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Optical storage in mixed Langmuir–Blodgett (LB) films of azopolymers and cadmium stearate

C.R. Mendonça, D.S. dos Santos Jr., D.T. Balogh*, A. Dhanabalan,
J.A. Giacometti, S.C. Zilio, O.N. Oliveira Jr.

Instituto de Física de São Carlos, Universidade de São Paulo, Caixa Postal 369, 13560-970 São Carlos, SP, Brazil

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Abstract

We present a comparative study on the optical storage characteristics of mixed Langmuir–Blodgett (LB) films from azobenzene polymers and cadmium stearate. The amplitude of induced birefringence depends on the azobenzene content in the polymer as well as on the rate of *trans–cis–trans* isomerization. Structural factors such as main chain rigidity seem to play an important role in the remaining stored information. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Langmuir–Blodgett (LB); *Trans–cis–trans* isomerization; Polymer

1. Introduction

The rich variety of organic materials has been exploited in an enormous number of basic research and technological investigations, especially because there are an equally large number of possibilities to control the properties of interest at the various stages of material processing. The first, obvious possibility lies in the chemical synthesis, where functional groups may be employed to achieve specific characteristics. This is the case of azoaromatic polymers that are promising for optoelectronic and photonic applications, as in optical switches [1–3], optical modulators [4], optical storage devices [3,5–10], surface relief gratings [3,10] and induction of liquid–crystals alignment [11], in which the property of interest is the reversible *cis–trans* photo isomerization of the azo group. In addition to being able to attach the azo group either in the polymer backbone (main-chain) or as a side chain (ramification), one can also tune the isomerization properties by choosing distinct azochromophores. Main-chain azoaromatic polymers (cf. poly(azobenzene)) do exhibit interesting semiconducting characteristics [12], but they usually possess poor mechanical properties and processibility. By attaching azobenzene moieties to a conventional polymer backbone as a side chain, one combines good mechanical and processing properties of the conventional polymer with the optical properties of the azo groups. Further control of material properties can be achieved by designing distinct molecular architectures if techniques such as the multilayer Langmuir–Blodgett (LB) [13] or self-assembly (SA) [14] methods are used. Even though one may not hope to obtain the same degree of order as in LB films of traditional amphiphiles, films may still have controlled thickness and surface uniformity, as in the LB films made from amphiphilic azobenzene-containing monomeric amphiphiles and azobenzene containing polymers [15–18]. The final properties obviously depend on several parameters whose influence may not be easily determined.

This state of affairs clearly calls for efforts towards establishing material design requirements. When we set out to investigate the optical storage characteristics of azopolymer LB films [3,15,16], we were guided by mere intuition, in addition to building upon experience of previous works by other researchers. Here, we pursue an investigation aiming at obtaining additional experimental information that may be used in guiding future systematic investigations on optical storage properties of LB films. In order to accomplish this task, we compare the results of four polymeric systems: a polyurethane prepared from 4-[*N*-bis-(2-hydroxy-ethyl)]-amino-4′-nitroazobenzeno (disperse red 19, DR19) and 4,4′-methylene-bis(phenylisocyanate), dubbed as DR19-MDI, the homopolymer of 4-[*N*-ethyl-*N*-(2-methacryloxy-ethyl)]-amino-2′-chloro-4′-nitroazobenzeno (HPDR13) [3], copolymers of 2-hydroxyethyl-methacrylate and of 4-[*N*-ethyl-*N*-(2-methacryloxy-ethyl)]-amino-2′-chloro-4′-nitro-azobenzeno (HEMA-DR13) [15], and another polyurethane

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* Corresponding author.
E-mail address: balogh@if.sc.usp.br (D.T. Balogh).

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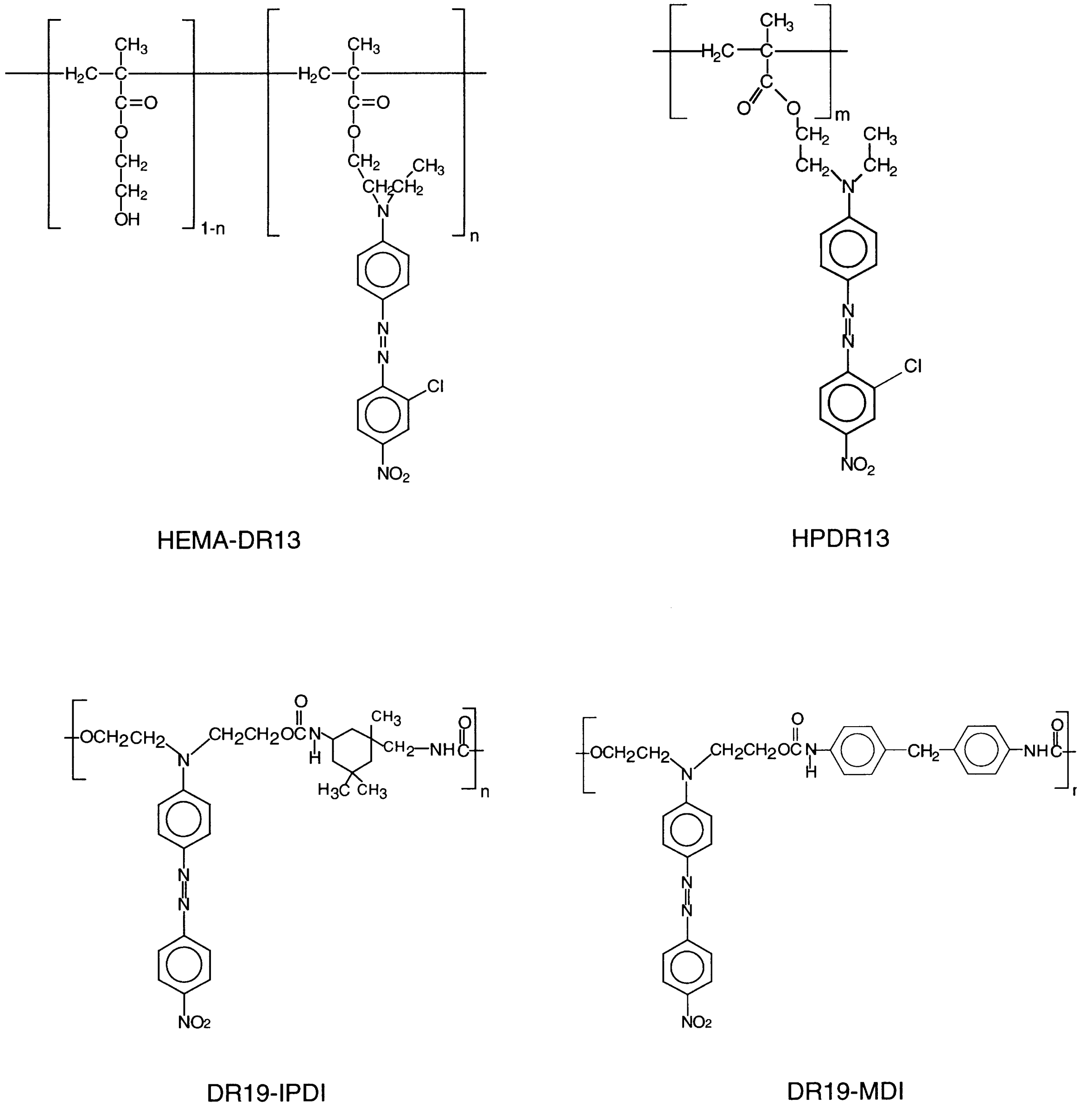

Fig. 1. Chemical strucutres of HPDR13, HEMA-DR13, DR13-IPDI and DR13MDI.

prepared with 4-[*N*-bis-(2-hydroxy-ethyl)]-amino-4′-nitro-azobenzeno and isophorone diisocyanate (DR19-IPDI) [16]. The chemical structures of these polymers are shown Fig. 1.

Before describing the experimental methods and results, let us briefly comment on the optical storage capabilities of azobenzene-containing materials. Information is stored in the form of optically induced anisotropy, dichroism or birefringence, which arise from the *trans–cis–trans* photoisomerization of the azo group and subsequent molecular reorientation. For example, upon impinging linearly polarized light (writing beam) of appropriate wavelength on an azopolymer film, the chromophore absorbs light and undergoes a *trans–cis* isomerization, unless it is oriented perpendicularly to the polarization direction. The cis form thermally relaxes to the more stable trans form, a process that is accompanied by a change in the chromophore orientation. The net result is an excess of molecules oriented perpendicularly to the laser polarization direction, thus inducing birefringence [6–10] that can be read with a probe beam in the transparent region.

2. Experimental details

This section emphasizes the synthesis and characterization of the newly developed DR19-MDI LB film [19]. The other polymers, namely HPDR13, HEMA-DR13 and DR19-IPDI, were discussed in Refs. [3,15,16], respectively, and no further details will be presented here. DR19-MDI was synthesized by the reaction of 4,4′-methylene-bis(phenylisocyanate) (MDI), with 4-[*N*-bis-(2-hydroxy-ethyl)]-amino-4′-nitroazobenzene (DR19), using cyclohexanone as solvent at 90°C for 48 h. The polymer was purified by dissolution and precipitation in a tetrahydrofuran (THF)/toluene/methanol system. The FTIR spectrum of DR19-MDI exhibited a vibrational absorption peak at 1721 cm^{-1}, characteristic of the carbonyl of a urethane group. No OH absorption at about 3400 cm^{-1} could be noticed. HPSEC analysis was performed in a Shimadzu HPLC chromatographic system, using THF as solvent and polystyrene standards. The molecular weights averages obtained were $Mw = 56{,}900\ g\ mol^{-1}$ and $Mn = 15{,}800\ g\ mol^{-1}$. The glass transition temperature (Tg) of the polymers investigated was determined by differential scanning calorimetry (DSC), in a Shymadzu TW50i Thermal Analyzer using a heating rate of 10°C min^{-1}, under nitrogen atmosphere.

The fabrication procedures for mixed LB films of DR19-MDI and cadmium stearate were similar to those reported in Ref. [18]. A DMSO/$CHCl_3$ (8:2) solution containing (0.25 mg ml^{-1}) of DR19-MDI and stearic acid was spread on an aqueous subphase that contained cadmium chloride (4×10^{-4} M) and sodium bicarbonate (5×10^{-5} M), to keep the pH at 6.0. Ultrapure water for the subphase was supplied by a Milli-RO coupled to a Milli-Q purification system from Millipore (resistivity 18.2 MΩ cm). Monolayer studies and multilayer LB film deposition were carried out with a KSV 5000 LB system placed on an antivibration table in a class 10,000 clean room at room temperature. BK7 glass plates were used as substrates, which were cleaned using the RCA standard method [20] prior to use. Mixed monolayers were transferred at 31 mN m^{-1} at a dipping speed of 3 mm min^{-1}. UV–Vis and FTIR measurements were carried out in a Hitachi-U2001 spectrophotometer and a BOMEM-MB102 Michelson series instrument, respectively. X-ray diffraction measurements were made with a Rigaku Rotaflex (Model RU200B) X-ray diffractometer in the 2θ range of 3–20° using a Cu target.

The optical birefringence was induced in the LB film using a polarized Nd:YAG continuous laser at 532 nm with a polarization angle of 45° with respect to the polarization orientation of the probe beam. The power of the writing laser beam was varied to study the influence of the intensity on the induced birefringence, for a 2 mm spot size. A low power He–Ne laser at 632.8 nm passing through crossed polarizers was used as the probe beam (reading light) to measure the induced birefringence in the sample.

3. Results and discussion

3.1. LB film deposition and characterization.

Emphasis is again placed on the film deposition and characterization of DR19-MDI because the other polymers were previously studied in Refs. [3,15,16]. DR19-MDI polymer formed a poorly stable monolayer that was not amenable to transfer by the LB technique. We have therefore adopted the mixed LB film approach, in which the DR19-MDI polymer was codeposited along with cadmium stearate [18]. This approach has been shown to be efficient for producing uniform and reproducible ultrathin LB films of polymeric materials. The mixed monolayers were transferred as Y-type films with a near unity transfer ratio at a constant surface pressure of 31 mN m^{-1}.

The UV–Vis spectrum of a 61-layer mixed LB film of DR19-MDI and CdSt is shown in Fig. 2. For comparison, the UV–Vis spectrum of DR19-MDI in a DMSO/$CHCl_3$ solution is also included. The absorption maximum (λ_{max}) of LB films is blue shifted by 10 nm (465 nm), in comparison to that in solution (475 nm), indicating a possible H-type aggregation of azobenzene chromophores in the LB film [21]. Such H-type aggregation is opposite to that of HPDR13 and DR19-IPDI azopolymers studied earlier [3,16] where λ_{max} was red shifted by 25 and 10 nm, respectively. In the case of the HEMA-DR13 copolymers, no significant shift in the λ_{max} was observed, because aggregation was precluded by increasing the spacing between chromophores. This difference in aggregation behavior may be related to the structure of the polymer and hence to their organization within the LB film. The X-ray diffraction pattern for this mixed LB film displayed a set of diffraction peaks (results not shown) with corresponding bilayer distance of 50 Å, which is similar to the values reported for other mixed LB films and also pure CdSt LB films. This means that in these mixed LB films, cadmium stearate and polymer molecules are present as separate phases. The diffraction peaks were broader and less intense than for pure CdSt films, pointing to a decrease in the stacking order of CdSt domains due to DR19-MDI.

Prior to going into the discussion of optical storage, we have also analyzed the bulk polymer samples by DSC. The glass transition temperatures (Tgs) obtained were 145, 56

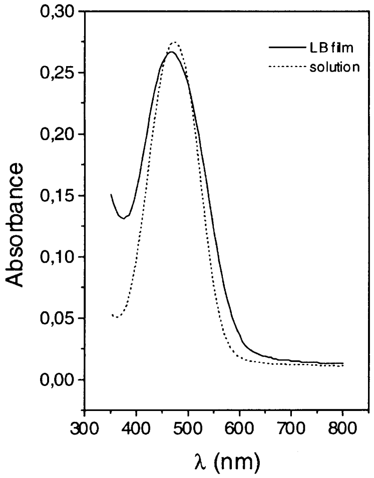

Fig. 2. UV–Vis spectra of a 61 layer mixed LB film of DR19-MDI and cadmium stearate (solid line) and a solution of the same polymer in DMSO/$CHCl_3$ (2:8 v/v).

and 138°C for DR19-MDI, HPDR13 and DR19-IPDI polymers, respectively, while for the copolymers Tg lied in the range from 64 to 82°C. Such distinct glass transition temperatures indicate structural differences among the polymers, which may affect their optical storage capabilities.

3.2. Optical storage experiments

The result of a typical optical storage experiment performed with a mixed LB film of DR19-MDI and cadmium stearate (50/50% wt, 61 layers) is depicted in Fig. 3. No transmission of the probe beam, which passes through two crossed polarizers placed before and after the film, is observed while the write beam is switched-off, indicating the random orientation of the chromophores. However, when the writing beam is switched on at point A, the transmission increases and reaches 50% of the saturation value in about 4 s. The increase in transmission is directly related to the induced birefringence in the film. The overall change in the transmitted signal was normalized between 0 and 1 for the sake of clarity of presentation. This light induced birefringence results from the orientation of some chromophores that are perpendicular to the laser polarization. When the writing beam was switched off at point B, transmission decreases sharply and in 0.9 s it reduces to 50% of the saturation value (point C). If the sample were left to relax, the transmission after point C would remain practically the same for several days. The induced birefringence could be optically erased by overwriting the test spot with a circularly polarized laser light that randomizes the chromophores orientation, thereby eliminating the macroscopic dipole orientation. The influence of the power of the writing laser on the induced birefringence has also been studied, as shown in Fig. 4. For a 61-layer LB film of DR19-MDI and cadmium stearate the induced birefringence increases with the laser power up to 8 mW or so, after which it tends to saturate (curve a), analogously to what was observed for mixed LB films of HPDR13 [3], HEMA-DR13 [15] and DR19-IPDI [16]. However, in the latter cases saturation was reached at approximately 2 mW, in comparison to 8 mW for DR19-MDI. This higher writing beam saturation power can be attributed to the DR19-MDI rigidity. The time to achieve 50% of maximum birefringence decreases drastically with increasing writing beam power, again up to 8 mW (curve b). For a fixed number of layers (say 61 layers) the amplitude of the induced birefringence obtained with a pump beam power of 9.5 mW was 0.026. The remaining birefringence (point C in Fig. 3) in such film is 80% of the maximum birefringence value independent of the pump laser power.

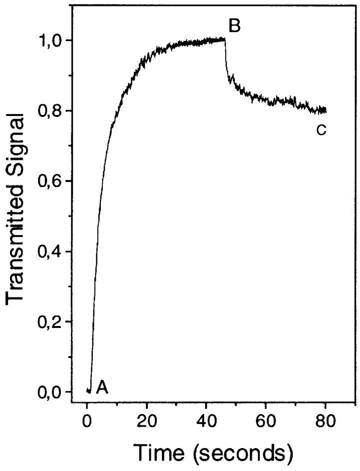

Fig. 3. Writing and erasing sequence on a composite LB film (61 layer) of DR19-MDI and cadmium stearate. The transmitted signal is normalized between 0 and 1 for the sake of clarity of presentation.

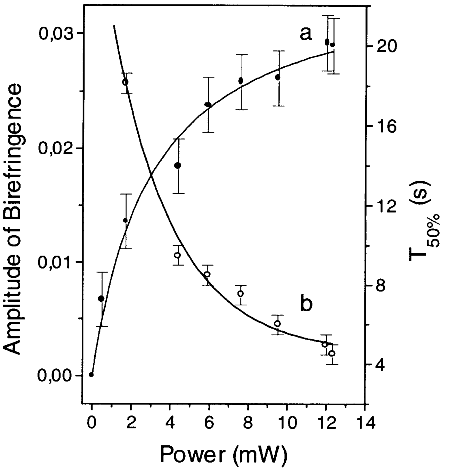

Fig. 4. Dependence on the laser power for the amplitude of the induced birefringence (curve a) and time to achieve 50% of the maximum birefringence (curve b), in a 61-layer mixed LB film of DR19-MDI and cadmium stearate (50:50 w/w). The lines are drawn to guide the eyes.

Table 1 summarizes some optical storage features of LB films from several azobenzene polymers. The residual signal for DR19-MDI is higher than for the other films, probably owing to the polymer rigidity, which is reflected in Tg measurements. Indeed, a dependence of the residual signal on Tg is clear for the copolymers HEMA-DR13. The residual signal is apparently related to the maximum birefringence (Δn), but this occurs because the latter also depends on the polymer rigidity, as can be seen in Table 1. The higher the polymer Tg, the lower the maximum induced birefringence was. The main factor affecting Δn is, however, the dye content in the azo-polymer, with Δn increasing with the amount of chromophore in the polymer, except for DR19-IPDI and DR19-MDI, as discussed below. This may be ascribed to the high absorbance of DR13 at the wavelength of the writing laser, thus leading to a more efficient *trans–cis* isomerization for the materials containing larger concentrations of the dye. The time required to achieve 50% of induced birefringence, which can be correlated to the polymer rigidity, is higher for DR19-MDI that displayed a higher Tg value. When the copolymers are analyzed separately, one also notes that $T_{50\%}^{\text{write}}$ increases with Tg. This is not the only important dependence, though.

Table 1
Optical storage characteristics of 61-layer LB films from the azopolymers HPDR13, DR19-IPDI, DR19-MDI and 15-layer LB films from copolymers HEMA-DR13 with four distinct dye concentrations

	Chromophore content (%w/w)	Maximum Δn	$T_{50\%}^{\mathrm{write}}$ (s)	Residual signal	$T_{50\%}^{\mathrm{relax}}$ (s)	Tg (°C)
HEMA-DR13	18	0.04	1.6	0.73	0.8	82
HEMA-DR13	24	0.05	0.9	0.64	0.7	79
HEMA-DR13	42	0.06	0.7	0.52	1.3	72
HEMA-DR13	64	0.07	0.5	0.48	1.6	64
HPDR13	83	0.12	1.0	0.35	3.0	56
DR19-IPDI	59	0.013	0.8	0.70	0.6	138
DR19-MDI	56	0.026	2.8	0.80	0.9	145

For isomerization rates, cooperative effects and sample heating may also affect $T_{50\%}^{\mathrm{write}}$, which probably cause the time for HPDR13 to be higher than expected from structural considerations only.

Relaxation processes are, in principle, easier to analyze because effects from heating and isomerization rates are small once the laser pump is switched off. The three remaining main factors are: (i) the rigidity of the polymer, where longer relaxation times are expected for materials with higher Tg; (ii) cooperative effects that may cause relaxation times to be longer when the amount of chromophore is increased; (iii) the free volume around the azo moiety. Table 1 shows that $T_{50\%}^{\mathrm{write}}$ (or more specifically the time required upon turning off the writing laser for the decrease in induced birefringence to reach 50% of the total decrease) increased with the chromophore concentration, and, at least for the copolymers, it decreases with increasing Tg. The latter finding rules out the hypothesis of the polymer rigidity (factor *i*). The availability of free volume for the azo group to relax and cooperative effects are the important factors. The free volume decreases with increasing chromophore concentration, thus making $T_{50\%}^{\mathrm{write}}$ longer. Cooperative effects, which increase with the chromophore concentration, also hinder relaxation.

Turning to the odd behavior of DR19-IPDI, whose maximum birefringence was lower than for DR19-MDI in spite of possessing a slightly larger chromophore concentration, one may ascribe this to the increase in the degree of electron delocalization in MDI, caused by introduction of phenyl rings instead of isophorones groups into the polyurethane polymer.

A similar investigation of the effects from the degree of chromophore functionalization and type of polymer backbone on storage properties of spin-coated copolymer films has been presented by Iftime et al. [22]. The increase in birefringence with the degree of functionalization was linear for the styrene-based copolymers but sublinear for the methacrylate-based ones [22]. In the latter series, the birefringence per mol of chromophore decreased with the amount of functionalization before reaching a saturation point, and this was attributed to dipolar interactions between neighbor chromophores [22]. The results presented here point to significant interaction among chromophores, as discussed above, for the increase in birefringence with the degree of functionalization was not linear. Also, in the copolymers analyzed by Iftime et al. [22], Tg was practically the same, unlike the polymers investigated in the present work. Indeed, the residual signal in the LB films of Table 1 decreased considerably with the degree of functionalization, for the copolymers as well as for HPDR13, whereas in Ref. [22] an increase was observed for the styrene copolymers and decreased only slightly for the methacrylate ones. The main reason for such a difference in behavior is in the large changes in Tg for the polymers used in the LB films, which play an important role in the relaxation processes, as discussed above.

4. Conclusions

On the basis of the results discussed above, one may suggest requirements for azopolymers to display optimized storage characteristics. First of all, one has to search for an ideal trade-off between efficient photoisomerization and relatively small relaxation (i.e. high residual signal). For an efficient isomerization the azoaromatic group should possess a large dipole moment, which may be achieved by attaching push–pull groups and the dye should absorb strongly at the wavelength of the writing laser. Moreover, the material should not absorb at the wavelength of the reading light. Polymers with high dye contents and low Tgs (which help in the orientation process), as HPDR13, do fulfill these requirements. However, low Tgs imply in low residual signals. We believe that polymers based on DR13 and with Tg of approximately 90°C would be ideal. In addition, large amounts of dye make chromophore aggregation more likely, but this may be minimized by designing polymeric structures where chromophores are kept apart, as in Ref. [15]. The time to write the information is also an important parameter for practical applications. In order to keep this time short, the requirements for an efficient isomerization apply, particularly a large dipole moment. The relaxation times are not that important, though, provided that the residual signal is sufficiently high.

In summary, the optical storage capability of DR19-MDI, HPDR13, HEMA-DR13 and DR13-IPDI LB films were measured and compared. The dependence of the amplitude and time of induced birefringence on the writing laser power was investigated. The structure of the polymer to which the azobenzene group is anchored seems to be one of the important factors influencing the optical storage features.

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