR19T film is much higher than in pDR1A. However, it takes tens of seconds to achieve saturation in a film of comparable thickness with pDR1A, where it takes about 100 ms. The difference appears from the fact that - as the laser starts reorienting the azo groups - whole crystalline domains are formed and oriented in the preferred direction. Indeed, at point B, where the laser is turned off, the birefringence increases, instead of decreasing as it does in amorphous polymers. The heat which has to be dissipated through the sample reinforces the thermodynamic tendency of the rigid groups to organize in crystalline domains. Erasing is very slow and rewriting never gives the same level of birefringence that was initially achieved in the amorphous film, because the disorder achieved by erasing is composed now of organized domains

randomly oriented.

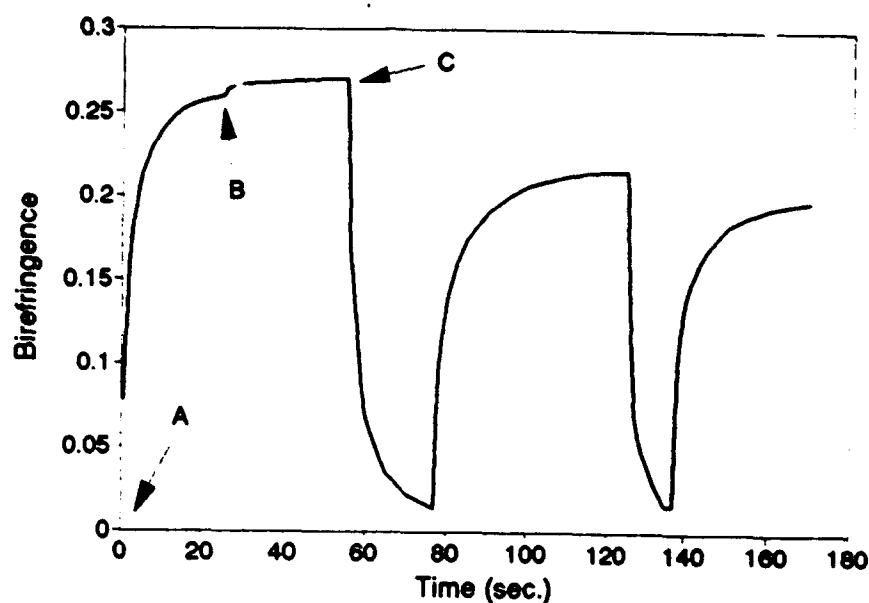


Figure 5. "Writing" curve on a freshly prepared pDR19T film. A: 514 nm planarly polarized laser ON; B: laser OFF; C: circularly polarized laser ON. Same procedure is repeated at 80 seconds and at 135 seconds.

An IR dichroism study (22) confirms that the dichroism of the azo groups is much greater in pDR19T than in pDR1A, but that - surprisingly - the other rigid groups in the polymer structure ($-\text{CH}=\text{CH}-\text{Ph}-\text{CH}=\text{CH}-$) also show a significant dichroism in the same direction as the azo groups. Thus, this reorientation by "sympathy" which has been reported in Langmuir-Blodgett films and liquid crystalline polymers is a much more general phenomenon and may involve rigid groups which are of a completely different shape and situated at a completely different site in a polymer structure.

POTENTIAL APPLICATIONS

Because of the potential of repetitive usage, an obvious application of the amorphous azo polymers is in erasable optical memory disks or cards. The rate of "recording" is in the milliseconds range. For read only memory, or write once read many times, liquid crystalline or semicrystalline polymers may be preferred, because the time to "write" the information is not critical, while the "contrast" (birefringence) is greater than in amorphous polymers.

Holographic storage also seems a fairly good potential use for these polymers. They are probably the only materials which can be reversibly recorded and which do not require any development of the image after recording. One advantage of these materials is that one could define a certain direction and store an image in that direction, then define another direction, at a fairly close angle to the first one, and store another image in the new direction. A multitude of directions could be defined this way, allowing a very high density of storage.

Some research groups have proven the waveguide properties of

the laser-induced "writing" on polymer films (23). One could imagine a "printed circuit" of waveguides on a polymer film having the main advantage that any connection could be erased or added at any time during the lifetime of such a device. Simplified versions of such waveguides can act as sensors in buried places. Second harmonic generation can also be obtained in these polymer films by using a combination of laser-induced reorientation and electric field poling (24). The advantage is that heating above T_g (as in "regular" poling) is not necessary.

CONCLUSIONS AND FUTURE WORK

A reversible order-disorder transition can be induced photochemically in amorphous high- T_g azobenzene-containing polymers. The mechanism of the reorientation process is still under study, but the most interesting aspect are the neighboring group effects and the cooperative motion between like and unlike rigid groups present in the polymer structure. The reorientation depends on the maximum absorbance of the polymer and its relation with the "writing" laser.

Our research group is investigating this phenomenon along a few lines. We are synthesizing new azobenzene-containing polymers with various absorbances in order to obtain high T_g and thermally stable polymers. We are studying the neighboring group effects on the efficiency of this process and are investigating new polymer structures which are liquid crystalline of a lower orientational order, or can become liquid crystalline by being subjected to polarized laser light.

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