

# Azobenzene Side-Chain Liquid Crystalline Polyesters with Outstanding Optical Storage Properties

S. HVILSTED\* & M. PEDERSEN

*Condensed Matter Physics and Chemistry Department*

N.C.R. HOLME & P.S. RAMANUJAN

*Optics and Fluid Dynamics Department*

*Risø National Laboratory,  
DK-4000 Roskilde - DENMARK*

Received 04.11.1997

A flexible azobenzene side-chain liquid crystalline (SCLC) polyester architecture employed for reversible optical storage is described. The modular design allows four structural parameters to be individually modified. These parameters: *i*- the methylene side-chain spacer length, *ii*- the substituent on azobenzene, *iii*- the methylene main-chain segment length, and *iv*- the polyester molecular mass, all influence the optical storage properties. A general synthetic route to novel mesogenic azobenzene diols comprising parameters *i* and *ii* is outlined. Polyesters with molecular masses (parameter *iv*) up to 100,000 are routinely obtained by melt transesterification of the novel diols and selected diacid precursors (parameter *iii*). Prominent storage features include no prealignment of thin SCLC polyester films prior to the writing process, and sensitivity in a broad laser wavelength window (415-532 nm). Additionally, information can be recorded either through polarization holography or as direct computer generated pattern (grey tones). Thus polarization holography results in high diffraction efficiency (> 50%) and high storage density (> 5000 lines/mm interference gratings) lasting presently well over 5 years without any sign of fatigue. The non-destructive read out is performed with red light (600-750 nm). Finally, erasing the information can be achieved by heating the polyester film to 80 °C or irradiating it briefly with UV-light. In the latter case at least 10,000 write, read and erase cycles are possible. Atomic force and scanning near-field optical microscopic investigations of gratings prepared with orthogonally polarized overlapping beams have demonstrated that the anisotropy is preserved in the film despite extensive mass transport and surface corrugation after the irradiation process. However, the observed surface roughness is strongly dependent on the laser polarization. Polarization Fourier-Transform infrared studies of laser induced segmental motion in selectively deuterated SCLC cyanoazobenzene polyesters have revealed that not only the azobenzene chromophores but also main-chain and side-chain spacers align preferentially perpendicular to laser polarization.

## Introduction

One new trend in polymer science during the last decade has been attempts to design polymer systems capable of responding to external stimuli e.g. light or an electric field and thus create advanced, functional

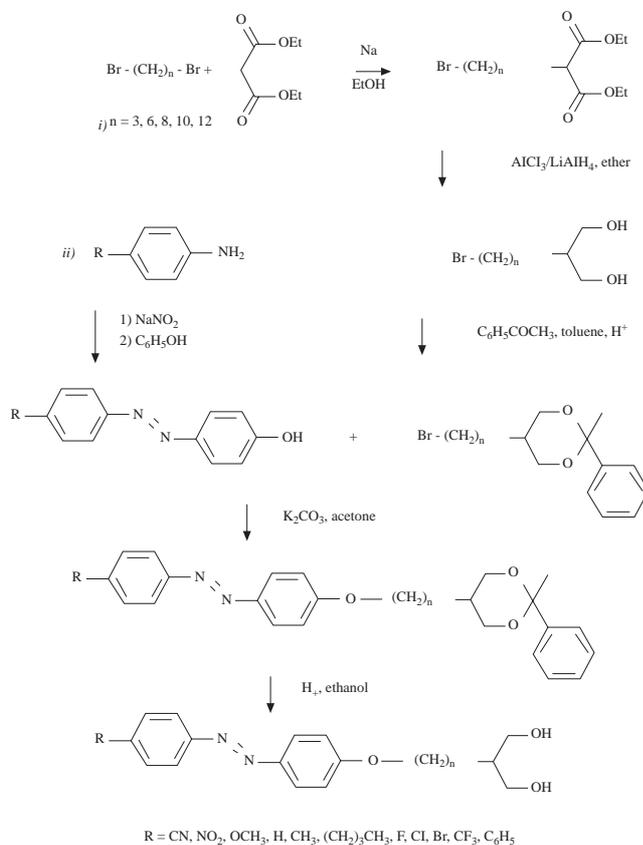
materials. In particular, the quest for optimal materials for optical information storage has been extensive during the last few years<sup>1,2</sup>. Efficient, high density and erasable optical storage can find important applications in computer industry, audio-visual entertainment systems, neural networks and page oriented memories. The search for polymeric materials capable of reversible optical information storage has accordingly escalated<sup>3,4</sup>. Especially, utilization of the photochromic properties of azobenzene (based on the light induced *trans-cis-trans* cycles)<sup>5</sup> has attracted tremendous attention. Many different systems with azo dyes dispersed in polymers<sup>6,7</sup> and azobenzene side chains in unoriented amorphous<sup>8,9</sup> or prealigned liquid crystalline polymers<sup>10–14</sup> have been proposed and investigated. Frequently, the cyanoazobenzene mesogen has been introduced and investigated in a number of different main-chain architectures such as side-chain liquid crystalline (SCLC) homo- or copolymers based on polyacrylates<sup>12,13,15–17</sup> and polymethacrylates<sup>11</sup>, polystyrene and poly( $\alpha$ -methylstyrene)<sup>18</sup>, polyesters<sup>10,17,19–21</sup> and polysulfones<sup>22</sup>. This initially motivated us to attempt the transformation of a synthetically very flexible and versatile comb-shaped polyester architecture<sup>23–26</sup> to photoaddressable polyester materials with pendant cyanoazobenzene chromophores in the side chains and to research possible reversible optical storage properties of these novel materials.

## SCLC Azobenzene Polyesters

The polyesters are prepared in a modular design allowing four structural parameters to be individually modified. The key parameter and cornerstone in the preparation of high molecular mass aliphatic polyesters<sup>26</sup> is the utility of an extensive, homologues series of crystalline diphenyl esters<sup>23</sup> comprising all even members from oxalate to hexadecanedioate and most of the odd members as well. These also provide the main-chain methylene segments of the novel SCLC azobenzene polyesters which we will term the polyester parameter *iii*. This necessarily moves the pendant azobenzene to the diol contrary to the early azobenzene polyesters which were all based on azobenzene substituted malonate<sup>10,17,19–21,27</sup>. The targeted diols are *para*-substituted azobenzenes linked through flexible methylene chains of varying lengths (polyester parameter *i*) to the 2-carbon of 1,3-propanediol. However, the coexistence of a number of different chemical functionalities in the 2-substituted propanediols required a special synthetic strategy to be developed. This approach, previously briefly outlined<sup>28,29</sup>, is shown in Scheme 1. A flexible methylene spacer is first incorporated through alkylation of diethyl malonate<sup>30</sup>. This furnishes a diethyl 2-( $\omega$ -bromo-alkyl)-malonate which is diligently reduced with mixed hydrides to the corresponding diol. Due to self condensation forming oligomeric ethers, the diol could not be sufficiently purified by vacuum distillation. Instead, the diol function is protected by reaction with acetophenone forming in all cases crystalline products which can be obtained in high purity. The ketal-protected diol is then reacted in a classical ether condensation with a properly substituted “azophenol”<sup>19</sup> (polyester parameter *ii*). The azophenol, in turn, is prepared by the conventional method by diazotation of the corresponding aniline and subsequent coupling with phenol. The azobenzene containing diol is finally recovered by short acidic alcoholysis. Careful purification by recrystallization and vacuum distillation ensures a liquid crystalline diol of high purity<sup>31,32</sup>.

The polyesters are prepared (as indicated in Scheme 2) in a base catalyzed (1-2 mol-%  $K_2CO_3$ ) transesterification between selected diphenyl ester main-chain precursors (polyester parameter *iii*) and azobenzene diols with an exactly stoichiometric match in a two step melt procedure in spherical and rotatable (providing effective reactant mixing) glass reactors under inert atmosphere<sup>26,28,29,31</sup>. During the first step, performed at 120-130°C and a relatively low pressure ( $\approx 5$  mbar), oligomeric products are produced and most of the phenol condensate removed by sublimation. In the second step, the temperature is slightly increased, the pressure lowered (0.05 mbar) and the final molecular mass is obtained as a highly viscous melt. The route for

preparation of polyesters is schematically illustrated in Scheme 2. The polyesters are isolated as a benzene solution and finally recovered by filtration allows the preparation of up to 2 g of polyester and results in almost quantitative yield of fine granulated or sometimes fibrous polyester material.

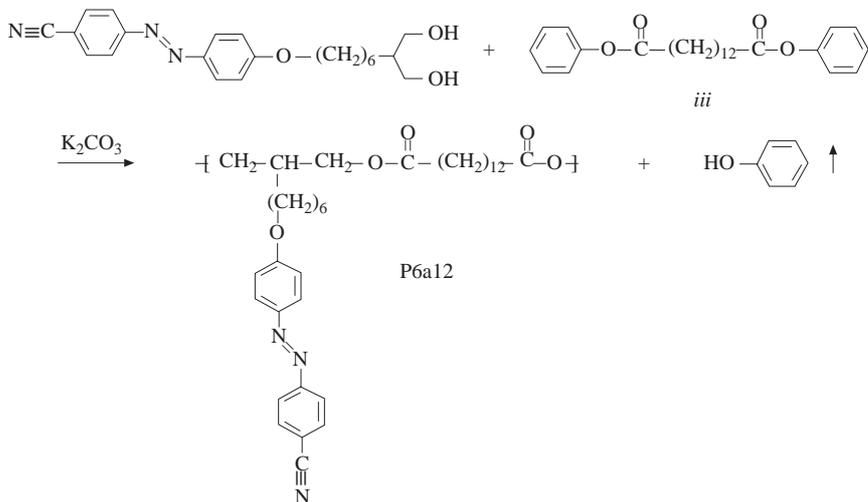


**Scheme 1.** Synthetic route for the preparation of the *para*-substituted azobenzene diols. *i*) and *ii*) indicate the introduction of parameters *i* and *ii*, respectively

An external range of SCLC polyesters has been prepared in this fashion by different combinations of ester precursors and azobenzene diols. A simple coding, **Pn<sub>x</sub>m**, has been adopted for each combination and thus describes a particular SCLC polyester. Here **Pn<sub>x</sub>** stems from the diol where **n** reflects the number of methylene groups in the flexible side-chain spacer and **x** (a, b, c, d ... k) refers to the *para*-substituent among: CN, NO<sub>2</sub>, OCH<sub>3</sub>, H, CH<sub>3</sub>, (CH<sub>2</sub>)<sub>3</sub>CH<sub>3</sub>, F, Cl, Br, CF<sub>3</sub>, or C<sub>6</sub>H<sub>5</sub> on the azobenzene. **m** derives from the number of methylene groups in the dicarboxylate of the precursor ester. Most investigations have been performed on poly(2-[6-[4-(4-cyanophenylazo)phenoxy]hexyl]-1,3-propylenetetradecanedioate) with the hexamethylene side-chain spacer which accordingly is designated **P6a12** (the structure of the repeating unit is shown in Scheme 2). It should be added that the utilization of either two diol monomers or two diphenyl esters in the same reaction is possible provided the correct stoichiometry is maintained. This use of either mixed diols or mixed diphenyl esters will naturally influence the polyester parameters *i*, *ii*, *iii*.

The azobenzene SCLC polyesters are soluble in many common organic solvents like benzene, toluene, chloroform, and tetrahydrofuran. The achieved molecular masses and molecular mass distributions are established by size exclusion chromatography (SEC) on tetrahydrofuran solutions by use of polystyrene calibration standards with refractive index detection. Weight average molecular masses up to 100.000 are routinely accomplished (polyester parameter *iv*). These values have been verified by independent laser light

scattering analysis<sup>29,32</sup>. The associated molecular mass distributions are close to 2 or slightly higher in line with theoretical predictions for condensation polymers at very high conversion<sup>33</sup>. In fact, these molecular characteristics have proved excellent mechanical strength necessary for the film forming ability. Free standing films and fibers of these polyesters have been produced; the fibers have been stretched as much as 1,000% before breaking<sup>34</sup>.



**Scheme 2.** Melt transesterification furnishing P6a12. *iii* indicates where polyester parameter *iii* is introduced

The polyester structures have been thoroughly investigated by different molecular spectroscopic techniques. Fourier-Transform infrared (FTIR) spectroscopy has been exploited as a tool for the identification of a number of polyester structural units<sup>26,31,35</sup>. More important and instrumental, however, is the possible use of polarized infrared light for investigation of segmental orientations and order parameters. The intensive FTIR analyses of laser induced segmental orientation on selectively deuterated SCLC cyanoazobenzene polyesters are discussed thoroughly in a later section on “Segmental Mobility”. Solution <sup>13</sup>C NMR spectroscopy normally allows identification of specific non-symmetrical carbons in branched<sup>36</sup> or comb-shaped polyesters<sup>25,26</sup>. Thus, all the carbons of the cyanoazobenzene, the hexamethylene spacer, the diol part and the main-chain carbons next to the carbonyl are unequivocally assigned in the corresponding polytetradecanedioate, **P6a12**<sup>29</sup>. Generally, <sup>13</sup>C NMR reveals a microstructure of the SCLC azobenzene polyesters corresponding exactly to the repeating unit of a linear main-chain polyester with an azobenzene side chain as expected from the starting building blocks. In some cases, the end-groups contemplated from the particular precursors utilized have also been verified<sup>29</sup>.

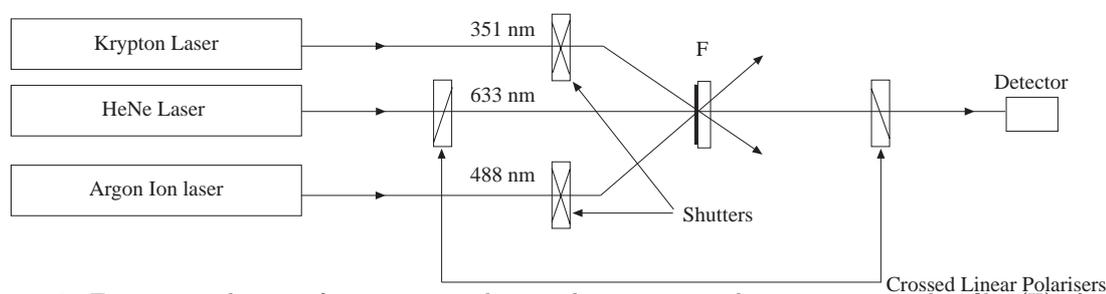
Phase characterizations have been performed by a combination of polarization optical microscopy (POM) and differential scanning calorimetry (DSC). The morphology of the SCLC azobenzene polyesters strongly depends upon the main-chain methylene spacing. Generally, the polyesters have a glass transition close to room temperature or lower, some mesophases, and, particularly in case of the long methylene spacing as dodecamethylene, aggregated or crystalline phases. The **P8a12** has been very thoroughly investigated and has been shown to have up to four higher order phases<sup>37</sup> which are strongly dependent on the polyester thermal history and strongly influenced by annealing effects. Due to the relatively high molecular masses the mesophases have been very difficult to identify especially in the polytetradecanedioates, **P6a12**, **P8a12** and **P10a12**<sup>29</sup>, however, in a low molecular mass sample of **P6a12** a smectic A phase has been verified.

All the azobenzene SCLC polyesters have absorptions in the UV-visible range characteristic of azobenzenes<sup>28,38</sup>. The spectra generally comprise two absorption bands, where the strongest absorption

with maximum (21,000 - 26,000 L/cm mol<sup>-1</sup>) in the near UV-region occurs in the range 348 - 379 nm (depending on the *para*-substituent: H, CH<sub>3</sub>, (CH<sub>2</sub>)<sub>3</sub>CH<sub>3</sub>, F, Cl, Br, CF<sub>3</sub>, OCH<sub>3</sub>, C<sub>6</sub>H<sub>5</sub>, CN, or NO<sub>2</sub>, on the azobenzenes) and can be assigned to the intense  $\pi - \pi^*$  transition of the (N=N) bond. The yellow to dark red colours of these polyesters, however, originate from a weak and broad band around 445 nm ( $\epsilon \approx 2,000$  L/cm mol<sup>-1</sup>) which is attributed to the corresponding  $n - \pi^*$  transition. In the present systems, the  $\pi - \pi^*$  and the broad  $n - \pi^*$  transitions overlap and cover relatively wide absorption regions with an extended shoulder on the long wavelength side.

## Optical Storage

The optical storage has been performed on 0.5 - 5  $\mu$ m polyester films. The best azobenzene SCLC polyester film quality is obtained from chloroform solutions cast or spin coated onto optical glass substrates<sup>34</sup>. After solvent removal by drying shortly at 85 °C the film is ready for use without any further treatment. However, a protective glass cover can be fixed on top of the film by use of a refractive index matching glue if wanted. The simplest storage process is conventional two-beam interferometry to record interference fringes in the film. The holographic efficiency is considerably improved, however, by use of polarization holography<sup>39</sup>. Fringes have been recorded in a broad wavelength window through the use of the 413 nm Krypton laser line and the 458, 475, 488 and 515 nm lines of an Argon ion laser<sup>28,31</sup>. Recently even the 532 nm line from a frequency doubled YAG laser has been exploited. The necessary laser intensity and irradiation time depend strongly on the particular polyester architecture. Typical laser powers range from 5 mW/cm<sup>2</sup> to 1 W/cm<sup>2</sup>. A grating produced in this way in **P6a12** at 488 nm with 5 mW/cm<sup>2</sup> for 180 s has typically a first order diffraction efficiency of approximately 5 %. The nondestructive read-out is performed with read light in the 600-750 nm range; typically a 4 mW HeNe laser at 633 nm is utilized for the read-out. Polarization holography has resulted in high grating diffraction efficiency (> 50% in the first order) and high storage density (> 5000 lines/mm). This holographic information is permanent, lasting presently well over 5 years without any sign of fatigue in a **P6a12**<sup>28,29</sup>. The holograms, on the other hand, can be globally erased by heating the film to about 80 °C for a few seconds. After cooling to room temperature the writing process can be repeated. Writing and erasure cycles have been reproduced hundreds of times in a polyester film with the same performance. Very recently it has been shown<sup>40</sup> that local erasure is possible with very brief UV-light irradiation from a Krypton laser at 351 nm as shown in Figure 1.

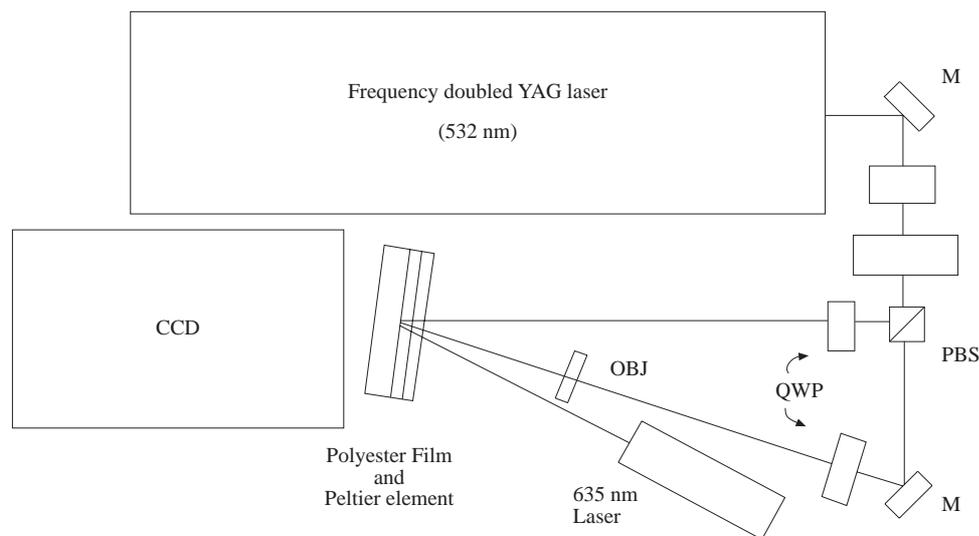


**Figure 1.** Experimental set-up for writing, reading, and erasing optical anisotropy in a thin film (F) of a side-chain liquid crystalline polyester

It was demonstrated that anisotropy (information) induced in 500 ms by 100 mW from the Argon ion laser line at 488 nm after a wait period of 300 ms could be totally removed (erased) in 200 ms by 200 mW at 351 nm from the Krypton laser. The cycle lasting 1 s could be repeated 10,000 times. Despite some overall

decrease in anisotropy probably due to increase in film temperature, sufficient anisotropy stable between erasures has been shown to exist and thus opens a great potential for optical storage applications.

The holographic process need not be performed with a big stationary system. We have constructed a portable holographic system which fills exactly an A-4 page sized breadboard<sup>41</sup> (schematically shown in Figure 2). This set-up includes the writing laser (a frequency doubled YAG laser, lasing at 532 nm with 35 mW), the read-out laser (red diode at 635 nm), all the optics and a CCD camera to collect the diffracted image. Only the power supply for the green laser and for the Peltier supply together with the screen are outside the breadboard.



**Figure 2.** A portable polarization holographic set-up. This occupies the area of an A4 page size (210 mm  $\times$  297 mm) in real life. HWP stands for half-wave plate, QWP for quarter-wave plate, PBS for polarization beam-splitter, M for mirror, OBJ for the object to be imaged, and CCD for charge coupled device camera to collect the diffracted image

During the course of the early investigations of the novel azobenzene SCLC polyesters a biphotonic holographic storage process has been discovered in several cyano-, methoxy- and unsubstituted azobenzene SCLC polyadipates (**P6a4**, **P6c4**, **P6d4**) and polytetradecanedioates (**P6a12**, **P6c12**, **P6d12**)<sup>42–44</sup>. The biphotonic high-density storage of text and gratings typically in 1 mm holograms<sup>42</sup> requires typically 488 nm from an Argon laser and 633 nm from a HeNe laser or 670 nm from a diode laser which do not necessarily need to be present simultaneously. Subsequently, we provided the first experimental evidence from optical and FTIR absorbance spectroscopy for a photoinduced transition of the *cis* state back to the *trans* state in azobenzene<sup>44</sup> caused by a red laser beam at 633 nm. Similar observations have very recently been made in the guest-host system 4-amino-4'-nitroazo-benzene/polycarbonate<sup>45</sup>.

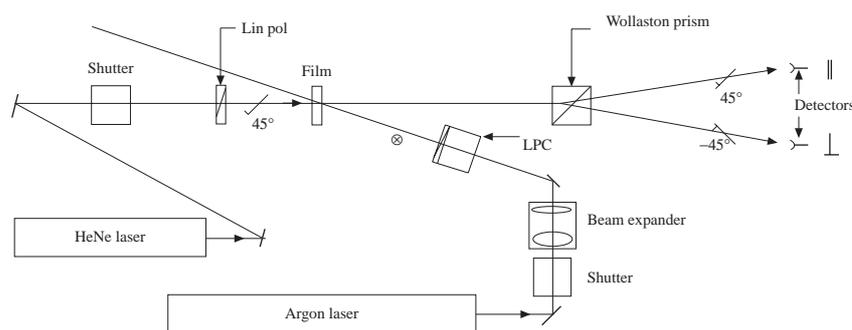
An alternative and different way of producing the storage is in form of computer generated patterns. Computer generated holograms (CGH) are useful in the fabrication of microoptical components such as microlens arrays, gratings etc. They have potential applications in aberration correction in optical systems, and as interconnects in optical neural networks. Especially as phase only optical elements, they are most useful as no energy is absorbed. Normally, CGHs are polarisation insensitive; however their usefulness is increased by making them polarisation sensitive. One such component could be an optical pick-up for compact disc players. Anisotropic materials provide such a substrate. CGHs are normally recorded as kinoform patterns in glass or photoresists, where the material is etched away in order to provide phase

changes of light. By making CGHs in side-chain polyesters, one has the additional advantages of no darkroom development, no wet processing and an erasable medium for storage. Previously, polarisation sensitive holographic elements have been recorded in dye-doped polymers, photorefractive crystals and dichromate gelatin<sup>46–48</sup>. However, these are optically recorded and hence lack the flexibility for producing arbitrary phase function. A 100 mW HeCd laser beam, linearly polarised at 442 nm was employed in writing CGHs in the SCLC polyesters. The beam is focused on the spin coated polyester film (**P6a12**, **P8a12** or **P10a12**) by means of a microscope objective mounted on a 10 kg turn wheel, after passing through a modulation of the laser beam, information is directly written in the polyesters. The set-up is capable of writing different grey scales with high resolution of the order of 500 lines/mm. Computer generated holograms for filtering (high or low pass, edge enhancement) and mapping (log-polar mapping) functions have been generated. Typically, a phase only Fresnel lens with a diameter of 2 mm and a focal length of 30 mm or a set of 6 Fresnel micro-lenses in an area of  $1.5 \times 2$  mm were produced. Text with letter sizes of  $50 \mu\text{m}$  and a Mandelbrot fractal figure ( $1.5 \times 2$  mm) were likewise written in the film.

## Anisotropy and Film Morphology

Initial time-dependent measurements of the induced optical anisotropy through simple recording of the transmitted HeNe power in the series **P6a12**, **P8a12** and **P10a12** at ambient temperature<sup>29,49</sup> demonstrated a complex dependence on both the spacer length and the recording laser power. The laser induced anisotropy - the basis for the holographic storage - has consequently been studied more systematically as a function of laser power and film temperature in a number of polydodecanedioates (**P6a10**, **P8a10**, **P10a10**) and polytetradecanedioates (**P6a12**, **P8a12**, **P10a12**). An automatic test system able to vary the pump Argon laser power and to control the film temperature by a Peltier element has been designed<sup>50</sup>.

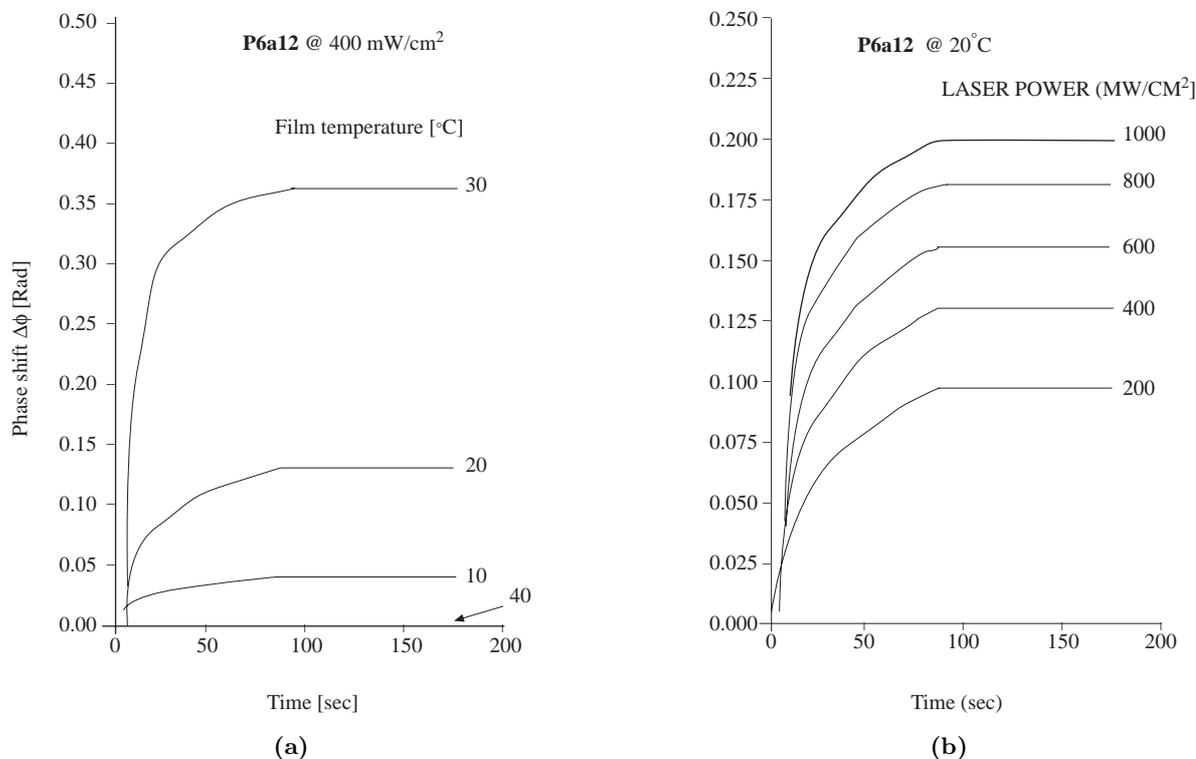
The induced anisotropy is probed by a polarized HeNe laser beam which after passing through the film is split by a Wollaston prism into two orthogonally polarized components whose intensities are monitored by photodetectors. A computer commands the laser beam control and the laser shutters, sets the Peltier temperature, repeats each analytic cycle three times, collects all the data and finally calculates the induced relative phase shift. This set-up is schematically shown in Figure 3.



**Figure 3.** Experimental set-up for measuring photoinduced anisotropy. LPC is a laser power control unit and Lin pol is a linear polarizer

The induced phase shift - taken as a measure of anisotropy - depends on laser power (200 - 1,000  $\text{mW}/\text{cm}^2$ ), irradiation time and film temperature. Generally, the highest laser power results in the highest phase shift; the phase shift drops to about half the value for the lowest laser power. However, the influence of temperature is more striking. Most of the polyesters easily achieve the maximum phase shift close to 0.5

rad at 30 °C with 400 mW/cm<sup>2</sup> for an exposure less than 100 s. At room temperature the phase shift is normally less than half of that, and at 10 °C even much less. No anisotropy can be induced at 40 °.



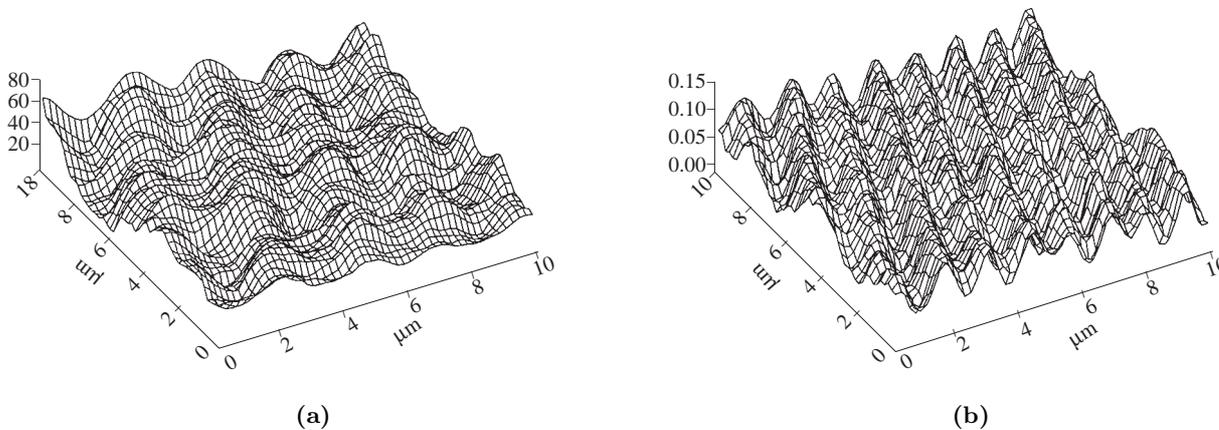
**Figure 4.** Temporal behaviour of induced anisotropy in **P6a12** films: a) at a constant laser intensity of 400 mW/cm<sup>2</sup> for different film temperatures and b) at a constant temperature of 20 °C for different laser intensities

Figure 4 illustrates both the dependence of film temperature and laser power on the phase shift in case of **P6a12**. The film cooling rate after erasure also plays a significant role; thus the maximum anisotropy in a film cooled at 0.025 °C/s is less than half as much as in the film cooled at > 0.5 °C/s. Measurements reveal that the erasing takes place at temperatures much higher than the glass transition temperature. In fact, this coincides with the temperature for transitions involving large enthalpies as observed by DSC. The induced anisotropy disappears completely when the polyesters enter the isotropic, melt-like state which happens in the temperature range 50-80 °C depending on the particular polyester architecture.

Thin phase polarization holographic gratings recorded with two waves with orthogonal linear polarization in these unusual polyester materials give rise to linear or circular birefringence depending on the illumination light source being linearly or circularly polarized<sup>51</sup>. It was additionally shown that polarization holography may be used for real-time simultaneous measurement of photoinduced linear and circular birefringence.

In order to further investigate the nature of the laser induced perturbations in thin polyester films atomic force microscopy (AFM) and scanning near-field optical microscopy (SNOM) have been resorted to<sup>52</sup>. The initially developed topographic grating prepared with orthogonally polarized overlapping beams in a **P6a12** has been followed by AFM for 20 hours by repeatedly scanning the same area of the film. The grating structure disappears after a few hours and a pronounced increase of surface roughness involving extensive mass transport is observed. However, a SNOM scanning of the grating reveals that the bulk of the

material remains optically anisotropic (Figure 5).



**Figure 5.** Surface topographic (a) and near-field optical microscopic (b) scans of an anisotropy grating in a **P6a12** film obtained with polarization holography. The scanned area is  $10 \mu\text{m} \cdot 10 \mu\text{m}$

The laser induced segmental ordering (see next section on “Segmental Orientation”) is the cause for the anisotropy in the film as well as a topographical modulation. Further detailed examinations of surface relief structures in **P6a12** generated by polarization holography with orthogonally circularly polarized laser beams have been performed<sup>53</sup>. We show that it is possible to separate the contribution to the diffraction efficiency into an anisotropic part and a surface relief part by examining the polarization content of the first order diffracted beam. By studying the dynamics of the growth of the grating, it is shown that the gratings due to anisotropy and surface relief appear at the same time. Surface gratings have now been observed and studied in many other azobenzene containing polymers. Thus recent investigations of relaxation of holographic gratings in SCLC polymethacrylates with different azobenzene content<sup>54</sup> is partly explained by the slow formation of light induced liquid crystalline microstructures. These are additionally believed to be primarily causing the modulation of the refractive index. Stable gratings have also been created by optically altering the surface profile of thin amorphous azobenzene polyacrylate<sup>55</sup> or azobenzene containing epoxy polymer<sup>56</sup> films. Based on AFM observations the surface transformation here is ascribed to the free volume requirement under *trans-cis* isomerization cycles. The resulting internal pressure has been argued to be above the yield point of the polymer<sup>57</sup>. We believe that the mechanism is more intricate. Our own recent investigations by AFM<sup>53</sup> have shown that irradiation of the film with two *s*-polarized beams causes only a weak surface relief, whereas two *p*-polarized beams produces a large surface relief. If the film is irradiated with two beams with orthogonal linear polarizations, the resultant field consists of regions with linear and circular polarizations. In this case, a surface relief grating with twice the original spatial frequency appears. In order to eliminate the influence of the out-of-plane component of the electric field when the two beams are incident at an angle to the normal to the film, single beam exposures through a linear grating mask were made. The lines of the mask were perpendicular (vertical) to the plane of incidence (horizontal). In this case there is a difference between *s*- and *p*-polarized light even at normal incidence. In the former case, practically no surface relief was observed, while for the latter, a surface relief of 200 nm was measured. One circularly polarized beam creates a surface relief of over 1000 nm. The unirradiated film thickness was 1.5  $\mu\text{m}$  in all these experiments. These indicate that the driving force for the surface relief formation depends strongly on the light polarization direction. In the case of linearly polarized light a surface relief appears

only if the polarization vector has a component perpendicular to the direction of the grating lines. The mass transport is influenced by the type of light polarization - linear or circular - probably due to different degrees of isomerization. In summary, we believe that the surface relief appears due to the modulation of the magnitude and direction of the interfacial tension between regions illuminated with light with different polarizations.

## Segmental Mobility

The anisotropy investigated and discussed in the previous section is a macroscopic effect involving many long molecular segments or entire chains. On the other hand, the statistical reorientation causing the final anisotropy of the polyester material initiates at the molecular level by the absorption of light in the azobenzene chromophore. The segmental motion of the azobenzene chromophore has long been studied by FTIR spectroscopy generally by focusing on specific aromatic vibrations with IR light polarized parallel and perpendicular to the original laser polarization<sup>29,31,35,43</sup>. In case of the cyanoazobenzene based polyesters the nitrile stretching vibration is particularly well suited. On the other hand, both the main-chain and the side-chain segments of the polyesters are methylene chains of varying length and therefore spectroscopically indistinguishable. One solution to this obstacle is specific labeling inducing significant and characteristic spectral band shifts. We have recently demonstrated<sup>58</sup> that selective deuteration by exchange and reduction reactions at various steps in the sequential preparation result in deuterium incorporation and furnish a set of strategic precursors and diols. Moreover, considerable spectral changes associated with deuterium presence are observed; especially the  $\nu_s(\text{CD}_2)$  and  $\nu_{as}(\text{CD}_2)$  vibrations are significantly shifted in comparison with their hydrogenated analogues. The proper combination of precursors and diols allows cyanoazobenzene SCLC polyesters with different deuterated segments to be prepared and spectroscopically thoroughly characterized<sup>38</sup>. Thorough polarization FTIR studies of laser induced segmental orientation in films of these selectively deuterated SCLC cyanoazobenzene polyesters reveal that in addition to the azobenzene chromophores both the main-chain and the side-chain segments align preferentially perpendicular to the laser polarization<sup>59</sup>. Polarization FTIR measurements performed on-line with the laser irradiation show that the segmental orientations develop simultaneously. In addition, the induced segmental order also decreases concurrently as a function of raising temperature. Moreover, the temperature at which the segmental order vanishes coincides with the disappearance of anisotropy (as discussed in the section on "Anisotropy and Film Morphology") and the entry into the isotropic, melt-like state as observed by DSC.

## Conclusions

The ideal material for erasable holographic storage should possess the following properties: high diffraction efficiency, high resolution, low-intensity response, high temporal sensitivity, no high fields in order to promote recording, no realignment of the molecules, no wet processing, permanent storage until erasure, and a fast erasure on the application of an external stimulus. The presented SCLC azobenzene polyesters fulfill almost all of the above criteria, although the immense structural potential is not yet fully exploited. Yet the chemical design possibilities are not exhausted. A new class of materials based on the same photochromic azobenzene side-groups but linked to peptide oligomers through amide bonds (designated DNO materials) has been shown to possess very prosperous optical storage properties, not least very high achievable diffraction efficiencies<sup>60,61</sup>. Basically the Merrifield synthesis amenable for these new structures has provided a vast number of homologues of oligomers in which oligomer length, linker length, back-bone "chemistry", and

chirality of back-bone unit conclusively influence the obtainable first order diffraction efficiency. In addition to the above mentioned storage features these new materials have an outstanding temperature resistance, thus holograms in these new DNO materials are preserved after long exposure to 180°C.

## Acknowledgement

M.P. and N.C.R.H. thank the Danish Research Academy for Ph.D. stipends. Financial support from the Brite/EuRam programme under contract BRE2.Ct93.0449: *LICRYPOIS* and the Danish Materials Technology Development Programme (MUP2) are gratefully acknowledged.

## References

1. Roth, J.P., *Rewritable Optical Storage Technology*, Meckler, Westport-London, U.K., 1991.
2. Kryder, M.H. *Ann. Rev. Mat. Sci.* **23**, 411 (1993).
3. McArdle, C.B., Ed., *Side Chain Liquid Crystal Polymers*, Blackie and Son Ltd., Glasgow, U.K., 1989, Chapter 13.
4. Chilton, J.A., and Gossey, M.T., Eds., *Special Polymers for Electronic and Optoelectronics*, Chapman & Hall, London, U.K., 1995.
5. Rau, H., *Photochemistry and Photophysics*, Rabek, J.F., Ed., CRC Press, Inc., Boca Raton, Florida, 1990, Vol.II, Ch. 4.
6. Gibbons, W.M., Shannon, P.J., Sun, S.-T., and Swetlin, B.J. *Nature* **351**, 49 (1991).
7. Chen, A.G., and Brady, D.J. *Opt. Lett.* **17**, 441 (1992).
8. Natansohn, A., Rochon, P., Gosselin, J., and Xie, S. *Macromolecules* **25**, 2268 (1992).
9. Xie, S., Natansohn, A., and Rochon, P. *Chem. Mat.* **5**, 403 (1993).
10. Eich, M., Wendorff, J.H., Reck, B., and Ringsdorf, H. *Makromol. Chem., Rapid Commun.* **8**, 59 (1987).
11. Anderle, K., Birenheide, R., Eich, M., and Wendorff, J.H. *Makromol. Chem.* **191**, 2133 (1990).
12. Wiesner, U., Antonietti, M., Boeffel, C., and Spiess, H. W. *Makromol. Chem.* **191**, 2133 (1990).
13. Stumpe, J., Muller, L., and Kreysig, D. *Makromol. Chem., Rapid Commun.* **12**, 81 (1991).
14. Haitjema, H.J., von Morgen, G.L., Tan, Y.Y., and Challa, G. *Macromolecules* **27**, 6201 (1994).
15. Ringsdorf, H., and Schmidt, H.-W. *Makromol. Chem.* **185**, 1327 (1984).
16. Ivanov, S., Yakolev, I., Kostromin, S., Shibaev, V., Läscher, L., Stumpe, J., and Kreysig, D. *Makromol. Chem., Rapid Commun.* **12**, 709 (1991).
17. Eich, M., and Wendorff, J.H. *J. Opt. Soc. Am. B* **7**, 1428 (1990).
18. Crivello, J.V., Deptolla, M., and Ringsdorf, H. *Liq. Cryst.* **3**, 235 (1988).
19. Reck, B., and Ringsdorf, H. *Makromol. Chem., Rapid Commun.* **6**, 291 (1985).
20. Engel, M., Hisgen, B., Keller, R., Kreuder, W., Reck, B., Ringsdorf, H., Schmidt, H.-W., and Tschirner, P. *Pure Appl. Chem.* **57**, 1009 (1985).
21. Reck, B., and Ringsdorf, H. *Liq. Cryst.* **8**, 247 (1990).
22. Braun, D., Herr, R.-P., and Arnold, N. *Makromol. Chem., Rapid Commun.* **8** 359 (1987).

23. Hvilsted, S., Andruzzi, F., Cerrai, P., and Tricoli, M. *Polymer* **32**, 127 (1991).
24. Hvilsted, S., Andruzzi, F., and M. Paci, M. *Polym. Bull.* **26**, 23 (1991).
25. Andruzzi, F., and Hvilsted, S. *Polymer* **32**, 2294 (1991).
26. Andruzzi, F., Hvilsted, S., and Paci, M. *Polymer* **35**, 4449 (1994).
27. Canessa, G.S., Aguilera, C., Serrano, J.L., and Oriol, L. *J. Polym. Sci. Part A: Polym. Chem.* **34**, 1465 (1996).
28. Hvilsted, S., Andruzzi, F., and Ramanujam, P.S. *Opt. Lett.* **17**, 1234 (1992).
29. Hvilsted, S., Andruzzi, F., Kulinna, C., Siesler, H.W., and Ramanujan, P.S. *Macromolecules* **28**, 2172 (1995).
30. Salmon-Legagneur, F., and Neveu, C., *Bull. Soc. Chim. Fr.* **1956**, 1345.
31. Zebger, I., Kulinna, C., Siesler, H.W., Andruzzi, F., Pedersen, M., Ramanujan, P.S., and Hvilsted, S. *Macromol. Symp.* **94**, 159 (1995).
32. Pedersen, M., *New Azobenzene Side-Chain Polyesters for Optical Information Storage*, Ph.D. Thesis, Technical University of Denmark, Lyngby, 1997.
33. Lenz, R.W., *Organic Chemistry of Synthetic High Polymers*, Interscience Publishers, New York, 1967. 62.
34. Ramanujan, P.S., Holme, C., Hvilsted, S., Pedersen, M., Andruzzi, F., Paci, M., Tassi, E.L., Magagnini, P.L., Hoffman, U., Zebger, I., and Siesler, H.W. *Polym. Adv. Techn.* **7**, 768 (1996).
35. Kulinna, C., Zebger, I., Hvilsted, S., Ramanujan, P.S., and Siesler, H.W. *Macromol. Symp.*, **83**, 169 (1994).
36. Hvilsted, S. *Makromol. Chem., Macromol. Symp.* **52**, 199 (1991).
37. Tassi, E.L., Paci, M., and Magagnini, P. *Mol. Cryst. Liq. Cryst.* **266**, 135 (1995).
38. Kulinna, C., Hvilsted, S., Hendann, C., Siesler, H.W., and Andruzzi, F. *Mol. Cryst. Liq. Cryst.* 1977, accepted.
39. Todorov, T., Nikolova, L., and Tomova, N. *Appl. Opt.* **23**, 4588 (1984).
40. Holme, N.C.R., Ramanujan, P.S., and Hvilsted, S. *Opt. Lett.* **21**, 902 (1996).
41. Ramanujan, P.S., Hvilsted, S., and Berg, R.H. *Holography*, SPIE Int. Techn. Working Group Newsletter, **6** (No.2), 2 (1996).
42. Ramanujam, P. S., Hvilsted, S., and F. Andruzzi, F. *Appl. Phys. Lett.* **62**, 1041 (1993)
43. Ramanujan, P.S., Hvilsted, S., Andruzzi, F., Kulinna, C., and Siesler, H.W., Organic Thin Films for Photonic Applications, *Technical Digest Series* **17** (Optical Society of America, Washington, D.C.), 244 (1993).
44. Ramanujan, P.S., Hvilsted, S., Zebger, I., and Siesler, H.W. *Macromol. Rapid Commun.* **16**, 455 (1995).
45. Bach, H., Anderle, K., Fuhrmann, T., and Wendorff, J.H. *J. Phys. Chem.* **100**, 4135 (1996).
46. Todorov, T., Nikolova, L., Stoyanova, K., and Tomova, N. *Appl. Opt.* **24**, 785 (1985).
47. Song, Q.W., Lee, M.C., Talbot, P.J., and Tam, E. *Opt. Lett.* **16**, 1228 (1991).
48. Kostuk, R., Kato, M., and Huang, Y.T. *Appl. Opt.* **29**, 3848 (1990).
49. Ramanujan, P.S., Andruzzi, F., and Hvilsted, S. *Opt. Rev.* **1**, 30 (1994).
50. Holme, N.C.R., Ramanujan, P.S., and Hvilsted, S. *Appl. Opt.* **35**, 4622 (1996).
51. Nikolova, L., Todorov, T., Ivanov, M., Andruzzi, F., Hvilsted, S., and Ramanujan, P.S. *Appl. Opt.* **35**, 3835 (1996).
52. Ramanujan, P.S., Holme, N.C.R., and Hvilsted, S. *Appl. Phys. Lett.* **68**, 1329 (1996).
53. Holme, N.C.R., Nikolova, L., Ramanujan, P.S., and Hvilsted, S. *Appl. Phys. Lett.* **70**, 1518 (1997).
54. Bieringer, T., Wuttke, R., Haarer, D., Gessner, U., and Rbner, J. *Macromol. Chem. Phys.* **196**, 1375 (1995).
55. Rochon, P., Batalla, E., and Natansohn, A. *Appl. Phys. Lett.* **66**, 136 (1995).

56. Kim, D.Y. Tripathy, S.K., Li, L., and Kumar, J. *Appl. Phys. Lett.* **66**, 1166 (1995).
57. Barrat, C.J., Natansohn, A.L., and Rochon, P.L. *J. Phys. Chem.* **100**, 8836 (1996).
58. Hendann, C., Siesler, H.W., Andruzzi, F., Kulinna, C., and Hvilsted, S. *Mol. Cryst. Liq. Cryst.* 1997, accepted.
59. Kulinna, C., Hvilsted, S., Hendann, C., Siesler, H.W., and Ramanujan, P.S., in preparation.
60. Berg, R.H., Hvilsted, S., and Ramanujan, P.S. 1996, *Nature*, **383**, 505 (1996).
61. Ramanujan, P.S., Holme, N.C.R., Nikolova, L., Berg, R.H., Hvilsted, S., Kristensen, E.T., Kulinna, C., Nielsen, A.B., and Pedersen, M. "Practical Holography and Holographic Materials XI", *Proc. SPIE* **3011** (1997) accepted.