

## Optical Storage Properties in Cast Films of an Azopolymer

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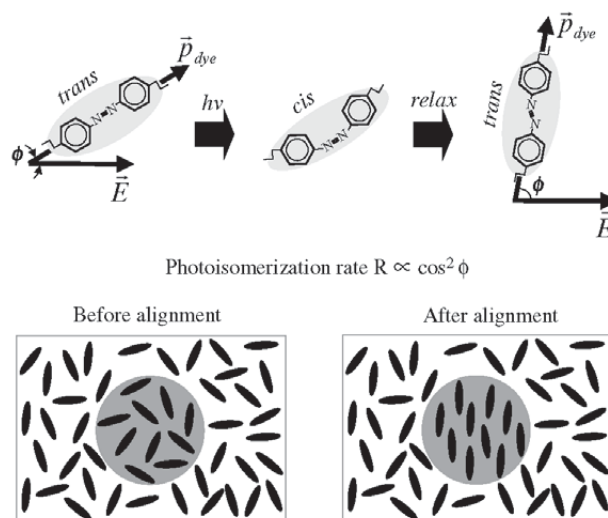
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In this paper we discuss the properties of optically induced birefringence in DR19-MDI cast films that may be used in optical storage applications. The selection of DR19-MDI cast films was based on a comparative study of optical storage properties of Langmuir-Blodgett (LB) films from various azopolymers. DR19-MDI possesses a high residual fraction of optical birefringence and good environmental stability, which was corroborated by the data from optical storage experiments. DR19-MDI cast films maintain a reasonable level of birefringence after the initial decay due to chromophore relaxation, thus making them promising candidates for optical storage devices.

**Keywords:** azopolymers, birefringence, optical storage

### 1. Introduction

Azoaromatic dyes have been widely investigated over the last few years due to their potential use in a variety of optical devices employing nonlinear optics, surface relief gratings and optically induced birefringence<sup>1</sup>. The latter process arises from the reversible *trans-cis-trans* photoisomerization and resulting molecular orientation, and allows organic polymers containing azo chromophores to be used in storing information optically<sup>2</sup>. When excited by linearly polarized laser light, azobenzene chromophores suffer *trans-cis-trans* isomerization, accompanied by molecular reorientation. Through the hole-burning mechanism, an excess of chromophores is formed in the direction perpendicular to the laser polarization after a large number of isomerization cycles. This causes birefringence in the film structure, thus representing a WRITE mechanism. As the light source is switched off, some molecular relaxation occurs, but a considerable number of molecules remain oriented. The stable birefringence pattern corresponds to the STORE step, which can be detected by measuring the change in transmittance of a weak probe beam that passes through crossed polarizers (READ). This birefringence pattern can



**Figure 1.** Optically induced birefringence diagram.

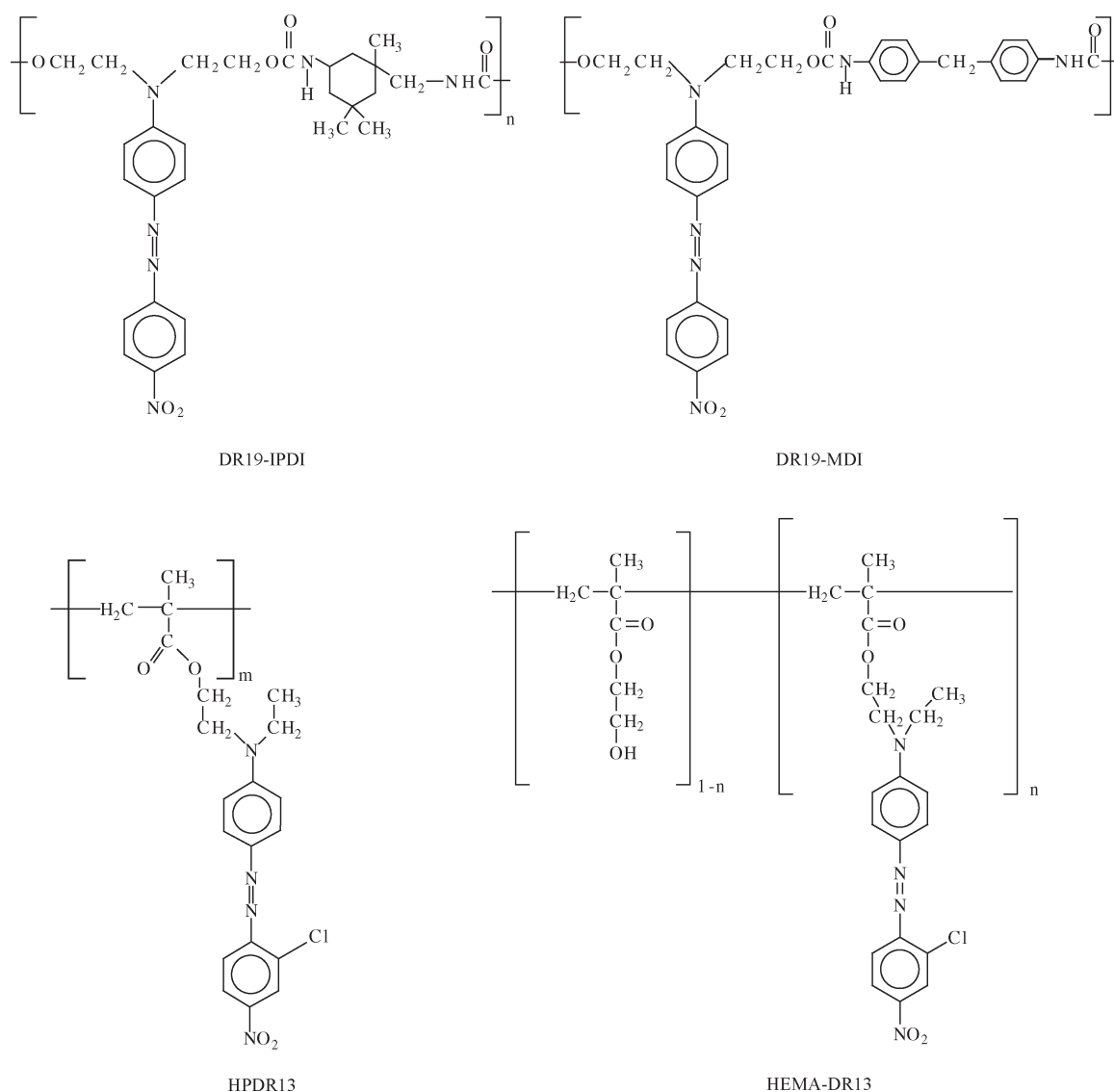
be completely erased by heating or overwriting the test spot with circularly polarized light (ERASE). Figure 1 shows a schematic representation of the orientation process<sup>3</sup>.

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In order to improve the optical storage features in azopolymers, a large number of fundamental and technology-driven studies have been made, by exploiting the rich variety of organic compounds and material processing methods available. The first possibility in this engineering process concerns the chemical synthesis, where different functional groups can be attached to azobenzene molecules, improving photochemical characteristics such as the isomerization rate<sup>4</sup>. Moreover, the azo group can be attached in different polymer backbones either in the main-chain or as a side chain<sup>5</sup>, allowing the mechanical and processing properties of conventional polymers to be combined with

the optical properties of azo groups. Extra control of the material properties can be achieved using film forming techniques such as the Langmuir-Blodgett (LB)<sup>6</sup> or layer-by-layer (LBL)<sup>7</sup> methods.

In an effort to establish materials with the desired optical storage properties, we have instituted a project to investigate a series of films from different azopolymers, particularly for obtaining experimental information to guide the development of optical storage devices. Four polymeric systems were found to provide good results in terms of optical storage and stability: polyurethane prepared from DR19 dye and methylene-diisocyanate (DR19-MDI), the



**Figure 2.** Chemical structures of DR19-IPDI, DR19-MDI, HPDR13 and HEMA-DR13.

methacrylic homopolymer of DR13 dye (HPDR13), copolymers of hydroxyethylmethacrylate and the methacrylic derivative of the DR13 dye (HEMA-DR13) and another polyurethane from DR19 dye with isophorone-diisocyanate (DR19-IPDI)<sup>6,8-10</sup>. The chemical structures of these polymers are shown in Fig. 2. These studies were performed with LB films to achieve better control of thickness and surface uniformity imparted by the LB method<sup>11</sup>. Guest-host systems from some polymers and chromophores were also studied. However, these latter systems are not suitable for applications owing to their small residual birefringence<sup>12</sup>. The low storage efficiency is typical of azoaromatic dyes in guest-host films, where the chromophores are not covalently attached to the polymer chain, resulting in an excessive freedom for rotational diffusion. The optical storage properties of LBL films of a series of anionic dyes and azopolymers alternated with different polycations were also investigated. In this kind of systems, the writing process takes much longer than in the spin-coated or cast films, due to the electrostatic and H-bonding interactions, which hamper the photoisomerization and molecular orientation<sup>7</sup>.

The studies involving the four systems in Fig. 2 pointed to a clear relation between the optical storage properties and the structure of the polymer to which the azobenzene group is attached. Since the writing and relaxation times for azopolymers are usually in the range of a few seconds, and are basically inherent to the mechanism of orientation, the following discussion will be focused on the maximum and the residual fraction of the induced birefringence. These two parameters are the most important for applications. Table 1 summarizes some optical storage features of LB films from the four azopolymers, and a full discussion of these results is given in Ref. 13. It is readily seen that the residual fraction for DR19-MDI is higher than for other films, owing to the polymer rigidity, which is reflected in  $T_g$  values. The maximum induced birefringence ( $\Delta n$ ) also depends on the polymer rigidity. The higher the polymer  $T_g$ , the lower the maximum induced birefringence. Of course, this value also depends on the chromophore concentration that is related to the chosen polymer.

**Table 1.** Optical Storage characteristics of LB films from azopolymers HEMA-DR13, HPDR13, DR19-IPDI, DR19-MDI (from Ref. 13).

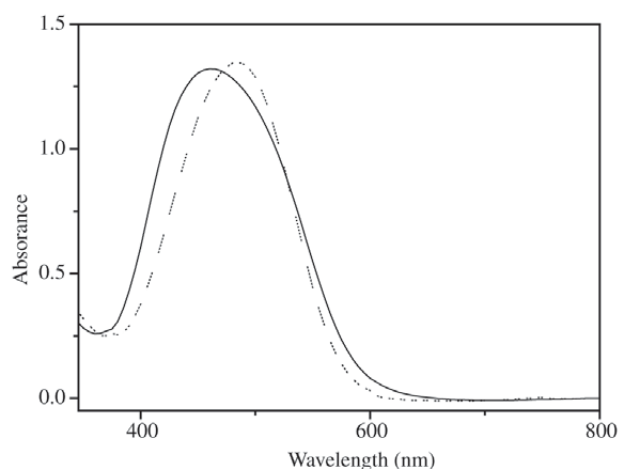
	Maximum $\Delta n$	Fraction of residual signal (%)	$T_g$ (°C)
HEMA-DR13	0.07	48	64
HPDR13	0.12	35	56
DR19-IPDI	0.013	70	138
DR19-MDI	0.026	80	145

On the basis of these results, DR19-MDI may be considered a good candidate for optical storage applications due to its high residual fraction in addition to environmental stability. One barrier to be overcome though is the low birefringence, which is 0.026 for a LB film. Better performance may be achieved with thicker films, produced by casting or spin-coating instead of the LB method. It is known that the birefringence of a LB film is usually higher than in a spin-coated film<sup>14</sup>, but the much larger thickness of the latter film can compensate and lead to an appreciable transmission signal. As a consequence, a higher light phase variation appears, which is important for optical storage devices. In this work we present data for DR19-MDI cast films, including the optical storage characteristics, writing/erasing stress tests and liability (relaxation) of the stored information.

## 2. Film Preparation and Characterization

The polymer synthesis was carried out as described in Ref. 8. The films were cast onto glass substrates, previously cleaned with the RCA<sup>15</sup> method. Initial attempts to produce thick films were made using volatile solvents, such as dichloromethane and chloroform. However, due to the low polymer solubility, it was impossible to obtain thick and visually uniform films. Thick, uniform films were obtained by using a high boiling point solvent, N-methyl-2-pyrrolidone (NMP). After several experiments, the optimized condition found was a 10/90 w/w solution (polymer/NMP), dried at 50 °C for 4 h. The film was characterized by UV-vis. absorption spectroscopy with a Hitachi-U2001 spectrophotometer.

The UV-vis. spectrum of a cast DR19-MDI film is shown in Fig. 3, which also includes the spectrum for DR19-MDI in a NMP solution. The absorption maximum of the film is



**Figure 3.** UV-vis. spectra of a DR19-MDI film (solid line) and a solution of the same polymer in NMP (dotted line).

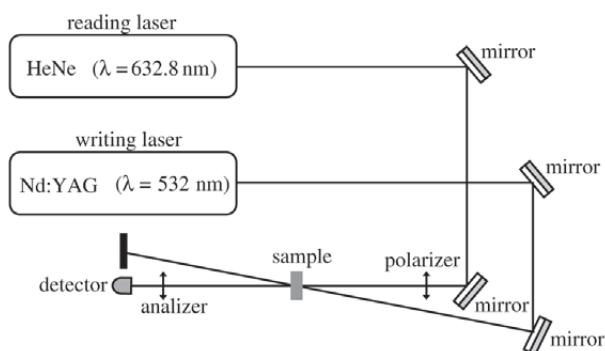


Figure 4. Optical storage experimental setup.

blue shifted in comparison to that in solution, indicating H-type aggregation of azobenzene chromophores in the film. Such a behavior is similar to that presented in Ref. 8.

### 3. Optical Storage Experimental Setup

The optical storage experiments were performed by producing the optically induced birefringence in the film using a diode-pumped frequency doubled, linearly polarized Nd:YAG continuous laser at 532 nm (writing beam) with a polarization angle of  $45^\circ$  with respect to the polarization orientation of the probe beam (reading beam). The power of the writing beam is varied to study the time and amplitude of the optically induced birefringence. A low-power He-Ne laser light at 632.8 nm passing through crossed polarizers was used as the reading beam to measure the induced birefringence in the sample. Figure 4 presents a diagram of the experimental setup. The optically induced birefringence can be determined by measuring the probe beam transmission ( $T = I/I_0$ ) according to:

$$\Delta n = \frac{\lambda}{\pi d} \sin^{-1} \sqrt{\frac{I}{I_0}} \quad (1)$$

where  $\lambda$  is the wavelength of the incident radiation,  $d$  is the film thickness,  $I_0$  is the incident beam intensity and  $I$  is the intensity after the second polarizer.

### 4. Results and Discussion

The result of a typical optical storage experiment with a DR19-MDI cast film is presented in Fig. 5, in which a writing power of 7 mW was used. Before the writing beam was switched on, there was no transmission of the probe beam that passes through the film and crossed polarizers. This indicates the random orientation of the chromophores. When the writing beam was switched on at point A, the transmis-

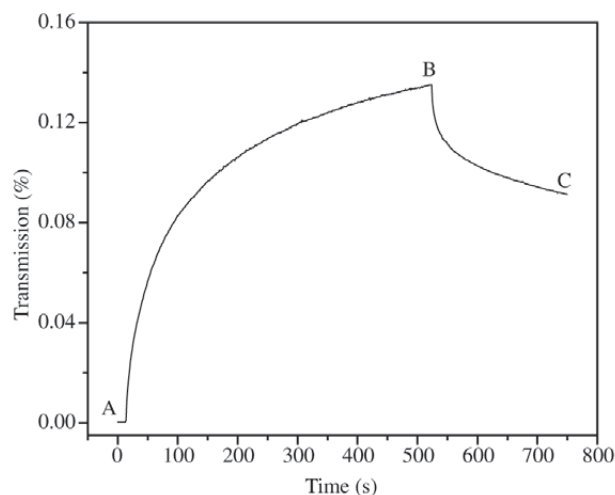


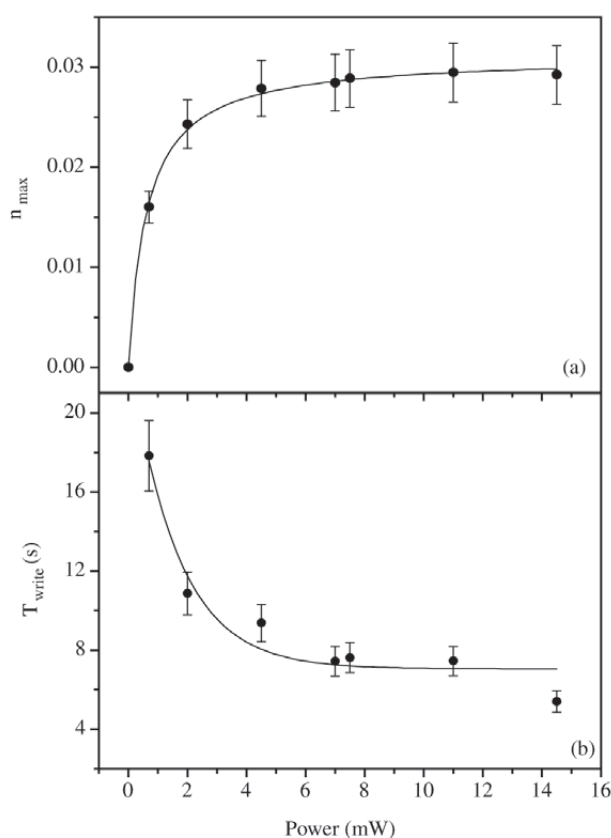
Figure 5. Writing sequence for a MDI cast film. The writing beam power was 7 mW.

sion increased and reached saturation in ca. 7 min. Such an increase in transmission is related to the induced birefringence due to the chromophore orientation. At point B the writing beam was switched off and the transmission decreased sharply, reducing to about 85% of the saturation value (point C) in about 4 min. This high residual rate, which is close to the one obtained for this polymer in the LB film<sup>12</sup> after the same time span, is one of the most important factors for using this material in optical storage applications. Noticeable also in Fig. 5 is the transmission level obtained with this film, about 13%, which allows its usage for applications. This high transmission value could be obtained due to the higher thickness ( $d = 3 \mu\text{m}$ ) of the cast film. Such a thicker film is hardly obtained by other film forming techniques, such as the Langmuir-Blodgett method.

The influence of the writing beam power has also been studied, as shown in Fig. 6. The maximum induced birefringence increases with the laser power up to 8 mW or so, after which saturation is reached (curve A). The characteristic time to induce the birefringence, obtained by fitting an exponential function to the writing sequence experimental data, decreases drastically with increasing writing beam power, again up to 8 mW (curve B).

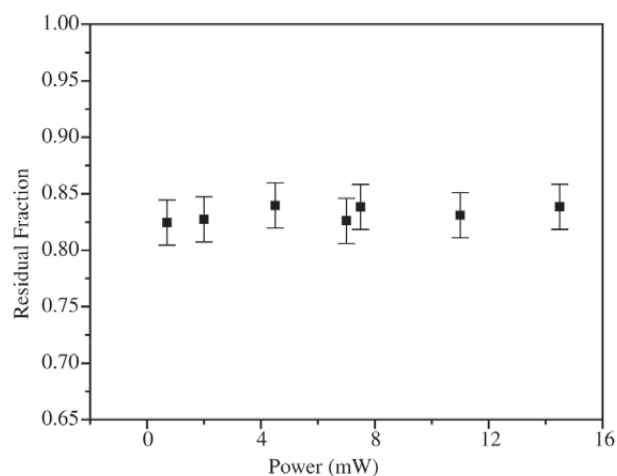
The remaining birefringence fraction, corresponding to the ratio between the maximum induced birefringence and that obtained at point C (after 4 min) in Fig. 5, is about 80% of the maximum birefringence for DR19-MDI film. This value is independent of the pump laser power, as shown Fig. 7.

If the sample were left to relax, the residual fraction shown in Fig. 7 corresponding to the transmission in the point C of Fig. 5 would remain in an appreciable value for

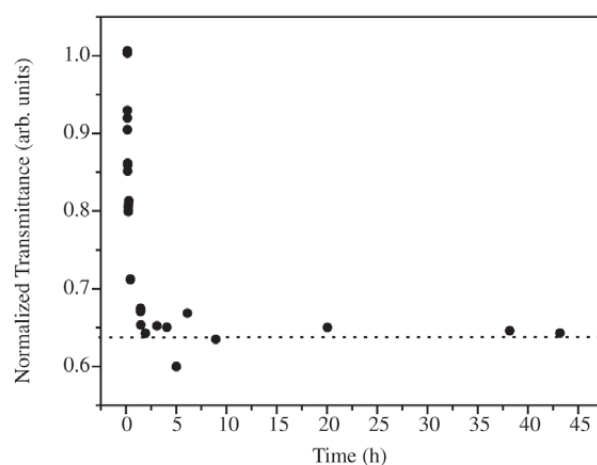


**Figure 6.** Dependence on the laser power for the amplitude of the induced birefringence (a) and writing time (b) for a DR19-MDI cast film. The lines are drawn to guide the eyes.

several days. That is to say, the induced birefringence is stable. In order to check the viability of the DR19-MDI as an optical storage device, in Fig. 8 we present a curve of the birefringence relaxation process taken during 50 h. Before the relaxation could be measured, the birefringence was induced using the writing beam (532 nm) operating at 6.5 mW for about 500 s. Although the sample absorption at the reading beam wavelength (632.8 nm) is very small, as the experiment takes a long time, it can also induce molecular orientation perpendicularly to its polarization direction, changing the birefringence already induced by the writing beam. In order to avoid this problem, the reading beam was blocked between two consecutive measurements. Any probe beam power fluctuation was canceled by using a reference detector. Figure 8 shows that after 2 h of relaxation the birefringence has reduced to 65 % of the maximum value. However, as shown in Fig. 8 this birefringence level stabilizes and remains the same for 2 days. Considering that no precaution was taken to protect the film from environ-



**Figure 7.** Residual fraction as a function of the writing beam laser power.



**Figure 8.** Optically induced birefringence relaxation measured during 50 h.

mental changes and from ambient light, the results of Fig. 8 indicate that the optically written information in this polymer can be used for storage purposes. Besides, multiple writing and erasing test (writing/erasing stress) was performed at room temperature on DR19-MDI film (results not shown here). The same birefringence levels were reached for every cycle, which again shows that this material is suitable for optical storage applications.

## 5. Conclusions

The procedures for preparing uniform, thick cast films from DR19-MDI were optimized. Photoinduced birefringence in these films were studied as a function of the writing laser power and the characteristic time to in-

duce the birefringence decreases with increasing writing beam power while the maximum induced birefringence increased with the laser power and begins to saturate with 8 mW. The remaining birefringence fraction is about 80% of the maximum birefringence for DR19-MDI film and is independent of the writing laser power. This value is relatively stable, decreasing to 65% after 2 h and remaining stable for more than 50 h. This relative stability and rather higher values of residual birefringence allied to the good film forming properties make DR19-MDI suitable for optical storage applications.

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