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Optical information can be stored, erased or overwritten on polymer thin films using polarized light. The information is in the power probe beam. We have measured the efficiency of the writing beam in a number of polymer and copolymer films containing azobenzene dyes as side groups. In this paper we compare the results amongst the polymers have synthesized. Preliminary results indicate that copolymers may be optimized to allow for the preparation of efficient thick films for erasable optical recording.

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EFFICIENCY OF REVERSIBLE OPTICAL STORAGE IN AZO POLYMERS

by

P. Rochon, J. Mao, A. Natansohn and S. Xie

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EFFICIENCY OF REVERSIBLE OPTICAL STORAGE IN AZO POLYMERS

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ABSTRACT

Optical information can be stored, erased or overwritten on polymer thin films using polarized light. The information is in the form of localized dichroism and birefringence and is read using a low power probe beam. We have measured the efficiency of the writing beam in a number of polymer and copolymer films containing azobenzene dyes as side groups. In this paper we compare the results amongst the polymers we have synthesized. Preliminary results indicate that copolymers may be optimized to allow for the preparation of efficient thick films for erasable optical recording.

2. INTRODUCTION

Azopolymers have been shown to exhibit long term stability in optically induced changes in their optical properties, in particular in induced birefringence and dichroism. Furthermore the optical information can be erased optically or thermally, or overwritten[1-2]. These qualities thus make films made of azopolymers very good candidates for erasable optical memories or for applications in electrooptics.

In recent years a concentrated effort has been made to understand, quantify and control the mechanisms involved in the optical recording[3-8]. The fundamental mechanism involves the reorientation of the optically anisotropic azoaromatic molecules in the polymer. This is accomplished by a selective photoisomerization of the molecules. It is well known that azobenzene can photochemically isomerize from the stable trans configuration to its cis configuration. The cis form can then isomerize back to the trans form either photochemically or thermally. One cycle of this trans-cis-trans isomerization will result in a reorientation of the trans molecule. The photoisomerization is induced using linearly polarized light which is absorbed by the azo dye. The probability of a particular molecule undergoing a reorientation will be proportional to the square of the angle between the molecular axis and the linear polarization direction. As the sample is exposed to the writing beam, the number of molecules lying parallel to the polarization direction will thus be decreased while those in the

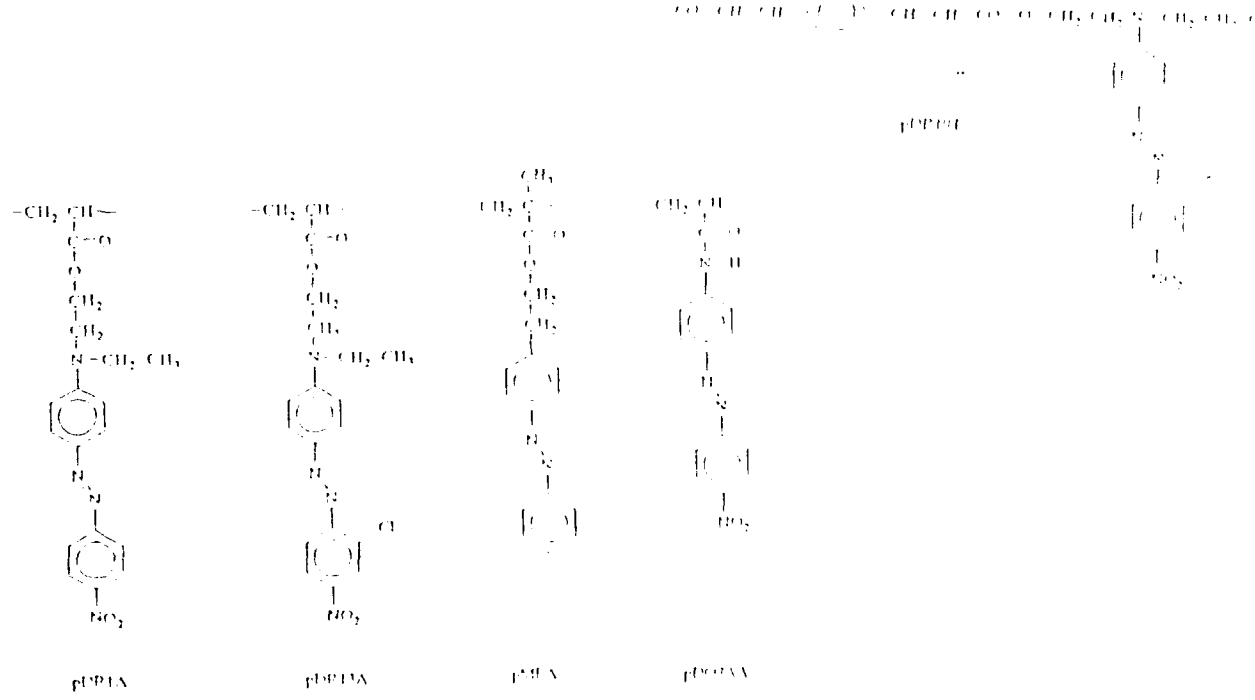
perpendicular direction will increase. The net result is an induced local birefringence and dichroism in the polymer film.

When the azobenzene groups are attached as side groups to long polymer chains, it has been found that the photoinduced anisotropy is maintained over long periods of time, at least for up to two years, with little degradation. Because the cis to trans isomerization can be optically induced and that the quantum yields for this process has been found to be greater than the trans to cis photoisomerization the time for reaching a saturation of the optical anisotropy can be relatively short, typically one second or less for a writing beam power of .1 W/cm^2. When the writing beam is turned off the induced birefringence can relax to about 80% of its saturation value and remains stable. The information can then be read nondestructively with a probe beam which detects the birefringence.

In the present work we report on the preliminary studies that we have done on several polymers and copolymers to characterize the efficiency of the writing process on the polymer films.

3. MATERIALS

The polymers that we have studied are amorphous polymers with high glass transition temperatures containing azoaromatic groups on the side chains. We have also studied a series of polymers made from the copolymerization of methyl methacrylate (MMA) with pDR1A as well as blends of pDR1A with PMMA. The structures of the various polymers are represented below:



4. EXPERIMENT

The polymers were dissolved in tetrahydrofuran (THF) and films were made by spin casting on glass substrates. The film thicknesses were selected such that at least 25% of the writing beam was transmitted through the sample. This was done in an attempt to avoid complications due to sample thickness.

The birefringence of the film at 632.8nm was measured by placing the sample between crossed linear polarizers. A 10 microwatt HeNe laser was used as probe. Optical anisotropy was induced in the film using a polarized Argon laser beam at 514.5 nm to write on the sample at a polarization angle of 45 degrees with respect to the probe polarization. The writing beam power was measured at 0.2 W/cm^2. The polarization state of the writing beam could be controlled using a Pockels cell. All measurements were performed at room temperature.

5. RESULTS AND DISCUSSION

The sample that we have studied were of varying thicknesses and had substantially different absorption coefficients at 514.4nm. We therefore define the efficiency of writing as the ratio on the net birefringence produced in the sample at saturation over the total energy absorbed by the sample to reach saturation. This definition is somewhat different than the usual definition of efficiency[8] which is the ratio of birefringence over the energy of the writing beam. We have attempted to compensate for the samples thickness and absorption coefficient in our definition in the hope that these parameters can be adjusted to maximize the net efficiency of a particular film.

The results that we have obtained are summarized in Table 1 where we report the saturation value of the birefringence Δn and the efficiency.

We note that all the samples have similar efficiency except for pDO3AA. The higher birefringence value of pDR19T can only be acheived by writing on the sample with more energy, in this case the exposure time increased in proportion to the increase in birefringence. These results reflect the semicrystalline nature of pDR19T[9]. The optical anisotropy is believed to be on a microdomain size rather than at the molecular level and this cooperative motion leads to an enhanced effect but requires more time to reach saturation. pDR19T also exhibits a hysteresis in that upon optically erasing the birefringence and rewriting, the subsequent levels of birefringence are lower.

Table 1
Birefringence and Efficiency

Polymer	Δn	Efficiency= Δn/Energy(absorbed) (10^{-6} cm^3/J)
pDR1A	.07	6.2
pDR13A	.08	4.4
pDO3AA	.06	0.4
pMEA	.01	3.2
pDR19T	.21	2.5

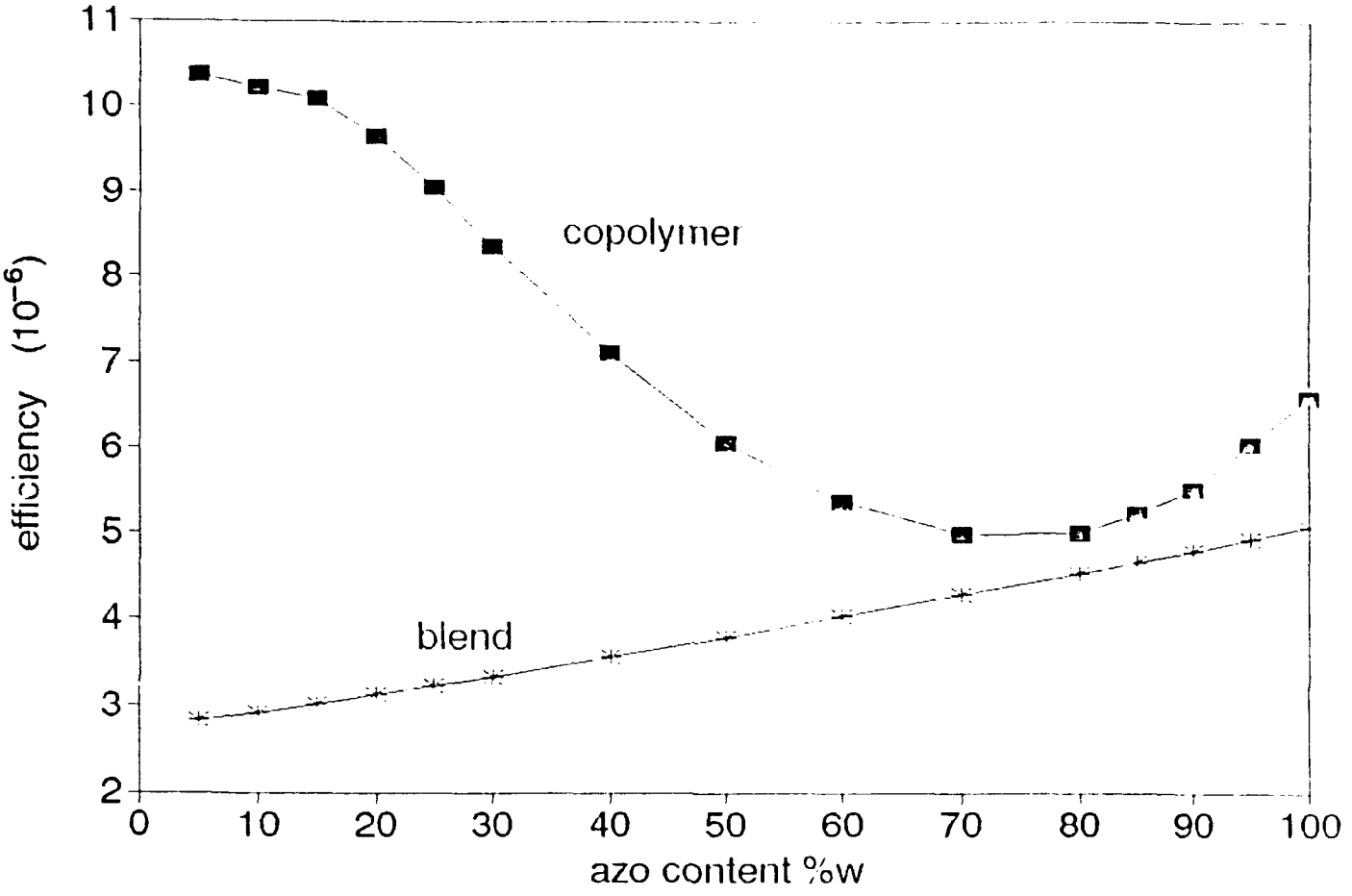
pDO3AA is an example of a polymer with no spacer between the azobenzene group and the main chain. The restricted internal motion reorientation results in a much slower writing process and consequently a much lower efficiency.

pDR1A, pDR13A, and pMEA have similar saturation values and efficiency even though their absorption coefficients at 514.5 are substantially different. Furthermore pMEA has no push-pull substituents on the azobenzene groups hence the cis isomer is relatively long lived for thermal reverse isomerization. The cis to trans isomerization is therefore probably optically induced at a rate that make pMEA as efficient as pDR1A. This reflects the higher quantum yield for the later transition[7].

pDR1A appears to be a most favorable candidate for reversible optical image storage, but its absorption coefficient at the writing wavelength is on the order of 10^5 cm^{-1} which means that the films should have a thickness of 500nm or less. This is too low to produce efficient films for holographic recording. We have therefore investigated blends of pDR1A in pMMA and copolymers of pDR1A with MMA in order to decrease the dye concentration in the polymer and allowing the production of thicker films.

Preliminary results on the efficiency of polymer films with varying azo content are presented in figure 1.

Figure 1.



The efficiency of the polymer blends decreases as the dye content decreases. This could be explained by assuming that the dye molecules in this case have a decrease in their ability to move when surrounded by the denser pMMA chains. Fewer of the azobenzene molecules along the pDR1A can be significantly re-oriented.

On the other hand, the copolymer exhibits an increase in efficiency as the azo content is decreased. This may be a consequence of the fact that each azo molecule now has fewer highly polar azo molecules along the pDR1A chain and that their individual motion is somewhat greater. Thus the writing time in such polymers is decreased because of lower medium range interactions. This effect could also result in less stability of the written information. We are presently studying the effects of nearest neighbor configurations and interactions in this regard and to aim towards an optimum composition.

6. CONCLUSION

We have evaluated the efficiency of a number of amorphous polymers and copolymers. The results indicated that an optimum copolymer configuration which has a high writing efficiency, which would permit the preparation of thick films, and which would still exhibit erasability and long term stability may soon be possible.

7. ACKNOWLEDGEMENTS

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8. REFERENCES

1. T. Todorov, N. Tomova and L. Nikolova, "High-sensitivity Material with Reversible Photo-induced Anisotropy", Opt. Commun, 42, pp123-126 (1983).

2. P.Rochon, J. Gosselin, A. Natansohn, and S.Xie,"Optically Induced and Erased Birefringence and Dichroism in Azoaromatic Polymers", Appl. Phys. Lett. 60, pp4-5 (1992).

3. A. Natansohn, P.Rochon, J. Gosselin and S. Xie, "Azo Polymers for Reversible Storage", Macromolecules 25, pp2268-2273 (1992).

4. P. Rochon, J. Gosselin, A. Natansohn, and S. Xie, "Kinetics for Reversible Optical Storage in Azo Polymers", Proc SPIE 1774, pp181-186 (1992).

5. Z.Sekkat and M.Dumont, "Polarization Effects in Photoisomerization of Azo Dyes in Polymeric Films", Appl. Phys. B53, pp121-123(1991).

6. M. Dumont and Z. Sekkat, "Dynamical Study of Photoinduced Anisotropy and Orientational Relaxation of Azo Dyes in Plymeric Films: Poling at Room Temperature", Proc. SPIE 1774, pp188-199, (1992).

7. R. Loucif-Saibi, K. Nakatani, J.A. Delaire, M.Dumont,and Z.Sekkat, "Photoisomerization and Second Harmonic Generation in Disperse Red One-Doped and Functionalized Poly(methyl methacrylate) Films"Chem. Mater. 5, pp229-236 (1993).

8. P.Rochon, A. Natansohn, J. Mao, C. Barrett ans S. Xie, "Efficiency of Laser-Addressed Optical Storage in some Azo Polymers", Science, submitted, June 1993.

9. A. Natansohn, P. Rochon, and D. Brown, "Induced Birefringence and Dichroism in Azo Polymers. Comparison Between Amorphous and Liquid Crystalline polymers", Polym. Prepr. ACS Div. Polym. Chem. 34, p739-740 (1993).

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