

POLYMER SCAFFOLDS BEARING AZOBENZENE — POTENTIAL FOR OPTICAL INFORMATION STORAGE

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Abstract The fundamental optical storage mechanism of the laser light addressable azobenzene moiety is briefly introduced. A modular and flexible synthesis design furnishes polyester matrices covalently integrating cyanoazobenzene in regularly spaced side chains. Thin films of these materials are particularly well suited for holographic storage. Notable figures of merits of liquid crystalline polyesters are response time to blue-green laser light of the order of nanoseconds, storage capacity expressed as 5000 lines/mm, and high, permanent (almost nine years) diffraction efficiency of the order of 50% or greater, and erasability. The implications of the main chain nature for polyester morphology and for the permanency of the induced anisotropy are discussed. The design and methods of preparation of other significantly different polymer scaffolds supporting cyanoazobenzene are elaborated. Oligopeptides always result in amorphous materials, whereas copolymethacrylates and dendritic or hyperbranched polyesters provide some materials that exhibit liquid crystallinity. However, none of these scaffolds affords materials that result in permanent anisotropy when exposed to interfering laser light.

Keywords Azobenzene side-chain polymers, Copolymethacrylates, Dendrimers, Holographic storage, LC and amorphous polyesters, Morphology, Oligopeptides.

INTRODUCTION

Materials capable of storing information optically are vigorously attracting increasing attention. The well-known photoresponsive ability of azo dyes has revitalized the interest in these century-old compounds and made them potential optical storage candidates. Especially the covalent linking of azo dyes to a polymer matrix through a flexible side chain as introduced by Ringsdorf *et al.*^[1] in the late eighties seems to be advantageous. During the last decade we have developed a range of significantly different polymer scaffolds bearing substituted azobenzene, with exploitable, exciting, and unexpected properties. Extensive investigations on the physical response to irradiation with polarized laser light, mainly in a holographic mode, have been performed. The polymers are LC and amorphous linear polyesters, and in collaboration with others copolymethacrylates and oligopeptides have been investigated (Fig. 1).

A last group comprises dendritic and hyperbranched polyesters. Within each polymer family a great number of structural variations have been made and their optical storage implications have been studied. It is the intention to provide a short timely review emphasizing the differences of the materials' light response and highlighting the superiority of the materials.

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investigated. In some cases, combinations of different substituents (X in Fig. 1a) both provide the highest achievable diffraction efficiency ($> 70\%$) and seem to complement the behavior of a corresponding material based on the single substituent. On the other hand, the initially raised questions on the influence of azobenzene dipole strength or substituent shape can not be answered by the conducted experiments. The azobenzene substituent, however, seems to strongly influence the particular poly(1,3-propylenetetradecanedioate) material morphology. That is crucial, and the temperature range open for inducing the anisotropy (corresponding to the writing process) is quite narrow. Creation of anisotropy is only possible in a narrow temperature range around T_g and seems to be performed most efficiently at T_g or slightly above. In other words, a most efficient temperature for the inscription of data exists for the individual LC polyesters. Whereas this temperature is 30°C for the cyano substituted polyester, the temperature is 35°C and 40°C for the trifluoromethyl and nitro analogues, respectively. In the evaluation of new materials it is therefore important to disclose the material optimum temperature response and not restrict the experiments to room temperature.

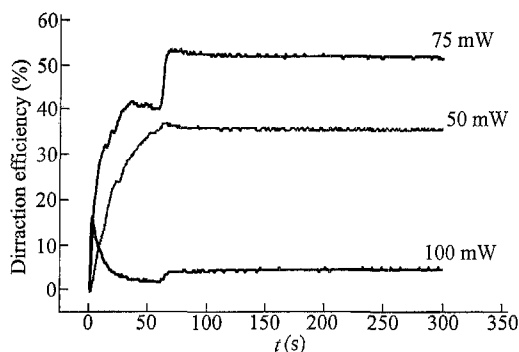


Fig. 2 Diffraction efficiency of a $2.7\ \mu\text{m}$ film of P(CN/NO₂)₁₂ (1:3) exposed for 60 s to 50, 75, and 100 mW (@ 488 nm)

An extensive number of polytetradecanedioates, -dodecanedioates and -adipates with cyanoazophenoxy alkylene (hexylene, octylene, and decylene) side chains, selectively deuterated at different positions, have been prepared as models for analogous non-deuterated materials^[4]. The polyester morphology is strongly dependent on the number of main-chain methylenes and differs from purely liquid crystalline (polyadipates) over semicrystalline (polydodecanedioates) to coexistence of mesomorphic and crystalline domains (polytetradecanedioates). Laser-induced anisotropy in thin films of these polyesters have been investigated with polarized FTIR spectroscopy. The analysis of the resulting segmental orientation is based on dichroic ratios of selected and characteristic absorption bands and calculations of order parameters according to a uniaxial orientation^[5]. In polyesters with the longest main-chain spacing (tetradecanedioates) not only the light sensitive azo chromophore but also the main-chain methylene segment and to a smaller extent the flexible alkylene spacer are preferentially oriented perpendicular to the laser light polarization. The extent of orientation increases with increasing alkylene spacer length. On the other hand, in the shorter polyadipates only the chromophore and the alkylene spacer behave similarly. In the polydodecanedioates the response to the laser seems to be somehow retarded although all three principally different segments are moderately oriented. Rapid-scan FTIR analysis performed on-line with the laser irradiation reveals that the alignment of the aliphatic segments occurs simultaneously with the chromophore orientation. Temperature dependent infrared investigations of the laser induced orientation shows that the preservation of the photoinduced anisotropy directly relates to the polyester phase behavior as monitored by DSC.

Since 1995 it has been observed^[6-9] that interfering laser beams on azobenzene containing polymers in general, as in the polarization holography set-up, create a surface relief as seen in Fig. 3. It turns out that the shape and appearance of such surface reliefs are very polarization dependent. Although a number of research groups are involved in the elucidation of these phenomena, no model among the many proposed so far has been

able to explain all the different, apparently contradictory observations made. As the storage process in these polymers involves the physical reorientation of segments of long polymer chains, this process was thought to take place over several seconds, if not minutes. The individual *trans-cis-trans* isomerization cycles of the cyanoazobenzene parts have long been speculated to be very fast^[10]. Recent investigations on thin films of the octyl-spaced cyanoazobenzene polytetradecanedioate have demonstrated^[11] photoinduced birefringence by use of one single 4 ns pulse. The maximum birefringence is attained at a moderate pulse strength (53 mJ/cm^2) in a dark reaction after excitation. Subsequently, in the course of minutes most of the birefringence is lost due to relaxation processes involving up to four different time constants, however, a small permanent birefringence remains (maximum values obtained with strengths $38\text{--}53 \text{ mJ/cm}^2$). It was furthermore observed that at high pulse energies the relaxation characteristics are strongly influenced by thermal effects and all processes take place in less than a μs leaving no permanent birefringence.

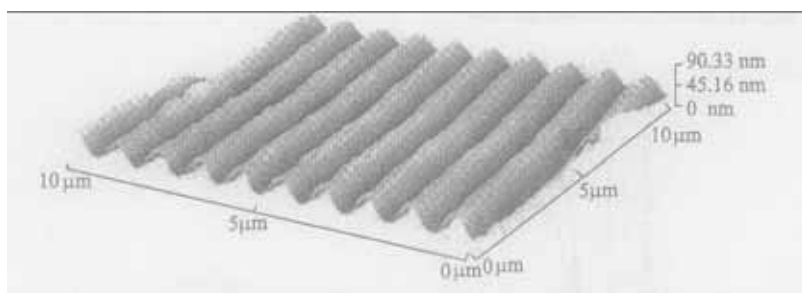


Fig. 3 AFM scan of $10 \mu\text{m}$ by $10 \mu\text{m}$ area exposed to two laser beams. The surface relief with a maximum roughness of 90 nm is observed after one 5 ns pulse. The interbeam angle between the recording beams is 28° , resulting in a spatial frequency of 900 lines/mm .

We have recently shown that holograms can be written in side-chain azobenzene polymers with a single pulse lasting 5 ns from a pulsed laser^[12]. The cyanoazobenzene side-chain polyester, P3aA is prepared by transesterification of the cyanoazobenzene containing diol and diphenyl phthalate in the melt under vacuum. Approximately 3 mg of the polyester material is dissolved in 150 microlitres of chloroform and cast on to a clean substrate. The film is dried in an oven at a temperature of 90°C for ten minutes. A polarization holographic set-up is used to record holographic gratings. We use a commercially available small frame frequency doubled YAG laser at 532 nm as the source. This laser delivers Q-switched pulses of $5\text{--}7 \text{ ns}$ duration at 20 Hz , with a peak power output of 1.6 MW/pulse . The two beams overlap on the polyester film. A HeNe laser is used to readout the diffraction gratings. We find that just after one pulse from the laser, several orders of diffraction of the HeNe laser can be seen. The diffraction efficiency in the first order exceeds 4% at a spatial frequency of 160 lines/mm . An atomic force microscopic (AFM) scan of the irradiated polyester shows considerable surface relief at the optical frequency (Fig. 3). A peak-to-valley value of approximately 90 nm was obtained at a spatial frequency of 900 lines/mm . In order to extend the scope of these investigations for practical holographic applications, the set-up was modified to fabricate Fraunhofer type holograms. The object beam was expanded to cover a transparency containing the word "Risø". The size of the object was 12 mm . The resulting hologram was about 1 mm in diameter. The image was quite bright enough to be viewed on a screen. The appearance of the image is instantaneous.

Copolymethacrylates

Optical storage of thin unoriented liquid crystalline and amorphous side-chain azobenzene copolymethacrylates was examined through polarization holographic measurements^[13]. The investigated materials are various copolymers obtained by free radical polymerization of two photochromic monomers, 1-methacryloxy-6-(4-oxy-4'-cyanoazobenzene)hexane ($n = 6$ in Fig. 1b) or 1-methacryloxy-8-(4-oxy-4'-cyanoazobenzene)octane ($n = 8$)

and a non-photochromic optically active comonomer, (–)-menthyl methacrylate; the fundamental composition of the copolymers is shown in Fig. 1(b). The thermal behavior and phase transitions of the polymers have been investigated in detail through differential scanning calorimetry and polarizing optical microscopy^[13]. Atomic force microscopy investigations have been carried out on the polarization holographic gratings recorded in the polymethacrylate films. A surface relief grating, comparable to the one depicted in Fig. 3, has been found to appear in all the films after irradiation. Surprisingly the copolymers with 50%~75% dye content exhibit the largest surface relief on the order of 1.2 μm in films originally 4 μm thick. The stored information is partially erasable in the copolymers characterized by an azo dye content of 75%~100% by heating the samples up to 80 °C. In the low azo dye content copolymers the optical information is not thermally erasable up to 80 °C.

Oligopeptides

In contrast to polymers molecular materials of relative small but well-defined sizes can often be prepared. One approach is the use of the peptide strategy exploiting the efficient solid-phase assembly of large numbers of diverse molecular structures by Merrifield synthesis. Through a targeted azobenzene design and by the proper choice of coupling strategy a vast number of new photoanisotropic azobenzene oligopeptides with the principle structure depicted in Fig. 1(c) were prepared^[14]. Holographic gratings with extraordinarily high diffraction grating efficiency can be recorded in thin films of most of these materials. The importance of the scaffold design among structures that can be considered structurally isomeric clearly demonstrated a strong template effect^[15]. Thus, a bis-trimer responded about 20 times faster than the corresponding linear hexamer. The notion here was the advantageous interaction of the two arms clearly influenced by the length of the linking amino acid acting as a template. In a later development the ornithine-based backbone was replaced with a proline-based one^[16] as shown in Fig. 1(d). This reduced the response time from 5 min to less than 1 s. The dimer with the fastest response could be prepared in solution in contrast to all the others (assembled by solid-phase synthesis). This allows the preparation to be easily scaled up to tens of grams. Most of the azobenzene oligopeptides demonstrated very high surface relief structures that actually account for the high diffraction efficiencies since no permanent anisotropy remains in the films after some weeks.

Dendritic and Hyperbranched Polyesters

Dendritic macromolecules, comprising dendrimers and hyperbranched polymers constitute a novel class of highly branched polymers with a multitude of end-groups. Whereas dendrimers are described by a well-defined, monodisperse structure, the related family of hyperbranched polymers consists of less well-defined, polydisperse molecules. A recent development^[17] has focussed on hydroxy-functional dendritic and hyperbranched aliphatic polyesters based on 2,2-bis(hydroxy-methyl)propionic acid (bis-MPA). The hydroxy surface of these dendrimers and hyperbranched polymers has been successfully functionalized with different end-groups^[18]. In a further development, dendrimers of generation 1 to 3 and a hyperbranched polymer of generation 3 were functionalized with azobenzene groups giving dendritic macromolecules bearing 6, 12, 24, and 32 chromophores, respectively. Different chromophoric units based on the cyanoazobenzene moiety substituted with alkoxy ω -carboxylic acid were coupled to the dendritic matrix by use of an acid chloride reaction as illustrated in Fig. 4 for the second generation with one methylene spacer. Investigations of these new materials' thermal and optical properties have demonstrated that no LC phase could be observed when the spacer length n is < 5 methylenes, whereas T_g decreases when n increases. When $n = 5$ or 10 a LC phase was observed. However, with the same n the broadness of the LC phase increases with increasing size of dendrimer generation. Permanent anisotropy of the order of 0.2 rad could be induced in thin film materials with laser light at 488 nm. Investigations by AFM have demonstrated surface reliefs (similar to Fig. 3) of the order of 1 μm in these films. The preliminary results have demonstrated that the spacer linking the chromophore to the dendritic core has a dramatic influence on the optical properties and is more important than the dendritic core.

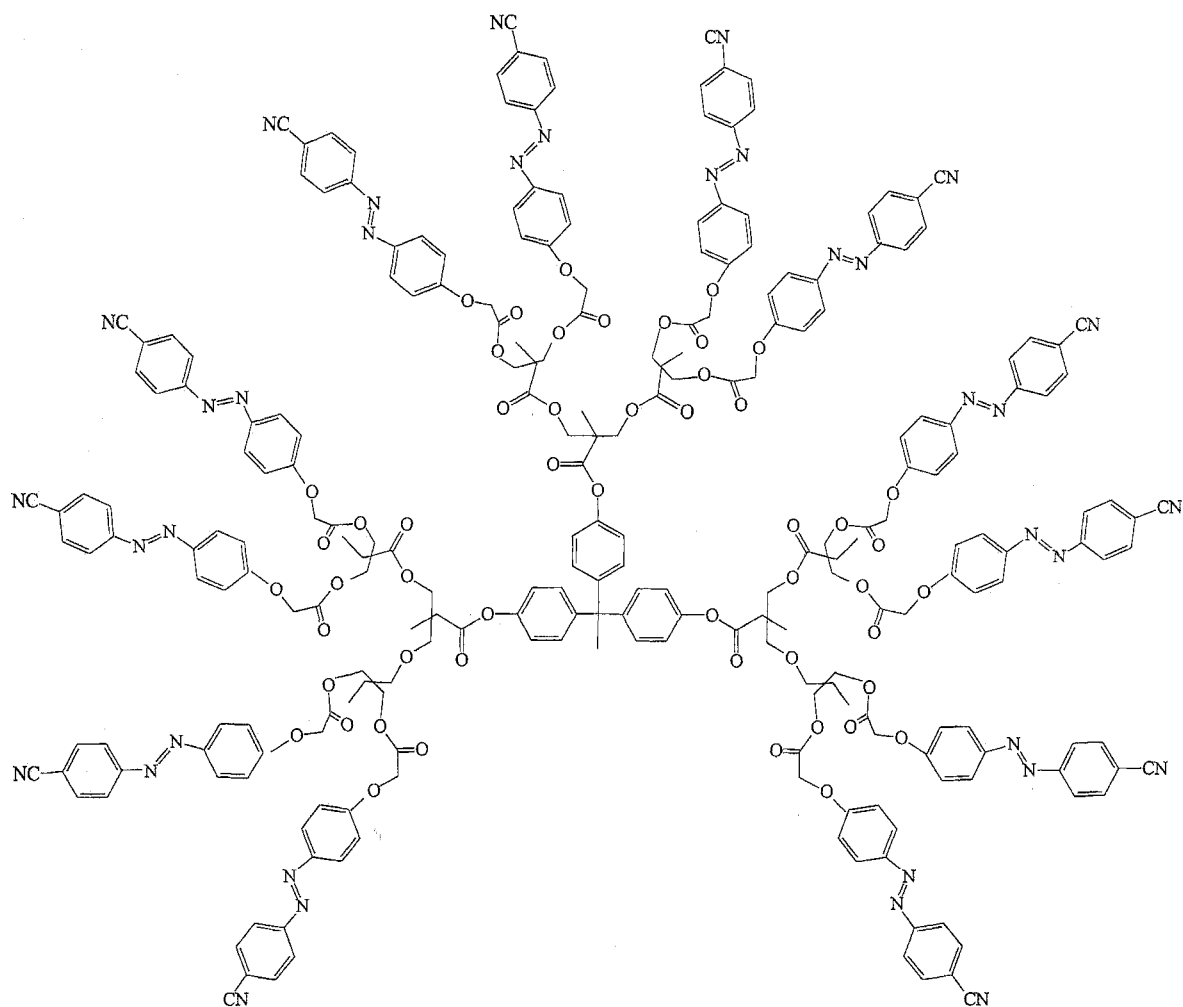


Fig. 4 Azobenzene dendrimer with a second generation aliphatic polyester scaffold and the cyanoazobenzene chromophore with one methylene in the spacer

CONCLUSIONS

LC azobenzene side-chain polyesters with aliphatic main chains respond very rapidly to laser light. A single nanosecond pulse can induce permanent birefringence. The basic, necessary processes, mimicking an optical storage process, are accomplished after such short laser exposures. All principle polyester segments contribute to the induced anisotropy. Instant holography can be performed in amorphous analogues with partly aromatic main chains after an only 5 ns short pulse from a YAG laser. It can therefore be concluded that thin films of the developed LC polyesters fulfill most of the expected requirements for future optical storage materials. Thus we have demonstrated the materials' sensitivity to moderate laser powers in the blue-green range, resulting in a very high resolution that has long-term permanency. Furthermore, the induced permanent anisotropy required for the storage can be inscribed in as short a time as a few nanoseconds.

A number of other cyanoazobenzene containing materials have interesting properties but develop no longer lasting anisotropy upon laser irradiation. Thus copolymethacrylates with (–)-menthyl and azobenzene ester side chains are either LC or amorphous but thin films of all materials form surface reliefs after irradiation. Molecular materials in the form of oligopeptides with azobenzenes allow very high diffraction efficiencies to be inscribed in short times strongly depending on the backbone structure and length. Template effects are pronounced in

comparable hexamers. However, proline dimers are superior and achieve maximum diffraction efficiency in 1 s. The diffraction efficiencies in all oligopeptides are due to very strong surface reliefs. Azobenzene dendritic or hyperbranched polyesters provide new materials with LC properties strongly depending on linker length and dendrimer size in which appreciable surface reliefs can be induced.

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