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

A. Natansohn,*,† S. Xie,† and P. Rochon‡

Department of Chemistry, Queen's University, Kingston, Ontario, Canada K7L 3N6, and Department of Physics, Royal Military College, Kingston, Ontario, Canada K7K 5L0

Introduction

In previous publications[1,2] we have shown that amorphous polymers containing azobenzene groups can be used as reversible optical storage media. Using a polarized laser beam, information can be written, read, erased, and rewritten on the same spot by means of induced birefringence and dichroism.[1] Liquid crystallinity is not a necessary condition for optical storage properties. In fact, liquid crystalline azo polymers have rather low glass transition temperatures, and thus lower storage stability at room temperature.[2] This is clearly seen in a recent publication[3] which describes similar writing procedures in the glassy state and in the liquid crystalline state for a series of azobenzene-containing liquid crystalline copolymers.

The mechanism of writing involves photochemical excitation of the azobenzene group, which undergoes a trans–cis isomerization. The cis–trans thermal isomerization is relatively rapid. An example of a write/erase curve is presented in Figure 1. An azobenzene group will be inert to photochemical excitation by the laser beam if its orientation is perpendicular to the polarization direction. The trans–cis photochemical transition rate can be described by a $I \cos^2(\phi)$ term, in which I is proportional to the laser beam intensity and ϕ is the angle between the azobenzene orientation and the laser polarization direction. All azobenzene groups which are not perpendicular to the laser polarization direction will undergo many trans–cis–trans isomerization cycles, without preserving their orientation. Those azobenzene groups which fall perpendicular to the laser polarization at the end of one of the cis–trans isomerization processes will remain in this position, because they cannot be reactivated when $\cos^2(\phi) = 0$. The net result of this process is an excess of azobenzene groups aligned perpendicular to the laser polarization. This translates in the birefringence read with a second laser beam, as seen in Figure 1.

When the writing laser is switched off, there is a certain relaxation process which eventually leaves about 60% of the signal intact. The decay at the moment of switch-off of the writing beam appears to be described by a relatively fast process and a slower one. The fast process may be associated with the cis–trans transition of the azobenzene groups which were in their cis configuration while the writing beam was on. While the excess azobenzene groups in the cis configuration do not contribute to the signal intensity, the sudden appearance of randomly oriented trans groups (from cis isomerization) has as an effect the decrease the overall birefringence of the written spot. The slower process is probably associated with the thermal diffusion of some of the molecules. The polymer used in our previous paper and in Figure 1—poly[4'-[[2-(acryloyloxy)ethyl]ethylamino]-4-nitroazobenzene] (pDR1A)—
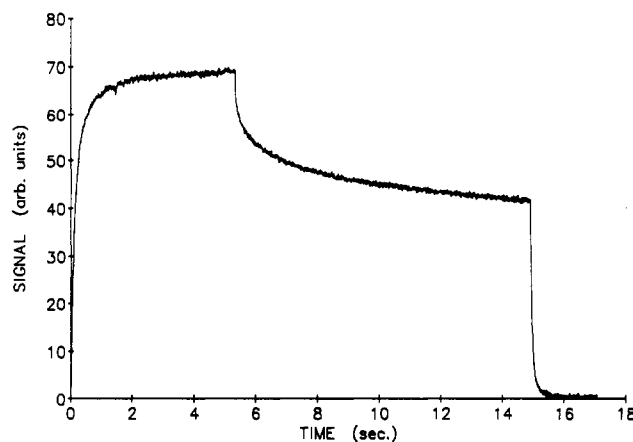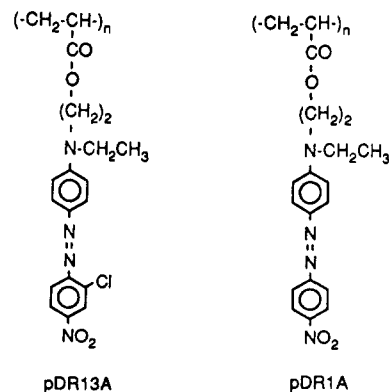
† Queen's University.
‡ Royal Military College.

Figure 1. Writing and erasing sequence on a pDR1A film. Writing beam is turned on at $t = 0$ s and turned off at $t = 5.5$ s; erasing beam is turned on at $t = 15$ s.

has a relatively low molecular weight, allowing for extensive motion, at least at the chain ends. Some thermal effects should also be considered as they obviously increase molecular motion.[2]

The erasure process is the fastest since circularly polarized light is being used to randomize the orientation of the azobenzene groups and fewer trans–cis–trans cycles are required to achieve randomization. Assuming that the cis lifetime is reasonably long for the molecule not to "remember" its previous orientation, a single trans–cis–trans cycle could be sufficient to randomize a previously oriented assembly of azo groups. For a random sample, with the same assumption of random distribution of orientations after isomerization, a significantly higher number of trans–cis–trans cycles will be necessary to achieve a preferred orientation. The erasure process is faster probably also because the circularly polarized light may heat the polymer more than the linearly polarized light.

The time to achieve birefringence, as well as the time to randomize the orientation, depends on a series of factors which we wanted to investigate. Light intensity is one of these factors. The more photons a sample absorbs, the faster the writing or erasing process.[2] The influence of film thickness is analyzed in another publication.[4] This paper presents a comparison between pDR1A and a polymer containing a slightly different azobenzene group: poly[4'-[[2-(acryloyloxy)ethyl]ethylamino]-2-chloro-4-nitroazobenzene] (pDR13A). The formulas of the structural units of the two polymers compared are as follows:

pDR13A　　　　　　　　　pDR1A

Experimental Section

The monomer was synthesized by the procedure described previously,[2] using Disperse Red 13 (Aldrich) instead of Disperse
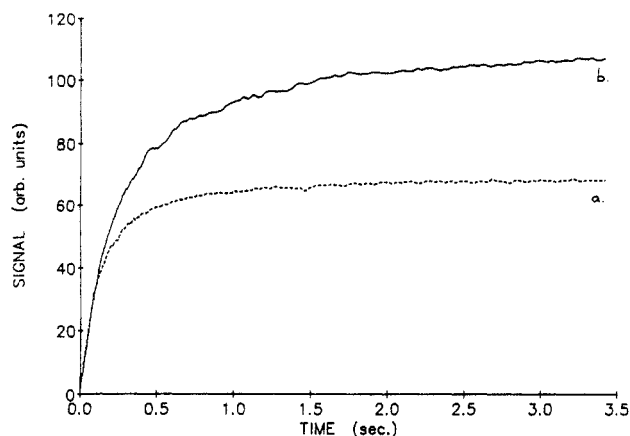
Figure 2. Writing curves for (a) a 106-nm-thick pDR1A film and (b) a 103-nm-thick pDR13A film.

Red 1. The NMR spectrum confirmed the monomer structure. The melting point of the monomer is 80 °C. The polymerization procedure was also identical, yielding 50% pDR13A with a DP_n of about 12, as determined by GPC. The glass transition temperature of pDR13A is 87 °C, as determined by DSC. Films of pDR1A and pDR13A were obtained by casting THF solutions of the two polymers on clean glass slides, allowing the solvent to evaporate, and heating the slides slightly above the glass transition temperature of each polymer. Film thickness was measured in each case by measuring the displacement of interference fringes produced by light reflected from the film surface with respect to light reflected from the film surface with respect to light reflected from the substrate. The procedure used for writing, reading, and erasing has been described previously.[1,2] The laser intensity was 5mW for a spot of 400-μm diameter.

Results and Discussion

To compare the rate of writing on pDR1A and pDR13A, it is essential that films of comparable thickness be used.[4] Figure 2 presents the writing curve for two films of the two polymers. The film thickness of the two samples is 106 nm for pDR1A and 103 nm for pDR13A. The glass transition temperatures for the two polymers are very close (91 °C for pDR1A and 87 °C for pDR13A). The saturation value is higher for pDR13A (105 arbitrary units in the experimental conditions employed here) than for pDR1A (64 arbitrary units). This can be explained by a higher refractive index of Disperse Red 13. Its maximum absorbance (502 nm) lies closer to the reading laser wavelength (632.8 nm) than the absorbance of Disperse Red 1 (λ_{max} = 464 nm). The ratio of the saturation values for the two polymers reflects the ratio of the measured absorbances (1.4×10^8 m^{-1} for pDR13A and 8.5×10^7 m^{-1} for pDR1A), as expected. The time to achieve 50% of the saturation value is 106 ms for PDR1A and 222 ms for PDR13A. This clearly indicates that the writing process is slower in PDR13A. In terms of the trans–cis–trans

isomerization processes which take place in order to achieve birefringence, the explanation for slower writing on PDR13A is straightforward. It has been shown that the activation energy for the trans–cis isomerization is similar for various substituents of the azobenzene.[5] There is a slight increase in the activation energy when bulky substituents are close to the azo group. The quantum yield of the isomerization can be very different. It decreases as bulkier substituents are introduced on the rings.[6] In our case, the chlorine atom in the ortho position to the azo group will increase the activation energy and decrease the quantum yield of trans–cis isomerization process; hence a longer exposure to the laser beam will be necessary to achieve saturation.

One important consideration regarding this pair and all possible azobenzene-containing polymers with potential optical storage properties is the type of azobenzene, as defined by Rau.[5] "Simple" azobenzenes have a relatively slow cis–trans thermal isomerization rate, and this may prevent their use as storage materials. Amino-substituted azobenzenes thermally isomerize back to trans relatively fast, and so do the donor–acceptor substituted azobenzenes. All the storage experiments reported in the literature are of the donor–acceptor substituted ("stilbene-type") azobenzenes. The most common one had oxygen (donor) and cyano (acceptor) groups.[7] Our studies involve an amino (donor) and a nitro (acceptor) groups. The strength of the push–pull electrons within the azobenzene group may have an influence on the actual rate of cis–trans isomerization, thus affecting the whole writing speed. The thermal cis–trans isomerization rate is normally very fast and not measurable, unless the group is bonded to a polymer.[5] We are studying a series of amorphous polymers and copolymers with different types of azobenzene groups and trying to correlate the writing rate with the known trans–cis and cis–trans isomerization rates.

References and Notes

(1) Rochon, P.; Gosselin, J.; Natansohn, A.; Xie, S. *Appl. Phys. Lett.* **1992**, *60*, 4.
(2) Natansohn, A.; Rochon, P.; Gosselin, J.; Xie, S. *Macromolecules* **1992**, *25*, 2268.
(3) Ivanov, S.; Yakovlev, I.; Kostromin, S.; Shibaev, V.; Lasker, L.; Stumpe, J.; Kreysig, D. *Makromol. Chem., Rapid Commun.* **1991**, *12*, 709.
(4) Rochon, P.; Bissonnette, D.; Natansohn, A.; Xie, S., submitted for publication in *Appl. Opt.*
(5) Rau, H. In *Photochemistry and Photophysics*; Rabek, J. F., Ed.; CRC Press, Inc.: Boca Raton, FL, 1990; Vol. 2, p 119.
(6) Reference 5, p 126, Table 2, structures 8–10.
(7) See, for example: Wiesner, U.; Reynolds, N.; Boeffel, C.; Spiess, H. W. *Makromol. Chem., Rapid Commun.* **1991**, *12*, 457.

Registry No. pDR13A, 142656-03-9; pDR1A, 139427-10-4.