Liquid crystals for holographic optical data storage

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A *tutorial review* is presented to inform and inspire the reader to develop and integrate strong scientific links between liquid crystals and holographic data storage, from a materials scientist's viewpoint. The principle of holographic data storage as a means of providing a solution to the information storage demands of the 21st century is detailed. Holography is a small subset of the much larger field of optical data storage and similarly, the diversity of materials used for optical data storage is enormous. The theory of polarisation holography which produces holograms of constant intensity, is discussed.

Polymeric liquid crystals play an important role in the development of materials for holographic storage and photoresponsive materials based on azobenzene are targeted for discussion due to their ease of photo-reversion between *trans*- and *cis*-states. Although the final polymer may not be liquid crystalline, irradiation can induce ordered domains. The mesogens act in a co-operative manner, enhancing refractive indices and birefringences. Surface relief gratings are discussed as a consequence of holographic storage.

Cholesteric polymers comprising azobenzene are briefly highlighted. Irradiation causing *cis*–*trans*-isomerisation can be used to control helix pitch. A brief mention of liquid crystals is also made since these materials may be of future interest since they are optically transparent and amenable to photo-induced anisotropy.

Introduction

This tutorial review is designed to inform and inspire the reader to develop and integrate strong scientific links between liquid crystals and holographic data storage, from a materials scientist's viewpoint. Holography is a small subset of the much larger field of optical data storage. In fact, both liquid crystals and optical data storage are enormous in their own right and impact modern day society from liquid crystals displays used in mobile phones to high quality music and films played on Compact Disk (CD) and Digital Versatile Disk (DVD). An in depth review of each subject is not the purpose of this article. The reader should consult relevant articles contained within this special issue for an overview of liquid crystals and ref. 1–7 for a thorough review of materials and mechanisms for optical data storage.

We aim to focus on the tenuous links that have been established between holographic data storage and liquid crystals following the seminal work of Wendorff *et al.*[8] who reported the formation of gratings with high diffraction efficiency (up to 4%) and high spatial resolution in a

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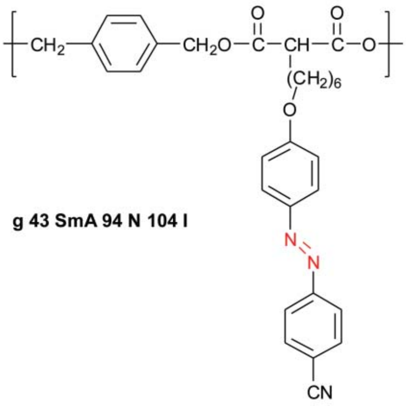
side-chain azobenzene polyester **1**. The polymer was aligned in an electric field above its T_g and irradiated at 514 nm. Heating the sample above its clearing point caused erasure. It may interest the reader to see the recent article by Tsutsumi,[9] commenting on the enormous impact of Wendorff's article to current developments in reversible holographic data storage (a reprint of Wendorff's original article may be found in this reference).



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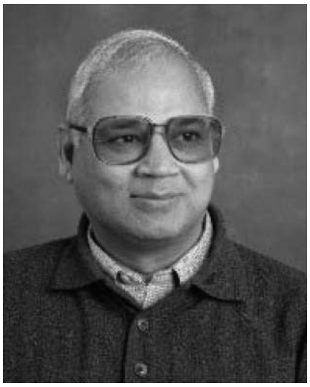
Furthermore, because of the enormity of the subject the reader is strongly encouraged to see the reviews, and references therein, of Natansohn and Rochon[2] on photoinduced motions in azo-containing polymers and the special issue on 'Photochromism: Memories and Switches' edited by Irie,[1] as certain topics such as photoinduced chirality will not be discussed. This tutorial overview highlights the theory and real-life application of polarisation holography. Materials, in particular the class known as photoaddressable polymers, are discussed together with the consequences of irradiation, such as photoinduced anisotropy and surface relief gratings. Photoresponsive polymer cholesterics are mentioned since they can be designed as dual materials, operating at different wavelengths to induce different responses. A brief mention of nematic glasses is made, which may be an exciting area because the materials are grain-less, defect-free and transparent, providing excellent optical clarity.



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Liquid crystallinity is not a pre-requisite for reversible holographic data storage but the role of liquid crystals (mesogens) as anisotropic structural units is very important in controlling birefringence, diffraction efficiency, co-operative motion, surface relief gratings and stability.[2] As summarised by Natansohn and Rochon[2] photoisomerisation in liquid crystalline polymers is thermodynamically favoured by the presence of a liquid crystalline or mesophase temperature range. A mesophase may be photo-induced if the film is in its initial isotropic amorphous state (relatively easy orientation and high birefringence), or the director of the liquid crystalline domains can be altered by the light polarization (energetically less favourable but of higher birefringence). There are two main ways of utilising liquid crystals in holographic data storage: either as a homogenous system where the liquid crystal moiety is an integral part of the molecule, or as a multi-component guest–host system exemplified by holographic photopolymer-dispersed liquid crystals (H-PDLC),[10] liquid crystalline elastomers,[11] and photorefractive mixtures.[3,12,13] Such multi-component systems will not be discussed and this tutorial will focus on systems comprising a liquid crystal (mesogenic) moiety as an integral part of the molecule.

Modern-day society lives in an information-obsessed world. The volume of information produced and stored annually is exponential in growth. The 'Information Age' has arrived in all its glory with on-line access to vast resources of electronic information never imagined less than two decades ago. On a daily basis we are bombarded with high resolution digitised images utilising mega- and giga-bytes of information. These terms will soon be redundant as the societal needs of the 21st century will demand for peta- and exa-bytes of information to be stored and retrieved on the click of a mouse button. Lyman and Varian[14] reported that five exabytes of information was produced globally by print, film, magnetic, and optical storage media alone in 2002. To put this in to context one must realise that digitized information is stored in terms of 'zeros' and 'ones' known as bits (1b). A letter of the alphabet utilises eight bits and is termed a byte (1B). One kilobyte (1 KB or 10^3 bytes) corresponds to approximately one page of A5 typewritten text. One megabyte (1 MB or 10^6 bytes) equates to an old style 3.5 inch floppy disk and the complete works of William Shakespeare can be stored on 5 MB. One gigabyte (1 GB or 10^9 bytes) corresponds to a large van filled with books, whereas 100 GB is a library floor of academic journals. One terabyte (1 TB or 10^{12} bytes) is nearly 50000 trees made into paper and printed. An academic research library stores approximately 2 TB of information. Moving in to the realms of peta- and exa-bytes, then the former is 10^{15} bytes (all the information contained within all US academic research libraries), whereas the latter is 10^{18} bytes. Five exabytes corresponds to all the words ever spoken by human beings or alternatively, an unbelievable 25^{10} trees made in to paper and printed!

However, a major problem exists since the storage needs of a modern-day society are incommensurate with the high volumes of information being processed. Although magnetic disk is still the best medium for storage of large amounts of information, it too has severe limitations. Magnetic disk, and conventional magneto-optical data storage technology, uses the surface of the medium to store and retrieve bits of data. The available area on a magnetic disk cannot be compressed indefinitely to record even smaller bits of information due to the superparamagnetic effect.[15] The diameter of the magnetic domains is limited to not much less than 10 nm otherwise, thermal self-erasure occurs. The magnetised bit flips randomly finding it difficult to attain a stable state.

The current consumer state of the art optical data storage device is BluRay DVD.[16] Unlike its counterparts, the CD (750 MB or 75 minutes music) and DVD (4.7 GB or 2 hour movie), BluRay DVD is capable of storing in excess of 27 GB. The success of BluRay DVD is due to the commercial availability of a blue laser light source (405 nm) combined with optics of numerical aperture 0.85, which allows for a smaller, focused spot-size, thus increasing the area available for storage. Researchers are already looking to the future by investigating the use of UV lasers at 266 nm to further enhance storage capacity,[17] which one day may become reality when technological advances to produce cheap commercially available UV lasers come to fruition.

To meet the societal needs of the 21st century a volumetric 3-D, rather than a surface 2-D, approach may be needed. Holography[18] may provide such a solution as exemplified by InPhase Technologies' Tapestry™ media,[19] which already boasts the ability to store and retrieve 200 GB on a standard 120 mm CD format at high speed, equivalent to a near tenfold improvement on optical BluRay DVD technology. Holographic storage provides the potential of storing in excess of a terabyte of information with transfer rates exceeding 1 GB/s and data access time of less than 100 μs.

Holographic data storage

The concept of holography was first introduced by Gabor[20,21] in 1948 but remained dormant for many years due to lack of technological advances in complementary optics and image processing instrumentation. In 1963, van Heerden[22] developed the technique of holographic data storage. Significant activity ensued in the early nineties due to major investment by the US Defense Advanced Research Projects Agency (DARPA) integrating academics and industrialists, mainly IBM, to capitalise on the technological advances available at the time: cheap semiconductor lasers; high resolution spatial light modulators and; CCD detector arrays. However, the lack of an appropriate material appeared to be, and still is, a major bottleneck in the acceptance of holography in the marketplace. Mention must be made here of two other materials that have been investigated for holographic storage: i) lithium niobate—volumetric storage has been demonstrated in single crystals of this material by D. Psaltis and his group;[23]ii) photorefractive polymers—this work has been pioneered by Peyghambarian's group.[24] The problem with the first material is that of growing large crystals of lithium niobate, while the photorefractive polymers required high voltages.

Any material suitable for holographic storage should possess:

i. fast optical switching between two states;
ii. high thermal stability over a wide temperature range;
iii. non-destructive read-out.

Holographic storage offers the unique potential for parallel storage and processing. In holographic storage, a page of information in the form of a bit-map is recorded at a time, instead of storing single bits as in digital storage. Typically, two laser beams derived from a single laser source are overlapped on a photosensitive material. One of the beams, called the object beam, passes through the object (bit-map) of interest, and the other beam called the reference beam, is a plane wave providing a phase reference. In conventional holography, the two beams have the same polarization. They create a complicated interference pattern in the film, which is characteristic of the object. The recorded information is read-out with a conjugate of the reference wave. In absorption or intensity holography, both the recording and the read-out beams are within the absorption band of the photosensitive material. The maximum diffraction efficiency that can be obtained in this process is on the order of 6%.[25] This is the case with silver halide photographic emulsions. The diffraction efficiency is defined as the ratio of the intensity of the diffracted beam to that of the incident beam. Theoretically many diffraction orders can result, however, mostly, only first order diffraction is used. If the absorption changes can be converted to optical phase changes, such as by bleaching the photographic plates, then an optical phase hologram results. This is the case with dichromated gelatin.[25] The maximum efficiency for such a hologram is on the order of 35%. If the holographic recording material is thick, then the interference fringes can be recorded in the bulk of the material, and the diffraction efficiency in phase holograms can reach 100%.

Sh. D. Kakichashvili[26] invented a new form of holography called polarization holography. In this case, the two overlapping beams can have different polarizations, and in the most important cases, they are orthogonally polarized. These beams are incoherent with respect to each other, and there is no variation in intensity across the hologram. No interference fringes result. However, if the material is sensitive to polarization changes, these can be recorded in the material. In particular, if two orthogonally circularly polarized light beams are employed to record a hologram, the resultant vectorial addition results in a linearly polarized light beam whose azimuth changes depending on the phase difference between the overlapping beams. If the molecules in the material, such as the case of azobenzene to be discussed, reorient due to the interaction with this linearly polarized light, a phase grating with a varying birefringence results. Reading this grating with polarized light produces the diffracted beams. If the photoinduced anisotropy (dichroism and birefringence) is large, a near 100% diffraction efficiency can be achieved even in thin films.[27]

A typical holographic optical bench is depicted in Fig. 1, where the incident linearly polarized beam is split into two beams with orthogonal polarizations by means of the polarization beam-splitter (PBS). A half-wave plate (HWP) before the PBS, is employed to make the intensities of the two overlapping beams equal, creating equal modulation. Optional polarizers (POL) are utilized in order to ensure complete plane polarization, followed by quarter-wave plates (QWP) to convert the linearly polarized light to circular polarization. One of the beams is a reference beam, and the other passes

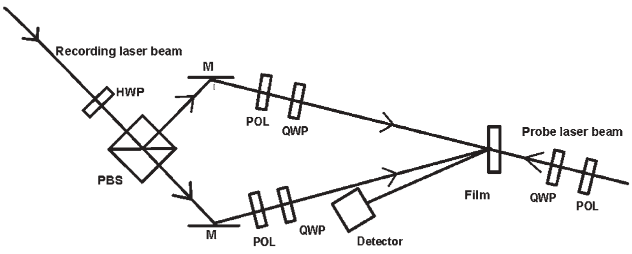


Fig. 1 Holographic set-up.

through the bit-map to be recorded. The probe laser beam, used for the read-out, is again circularly polarized through a quarter wave plate; the diffracted beam can be detected with a detector.

Fig. 2 displays a method of recording a hologram of a bitmap.

The bitmap in question can be an image, a physical transparency, a piece of film containing the information to be recorded or a spatial light modulator (SLM) containing black and white pixels that represent 0's and 1's of a binary file. The object beam circularly polarized passes through the SLM and impinges on the recording film. The reference beam orthogonally circularly polarized likewise falls on the film overlapping the object beam. The resultant elliptically polarized light aligns the photoresponsive molecules, for example azobenzenes, predominantly perpendicular to the major axis, creating a birefringence. This pattern can be seen under a polarization microscope between crossed-polarizers.

It should be noted that holographic storage using laser addressed *via* heat-mode recording is also possible and was first reported in 1983 by Shibaev *et al.*[28] The heat from a focused laser beam impinging on an area of an aligned anisotropic SCLCP causes the local temperature to exceed the clearing point of the polymer. An isotropic state is created, which is frozen-in by rapidly quenching below the glass transition, T_g. Photo-mode recording is far superior to heat-mode recording because of higher resolution, fast writing speed and the possibility of multiplexing, *i.e.*, the ability to record multiple holograms in the same volume of space. This article will not further discuss heat-mode recording.

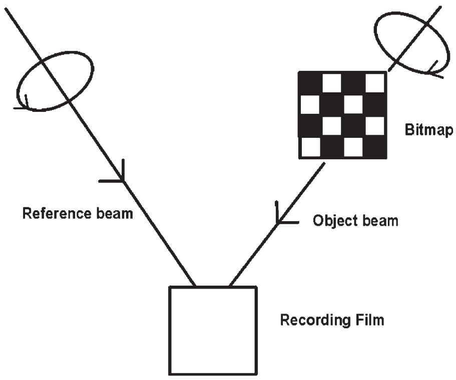


Fig. 2 Recording a bitmap.

Theory—recording

Let us assume that there is only photo-induced birefringence in the material (no photodichroism). Furthermore, let us assume that the two interfering plane waves $\boldsymbol{E_1}$, and $\boldsymbol{E_2}$, propagate with an inter-beam angle, 2θ.

If the two waves are orthogonally circularly polarized, in paraxial approximation their Jones vectors can be written as:

$$E_1=\frac{1}{\sqrt{2}}\begin{vmatrix}1\\-i\end{vmatrix}\exp(i\delta_1)\text{ and }E_2=\frac{1}{\sqrt{2}}\begin{vmatrix}1\\i\end{vmatrix}\exp(i\delta_2)\qquad(1.1)$$

Here $\left|{}^{1}_{-i}\right|$ is the Jones Matrix for a left-circularly polarized beam, and $\left|{}^{1}_{+i}\right|$ represents a right circularly polarized beam, δ_1 and δ_2 are the phases of the incident beam.

The interference field is:

$$E=E_1+E_2=\sqrt{2}\begin{vmatrix}\cos\delta\\\sin\delta\end{vmatrix}\text{ where }\delta=(\delta_2-\delta_1)/2\qquad(1.2)$$

A photo-birefringent material can record this pattern resulting in a polarization hologram. The transmission matrix of the recorded hologram T_{ani} as a function of δ can be written as:

$$T_{\text{ani}}=R^{-1}.T.R=$$
$$\begin{pmatrix}\cos\delta & \sin\delta\\-\sin\delta & \cos\delta\end{pmatrix}\begin{pmatrix}e^{i\Delta\varphi} & 0\\0 & e^{-i\Delta\varphi}\end{pmatrix}\begin{pmatrix}\cos\delta & -\sin\delta\\\sin\delta & \cos\delta\end{pmatrix}\qquad(1.3)$$

where $T=\begin{pmatrix}e^{i\Delta\varphi} & 0\\0 & e^{-i\Delta\varphi}\end{pmatrix}$ is the transmission matrix caused by linearly polarized light and R = $\left({}^{\cos\delta-\sin\delta}_{\sin\delta\cos\delta}\right)$ is a matrix describing a rotation by an angle δ.

Simplifying the above equation, the Jones matrix describing anisotropic transmission is:

$$T=\left|{}^{\cos(\Delta\varphi)+i\sin(\Delta\varphi)\cos2\delta-i\sin(\Delta\varphi)\sin2\delta}_{-i\sin(\Delta\varphi)\sin2\delta\cos(\Delta\varphi)-i\sin(\Delta\varphi)\cos2\delta}\right|\qquad(1.4)$$

Here $\Delta\varphi$ = $\pi(\Delta n)d/\lambda$ is the induced anisotropic phase difference in the material, Δn is the photo-birefringence and d the material thickness. This matrix is a superposition of three matrices (T= T_1 + T_2 + T_3) that determine the existence of three waves after the hologram:

$$T_1=\cos(\Delta\varphi)\left|{}^{10}_{01}\right|\qquad(1.5)$$

is the directly transmitted wave (0th order).

$$T_2=i\frac{\sin(\Delta\varphi)}{2}\begin{vmatrix}1 & -i\\-i & -1\end{vmatrix}\exp(2i\delta)\qquad(1.6)$$

is a wave with a left circular polarization in the -1 order, and

$$T_3=i\frac{\sin(\Delta\varphi)}{2}\begin{vmatrix}1 & i\\i & -1\end{vmatrix}\exp(-2i\delta)\qquad(1.7)$$

is a wave with right circular polarization in the +1 order.

Read-out—theory

Let us assume a normally incident plane wave R with left circular polarisation

$$R=\left|{}^{1}_{-i}\right|\qquad(1.8)$$

for the read-out.

The diffracted amplitude can be found as the result of the product of T and R. The only diffracted wave in this case is

$$E_{+1} = \sin(\Delta\varphi)|_i^1|\exp(-2i\delta), \tag{1.9}$$

The diffracted intensity is obtained by multiplying eqn. (1.9) with its complex conjugate.

$$I_{+1} = \sin^2(\Delta\varphi)|_i^1| \tag{1.10}$$

which shows that for a photo-induced anisotropy of π/2, a 100% right circularly polarized, +1 order wave can be obtained. This is the case if the overlapping circularly polarized beams have equal intensity. If the object beam is passed through an amplitude mask, the intensity ratio is no longer equal to 1, resulting in a resultant elliptically polarized beam. In this case, detailed theoretical calculations show that the resulting even and odd order diffracted beams will be orthogonally polarized. Thus, the zeroth order diffraction beam can be removed through a combination of a quarter wave-plate, and a suitable polarizer

If, in addition, there is a surface relief, there will be an additional diffraction due to this. The readers are referred to Holme *et al.*[29] for further detailed treatment of gratings with both anisotropy and surface relief. However, it has been found that a surface relief is detrimental to the read-out process in holographic storage, resulting in a decreased to signal-to-noise ratio.

Azobenzene photoresponsive polymers

Azobenzene. Polarization holography, of course, demands storage materials that are sensitive to the polarization of light. Ramanujam and co-workers[30] have championed polarisation holography using materials based on azobenzene, which has been the workhorse in the development of photosensitive materials for holographic or photo-mode data storage following the seminal work of Wendorff *et al.*[8,9] Azobenzene polymers are easy to fabricate, and extremely good quality thin films can be obtained with an initial isotropic distribution of the chromophores. After irradiation with linearly polarized light, a rather large birefringence can be created. Polymers serve as excellent media for holographic data storage rather than single crystals, *e.g.*, lithium niobate, because of ease of fabrication and processing. Polymers allow a wide number of structural permutations and combinations by varying the nature and type of subunits comprising the polymer. Single crystal engineering is a difficult, skilled art and unlike polymers, single crystals are prone to mechanical fragility.

Azobenzene is a long and flat molecule, with a transition dipole moment. The molecule is, in its most stable form, in the *trans*-state. On excitation with blue light, the molecule isomerises to the *cis*-state. The absorption spectra of the *trans*- and *cis*-states of the azobenzene attached to a polyester chain are shown in Fig. 3.

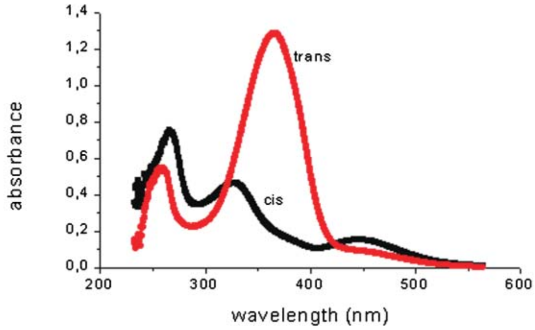


Fig. 3 Typical UV-vis absorption spectrum of polymer bound azobenzene.

The strong absorption at 360 nm in the *trans*-state is due to a π–π* transition. This transition occurs at approximately 320 nm in the *cis*-state. The absorption at 450 nm both in the *trans*- and *cis*-states are due to n–π* transitions. If the molecule is excited at 360 nm, it isomerises to the *cis*-state, from where it will return to the *trans*-ground state through non-radiative transition. However, exciting the molecule at 450 nm will cycle the molecule through *trans*- and *cis*-states several times as depicted in Fig. 4.

The probability of the molecule in the *trans*-state absorbing a photon is proportional to $\left|\vec{\mu}.\vec{E}\right|^2$, where $\vec{\mu}$ is the transition dipole moment of the molecule, and $\vec{E}$, is electric field vector, and thus is proportional to $\mathrm{Cos}^2\vartheta$, where ϑ is the angle between the transition dipole-moment and the electric field vector. Due to the continued optical pumping process, the molecule after a number of *trans–cis*-transition cycles, will re-organise orthogonal to the electric field vector, and hence will be unable to absorb the photons, thus creating an anisotropy in the material. Excitation of azobenzene with elliptically polarized light will result in the azobenzenes orienting predominantly orthogonal to the major axis of the elliptical vibration.

The mechanism of photoisomerisation of azobenzene is wavelength dependent. The *trans–cis* isomerisation proceeds *via* an inversion mechanism when irradiated in the n–π* region, whilst a rotational mechanism for *trans–cis* isomerisation is proposed during irradiation in the π–π* region.

If the polymer is liquid-crystalline, the rotated domains are stable at room temperature preserving any information stored in the material. The information stored in liquid crystalline azobenzene side-chain polyesters has been found to be stable for over 15 years. However, the domain structure in the polymers introduces background scattering, reducing the signal to noise ratio. If the polymers are glassy, then the stability of the stored information has been found to depend on the glass transition temperature of the polymer.[31]

Holographic memory card system. A compact holographic information storage system has been constructed with the above-mentioned principles in mind.[32]

Fig. 5 shows the optical arrangement of the polarization Holographic Memory Card (HMC) system. The 8f Fourier system consists of two identical Fourier objectives and two polarization beam splitters. The small mirror at the back focal plane of the first Fourier objective, which serves as the aperture stop of the 8f system, allows for suitable Fourier filtering. Between the two polarization beam splitters, a random phase mask for decreasing undesirable intensity peaks in the Fourier plane is placed. In order to increase the data

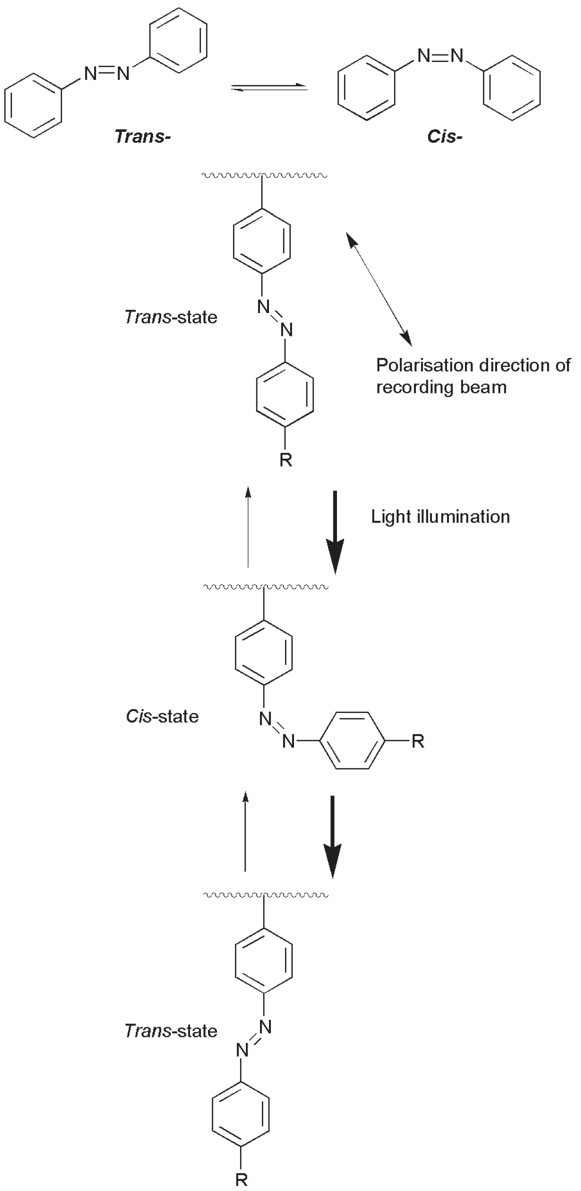


Fig. 4 *Trans–cis–trans* photoreversion in polymer-bound azobenzenes.

density, the axis of the large angle (47°) object wave cone and the plane reference wave is parallel. These waves are circularly polarized in the opposite directions. Two-element (spherical and biaspherical) reading/writing objective with 0.73 NA in the Fourier space is used. A small-frame frequency doubled YAG laser at 532 nm is used as the source. The holograms are recorded in an azobenzene polyester film.

A typical bitmap of a data page recorded and recovered is shown in Fig. 6. The hologram size is about 0.26 mm in diameter, corresponding to a data density of ~ 1 bit μm^{-2}. Powerful error correction codes based on the Reed-Solomon procedure help the written data page to be recovered without errors. Further details of data recording and read-out are provided Lörincz *et al.*[32] Data density enhancement is possible with special data encoding techniques and Fourier filtering. These improvements require minor hardware changes of the HMC system and slight modification of the signal processing algorithm. Deterministic phase coded multiplexing can further increase the storage density. The storage capacity can be increased several-fold if one could utilize multiplexing techniques.

PAPs - photoaddressable polymers. Photoaddressable polymers (PAPs) have played a key role in the development of holography and the use of liquid crystalline structural entities.[2,33,34] PAPs are amorphous or liquid crystalline side-chain copolymers functionalised with azobenzene chromophores and mesogenic side groups, which may also be photoactive. PAPs exhibit high photo-induced birefringence as a result of repeated *cis–trans–cis* photoisomerisation, inducing strong molecular reorientation (see Fig. 4). The role of the mesogenic group is to undergo co-operative or synergistic molecular motions, thus inducing a higher birefringence, and to stabilize their orientation after the illumination process. The process is reversible and exhibits excellent long-term stability.

The concept of PAPs, combination of photoactive chromophore and co-operative mesogenic unit, is best summarised by Zilker *et al.*,[34] who rationalizes two fundamental design philosophies as exemplified by the CP1 and K1 polymer

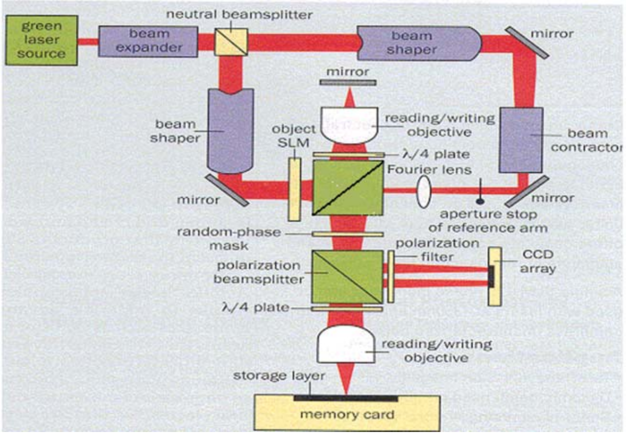


Fig. 5 Holographic Memory Card system.

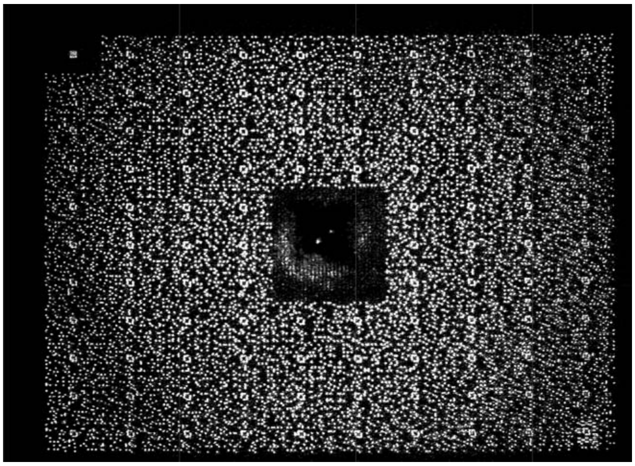


Fig. 6 Recovered data page with the HMC system.

systems shown in Fig. 7. The CP1-50 polymer system comprises two distinct units: a photoactive chromophore and; a co-operative mesogen. In the K1-40 polymer system a clear distinction between chromophore and mesogen is no longer apparent. The mesogen is itself an azo compound, which can be addressed by light. Thus, the distinction between fast-chromophore and slow-mesogen reorientation is lifted leading to a higher of orientation of the mesogenic units.

In the K1-40 system, donor–acceptor substitutions lead to an increase of the interaction between azo and mesogen groups. The overall effect of the K1-40 polymeric system is an increased photo-induced birefringence due the large anisotropy of molecular polarisabilities, $\Delta\alpha$, of both side chains, resulting in high modulations of the refractive index obtained with illumination energies of only 40 J cm^{-2}.

Dipolar contributions are believed to play a major role in high photo-induced anisotropy exhibited by amorphous K1-40 polymers (G 143 I). The dipole moment of K1-40 is approximately two to three times greater than CP1-50. In the less polar CP1-50 polymer system, steric forces are assumed to be the driving force for reorientation of the mesogenic units. The speed and maximum photo-induced birefringence is limited in CP1-50-type polymers because the reorientation of the chromophore and of the mesogen occurs sequentially. This manifests itself in the holographic growth, in the relaxation dynamics and also in the thermal-gain effect. The latter arises due to an increase of the free volume available to the mesogens and on their increasing thermal movements at higher temperatures leading to a collective orientation of the side chains along the direction which is given by those groups that were pre-aligned for the recording laser. Polymers that do not have a liquid-crystalline phase do not exhibit this gain effect. The decrease of the diffraction efficiency occurring inside the liquid crystal phase arises from the overall orientation of the liquid crystal, which decreases the modulation depth of the birefringence grating.

In the absence of any chromophore, for example, a homopolymer comprising 100% mesogenic groups (nominally known as K1-0; G 149 LC 249 I), the photo-induced birefringence is rather low (Δn = 0.10). Similarly, in the absence of any mesogen, for example, homopolymer comprising 100% chromophore units (nominally known as K1-100; G 122 I), the photo-induced birefringence is also low (Δn = 0.11). Thus, confirming the need for both chromophore and mesogen working in a synergistic or co-operative manner for high birefringence values (K1-40, Δn = 0.23). Small angle X-ray scattering reveals the formation of small domains consisting of supermolecular aggregates with a high degree of orientational order. As the illumination time is increased, the degree of ordering increases, whilst the domain size remains constant. Thus scattering is due to re-ordering and not density fluctuations as in guest–host systems where diffusion processes are dominant.

Tolanes as mesogenic units (**2**) have been used to enhance the diffraction efficiency (η) and the modulation of the refractive index ($\Delta\eta'$). Ikeda *et al.*[35] prepared materials comprising tolane mesogenic units which are known to exhibit high birefringence with photoresponsive azobenzene groups. Tolanes are conjugated, linear aromatic molecules

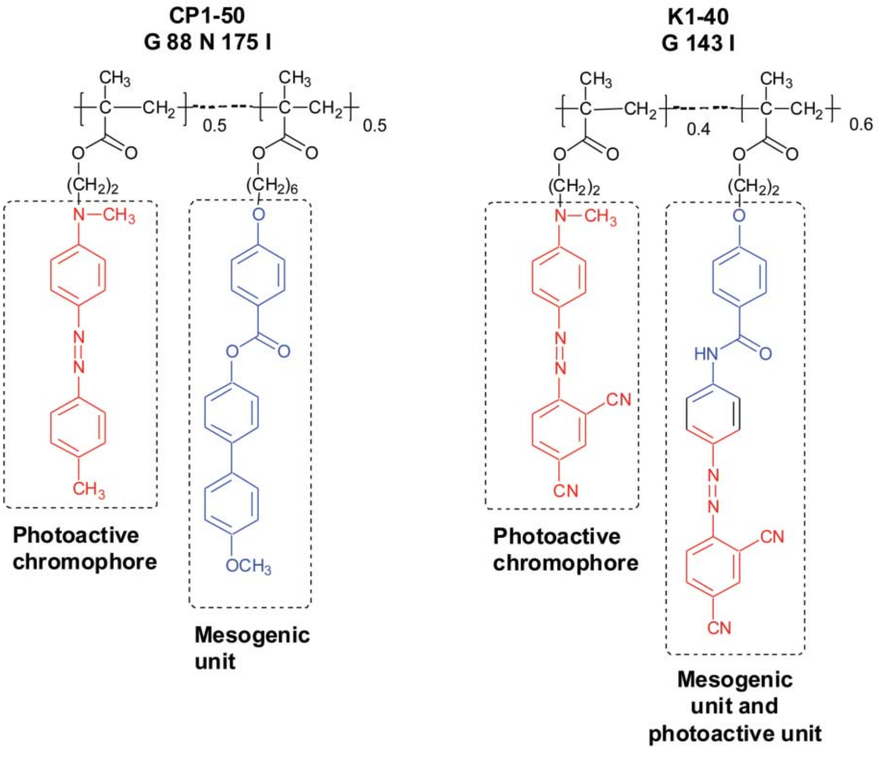
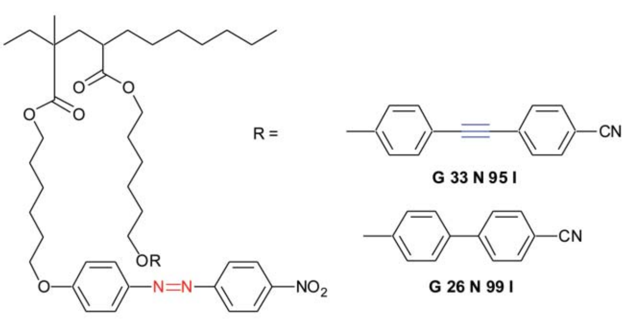


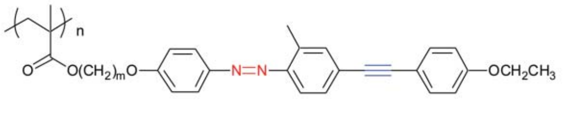
Fig. 7 CP1-50 and K1-40 structural assemblies.

bridged by a sp-hybridised carbon–carbon triple bond unit, *i.e.*, diphenylacetylenes.



2

Gratings were formed at 60 °C (nematic phase) and under the polarisation conditions used (s + s), the value of η for the tolane-based polymer reached a maximum value of 20% after 4 minutes irradiation whereas, the biphenyl-based polymer reached a maximum value of η of 4% after 1 hour. Attachment of both tolane and photoresponsive azo-group through a common central benzene ring (**3**) further improves photosensitivity.[36] In other words, the mesogen and photoresponsive unit were the same, similar to the earlier concept of PAPs.

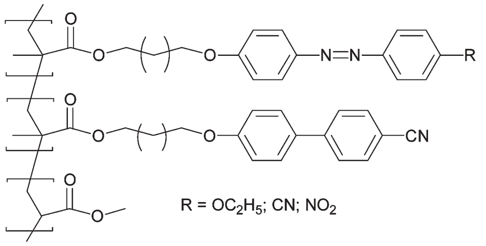


3

m = 6: G 47 N 220 I
9: G 39 N 212 I
12: G 34 N 229 I

Such materials show improved photoinduced birefringence (approximately 0.35). Surface relief gratings were observed due to structural photo-induced changes in order and disorder of the azo-tolane side-chains. Interestingly, grating formation takes place faster in liquid crystal polymers comprising short alkyl tethers because of low packing density and thus a higher propensity to undergo order–disorder transformations. Long alkyl tethers have a high packing density and show the highest resistance to grating formation or disruption of an ordered structure.

Hvilsted and Ramanujam[37] have extensively studied azobenzene polymers comprising a variety of scaffolds. They concluded that liquid crystalline polyesters responded very fast to laser light. A single nanosecond pulse was able to induce high permanent birefringence, stable for more than ten years with a storage capacity of 5000 lines mm^{-1}, and showed erasability. The scope for azobenzene polymers with mesogenic groups is endless and recently Ikeda *et al.*[38] have demonstrated multiple data storage simultaneously utilizing polarisation and angular selectivity by reporting holographic multiple data storage of 55 holograms using angular multiplexing in an optically transparent, 200 μm thick, methacrylate copolymer comprising donor–accceptor-type azobenzene and mesogenic cyanobiphenyl moieties (**4**). The polymer is amorphous and the mesogenic groups undergo co-operative movement.

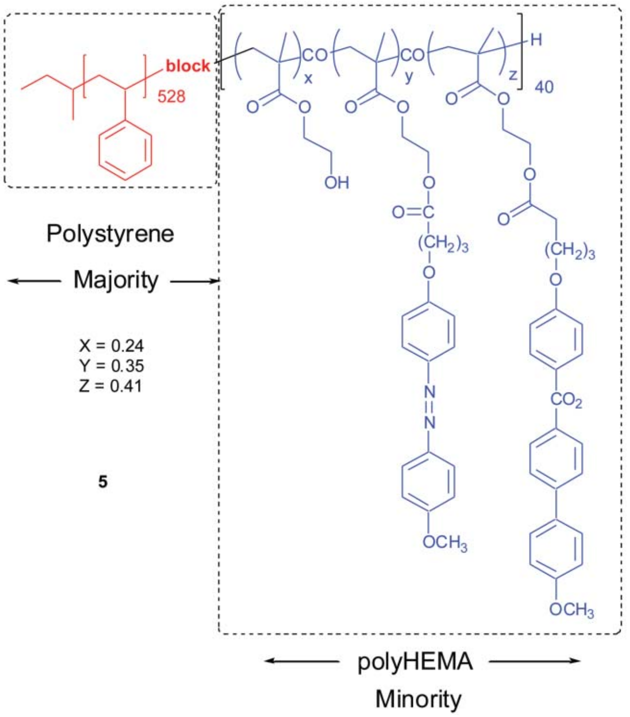


R = OC_2H_5; CN; NO_2

4

A stumbling block to the wider success of PAPs for high capacity volumetric storage is their difficulty to form thick films in the absence of diluents. Thick films cannot be simply fabricated by increasing the concentration of chromophore in a solution that is to be spin-coated or solution cast since the resultant high optical density would limit light penetration. The maximum thickness of a homopolymer film should be approximately 4/absorptivity, or about 320 nm, otherwise thicker films will completely absorb the incoming light beam.[2] Many attempts have been made to fabricate thick films of low optical density, relying on a strategy that embeds the PAP in an inert matrix or diluent, with moderate success.

An elegant way of controlling the optical density is by using a concept of macroscopic dilution of the chromophores as part of a block copolymer system.[39] Thick films can be prepared with multiplexing capability and read–write–erase longevity. The block copolymers contain azobenzene side-chains in one block (minority) combined with a block of mesogen material (majority) (**5**). When there is less than 15% of the chromophoric segment, the block copolymers form spherical microphases of 10–20 nm diameter in size. The chromophores become confined in a narrow environment aiding stability of the inscribed grating and minimising surface relief grating formation.[39]



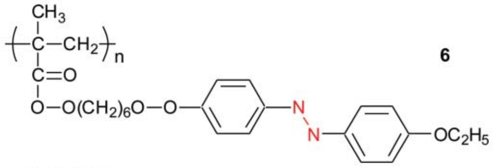
5

The optical density may be manipulated by blending the copolymer with polystrene (PS) homopolymer, producing a polymer amenable to injection moulding. Schmidt *et al.*[39] have prepared a high molecular weight blend (95 wt% PS and 5 wt% block copolymer, M_n = 124 000 g mol^{-1}) with domain sizes 10–20 nm equating to a concentration between 3000 and 10 000 spheres μm^{-1}. The unreacted hydroxyethylmethacrylate (HEMA) segments does not affect side chain orientation but favourably enhances phase separation. The mesogens in the microspheres exhibit cooperative motion inducing strong, stable birefringence. However, long writing times are required which could be reduced using mesogenic azobenzene chromophores that form a liquid crystalline phase without additional mesogenic side chains.[39]

Surface relief gratings

The phenomena of surface relief gratings (SRGs), which form post irradiation due to massive macroscopic molecular motions, have been thoroughly investigated by the groups of Natansohn[2] and Tripathy.[40] Oliveira Jr. *et al.*[7] has recently reviewed optical storage and surface relief gratings in azobenzene-containing nano-structured films derived by Langmuir Blodgett and/or layer by layer electrostatic deposition.

Ikeda *et al.*[41] reported observation of unique characteristics in phase-type gratings that were formed in a polymer azobenzene liquid crystal film. Two unpolarised writing beams were used in their study to create surface relief gratings. Comparison of the diffraction efficiency with the surface modulation revealed that the gratings could not be characterised only as conventional surface-relief gratings. In the glassy state of the film, moderate efficiency (approx. 18%) was obtained with large surface modulation (68–76 nm), whereas the gratings recorded in the nematic phase showed higher diffraction efficiency (approx. 28%) with slight surface modulation (33–53 nm), concluding that the diffraction efficiency was enhanced in the liquid-crystalline state, *i.e.*, the large enhancement of the efficiency was attributable to spatial modulation of molecular alignment (refractive index). Comparison of films with a similar modulation (30–35 nm) revealed that those in the recorded in the nematic phase had diffraction efficiency three times larger than the glassy state, 7% compared with 21%, respectively. Dynamics of the first-order diffraction beam exhibited that the grating formation was associated with photochemical phase transition (N–I) of the polymer azobenzene liquid crystal (**6**). Supported by atomic force microscopy and polarizing light microscopy data, Ikeda *et al.*[41] proposed that isotropic phases were formed by photochemical reaction of azobenzene moieties in the interference pattern at an appropriate level. The grating was formed by alternate arrangement of isotropic and nematic phases as well as slight modulation of surface structure.



6

g 68 N 150 I
Mw = 79, 000; Mw/Mn = 4.4

SRG formation and suppression may be controlled using semi-fluorinated azobenzene polymers.[42] Semi-fluorinated azobenzene liquid crystalline side-chain polymers, of sufficient fluorinated side-chain lengths, can completely suppress surface relief grating formation due to a self-assembled liquid crystalline order at the surface as shown in Fig. 8.

Using wide-angle X-ray scattering (WAXS), Ober *et al.*[42] revealed that polymers with perfluorohexyl- (n = 6) and perfluorooctyl-chains (n = 8) based solely on compositions of photoresponsive group **I** exhibited a smectic A phase with clearing points of 105 and 160 °C and d-spacings of 46 and 52 Å, respectively. The perfluorohexyl-azopolymer showed strong surface relief grating formation whereas, no SRG was formed in the perfluorooctyl-azopolymer as evidenced by AFM. However, the perfluorooctyl-azopolymer did show diffraction of the reading laser implying re-orientation of the

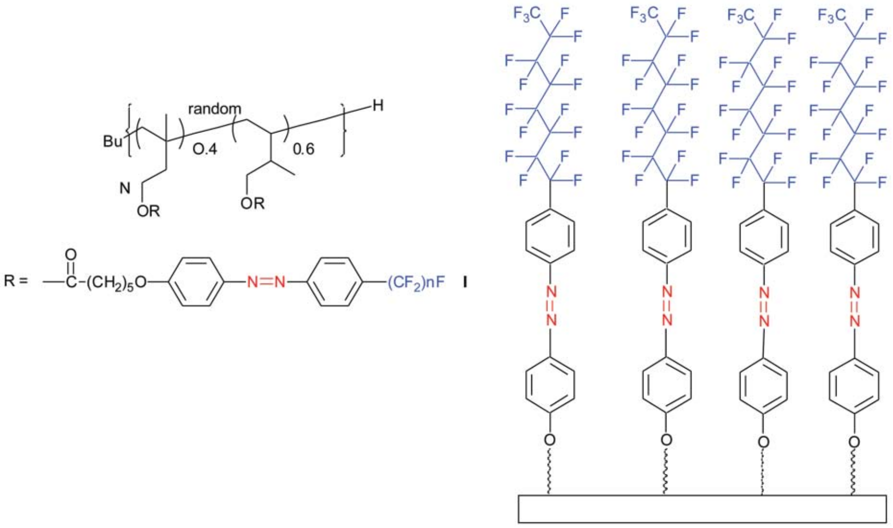


Fig. 8 Molecular structure and surface organisation of semi-fluorinated polymers.

chromophores and photo-induced birefringence. Ober *et al.* postulate that localised liquid crystalline ordering of the perfluoroalkyl chains at the surface hampers SRG formation. The desire to form liquid crystalline assemblies increases with increasing perfluoroalkyl chain length. Hence, SRG formation diminishes as the chain length increases from $n = 4$ to 6 to 8.

An understanding of holographic-induced surface relief gratings has been used to create micropatterned structures. Seki *et al.*[43] have used holographic recording modes (s-: s-) and (p-: p-) to engineer macroscopic alignment and micropatterning of nanoscale periodic structures in block copolymer thin films (see Fig. 9). They report a new 3D (both out-of-plane and in-plane) alignment of nanocyclinders of a diblock copolymer comprising liquid crystalline photoresponsive block chains and poly(ethylene oxide) (PEO) by applying the process of photoinduced mass migration.

The copolymer (Fig. 9), after annealing and successive cooling to room temperature, forms hexagonally close-packed PEO cylinders oriented normal to the substrate plane due to its liquid crystallinity. Seki *et al.*[43] show that in films of thickness greater than 70 nm, and following annealing at 110 °C and subsequent exposure to hexane vapour, H-aggregation is dominant. The azobenzene chromophores align parallel with the PEO cylinders, which are perpendicular with respect to the substrate surface. As they attempted to induce mass migration *via* holographic irradiation at 488 nm, they observed no surface relief grating. However, on softening the material with 5 CB, also acts a diluent, efficient surface relief formation was detected. Post treatment effectively removed the 5 CB molecules *via* evaporation leaving a stable, corrugated surface relief gratings due to mass migration. The direction of the PEO cylinders is dependent upon the holographic recording mode either the electric field vectors were perpendicular (s-: s-) or parallel (p-: p-) to the plane of incidence.

Polymer photochromic cholesterics

The vast majority of studies on photochromic systems are based on azobenzene derivatives as discussed earlier. An interesting evolving area is polymer photochromic cholesterics as highlighted by Bobrovsky *et al.*[44] who discuss the combination of azobenzene with chiral photochromic groups, *i.e.*, dual photochromic materials (see Fig. 10). They report optical properties of binary and ternary copolymers comprising various monomer units, each of which plays a certain 'functional role'.

The methoxyphenylbenzoate groups (**a**) are expected to induce liquid crystallinity (nematic phase). The photoresponsive azobenzene moiety (**b**) will undergo *trans–cis*-photoisomerisation leading to photoinduced birefringence and the chiral photochromic benzylidene-*p*-menthanone fragment (**c**) was expected to form the cholesteric phase. The absorption bands of the azobenzene groups lie in the visible and near UV-spectral regions, whereas the absorptions bands for the chiral menthanone (**c**) occur in the UV spectral region. Thus, they were able to control the type of process for varying the optical properties of the polymer such as birefringence or untwisting of the cholesteric helix to record data. For example, UV irradiation (313 nm or 366 nm) induces *E–Z*-photoisomerisation of the menthanone groups causing the linear *E*-isomer, conducive for liquid crystallinity, to alter shape to the non-linear, less conducive, almost bent structure of the *Z*-isomer (see Fig. 11). A significant change in the helical twisting power, β, is observed as a result of helix unwinding with the pitch tending towards longer wavelengths. Unfortunately, this process is irreversible and the image cannot be rewritten.

Alternatively, irradiation at 514 nm probes the n–π* absorption of the azobenzene moiety resulting in *cis–trans–cis*-photoisomerisation cycles, without affecting the menthanone group. Helix unwinding occurs and a bathochromic shift is detected. However, this process is reversible and heating the sample causes twisting of the helix. Many record-erase cycles can be performed with minimal fatigue or bleaching.

Although it is not our intention to discuss photopolymer mixtures, the work of Strohriegel *et al.*[45] is worth mentioning since they were able to store polarization holograms in a cholesteric liquid crystal/monomer mix post following polymerisation. The individual monomers are very similar to what are perceived as reactive mesogens, which are attracting considerable attention in the liquid crystal community.

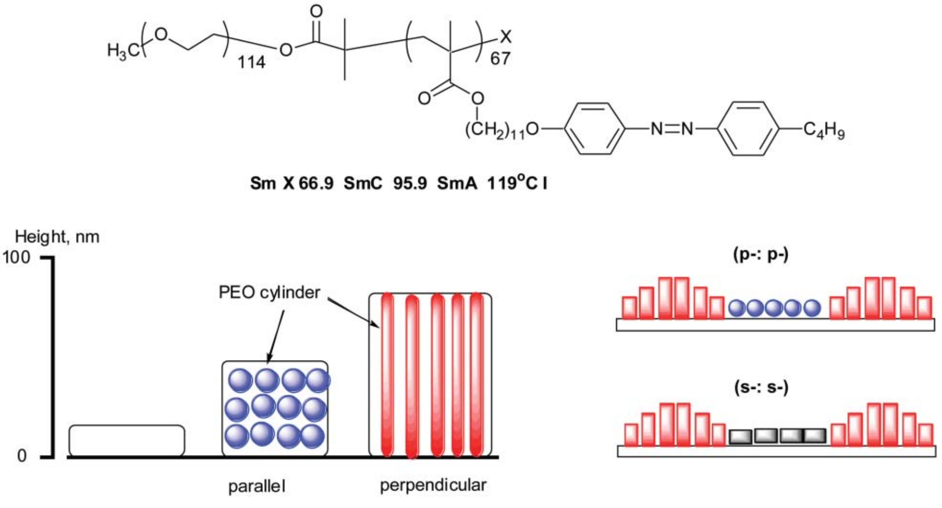


Fig. 9 Molecular structure and surface organisation of photoresponsive PEO comprising block copolymers.

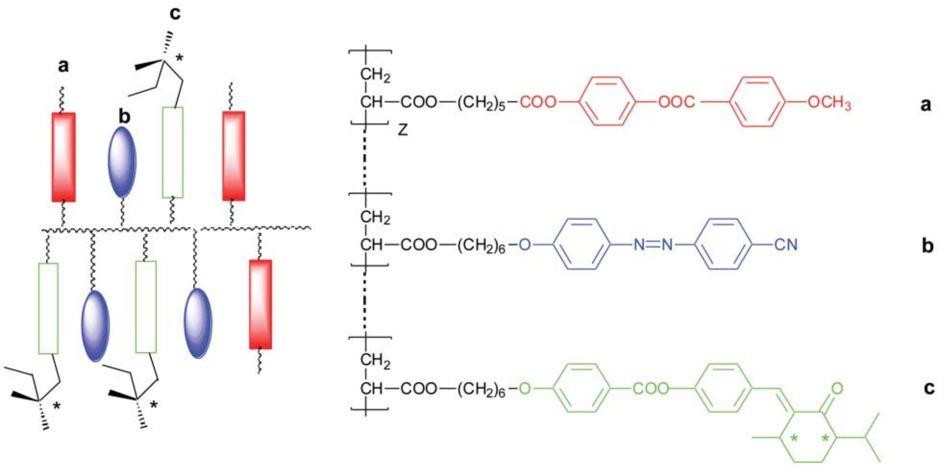


Fig. 10 Composition of a ternary system with dual properties.

Holographic phase gratings are produced by one s- and one p-polarised writing beam. If the helicity of the writing beam matches the helicity of the cholesteric liquid crystal then, light is transmitted. Alternatively, if there is a mis-match then, light is reflected. Thus, bright and dark regions are created and between these two states the polarisation state changes from elliptic to linear and then back to elliptic with opposite helicity. In the bright regions monomers diffuse from the dark areas as polymerisation proceeds, forming a refractive index gradient. This forms a grating that diffracts the reading beam independent of its wavelength. As shown in Fig. 12, the photopolymer comprises: a nematic bisacrylate with two mesogens **e** (46%); a nematic bisacrylate with one mesogen **d** (46%) and; a chiral sorbitol derivative **f** (7%) which controls the pitch of the helix.

Glassy nematics—an interesting concept. Glassy nematics offer similar advantages of polymeric films over single crystal materials in that they have the ability to form of optically transparent, grainless, defect free films. Large area monodomain films can be fabricated with various modes of molecular order frozen in the glassy state rendering glassy nematics useful for photonic applications. Glassy liquid crystals are composed of mesogens covalently attached to a volume-excluding core, which prevents crystallisation but promotes vitrification on cooling.[45]

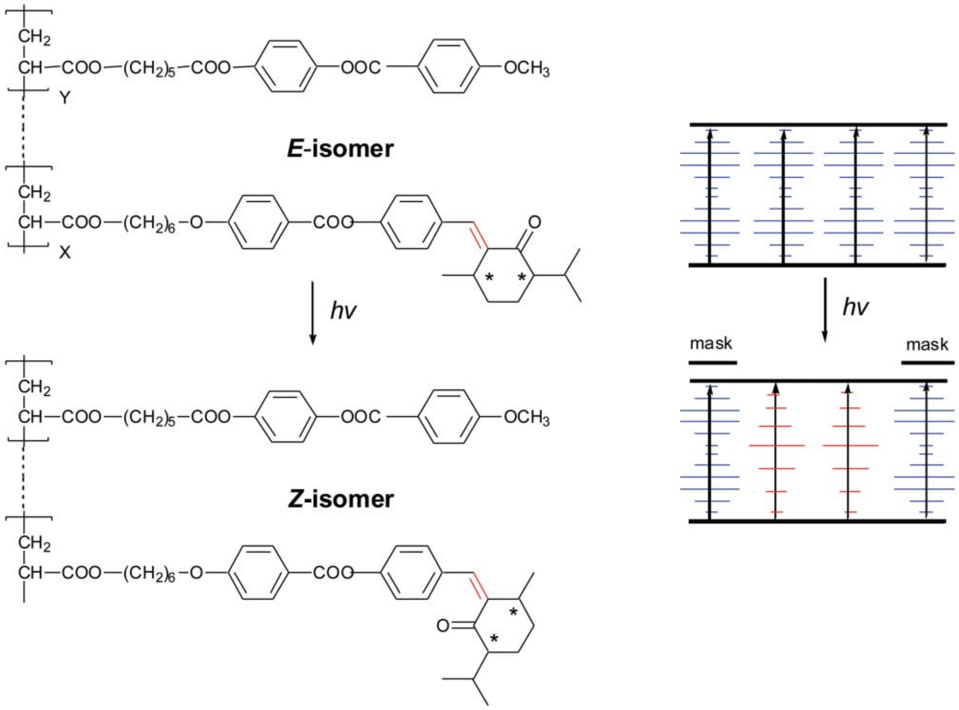


Fig. 11 Photo-controlled helix unwinding.

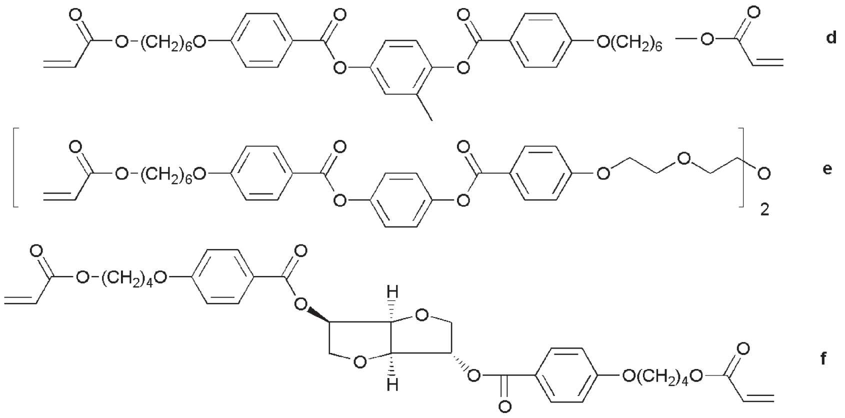
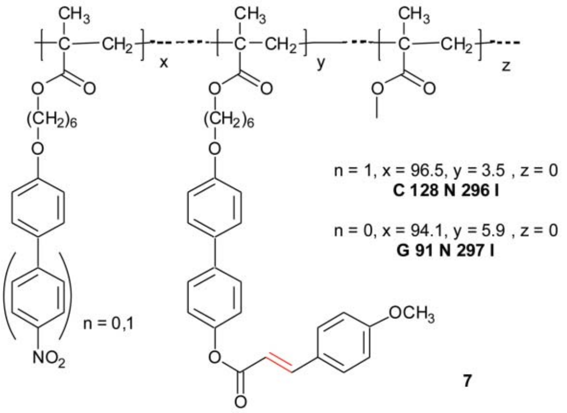


Fig. 12 Structural composition of a reactive photopolymer.

As reported by Chen *et al.*[46] the use of a photoresponsive moiety (see Fig. 13) as the volume-excluding core is the key to introducing additional functionalities in to glassy liquid crystals.

Such materials form macroscopically ordered films in which the photoresponsive groups can align with the nematic director. Thus, such materials present new opportunities for data storage since the refractive indices and optical birefringences can be photo-modulated.



7

Non-azobenzene systems. Although there are many non-azobenzene materials used for optical data storage,[1] we highlight a material capable of optical recording at 405 nm, which may be important since the advent of the Blu-ray technology. Kawatsuki *et al.*[47] have recently reported the first example of multiple optical data storage using linearly polarised 405 nm laser light in a polymethacrylate liquid crystalline polymer (**7**), comprising photo-cross-linkable 4-(4-methoxycinnamoyloxy)biphenyl (MCB) and photosensitising 4-nitrobiphenyl or 4-nitrophenyl side groups. The liquid crystal nature of the material allows the axis-selective photoreaction of the MCB side groups to generate the photoinduced optical anisotropy of the film, while a thermal

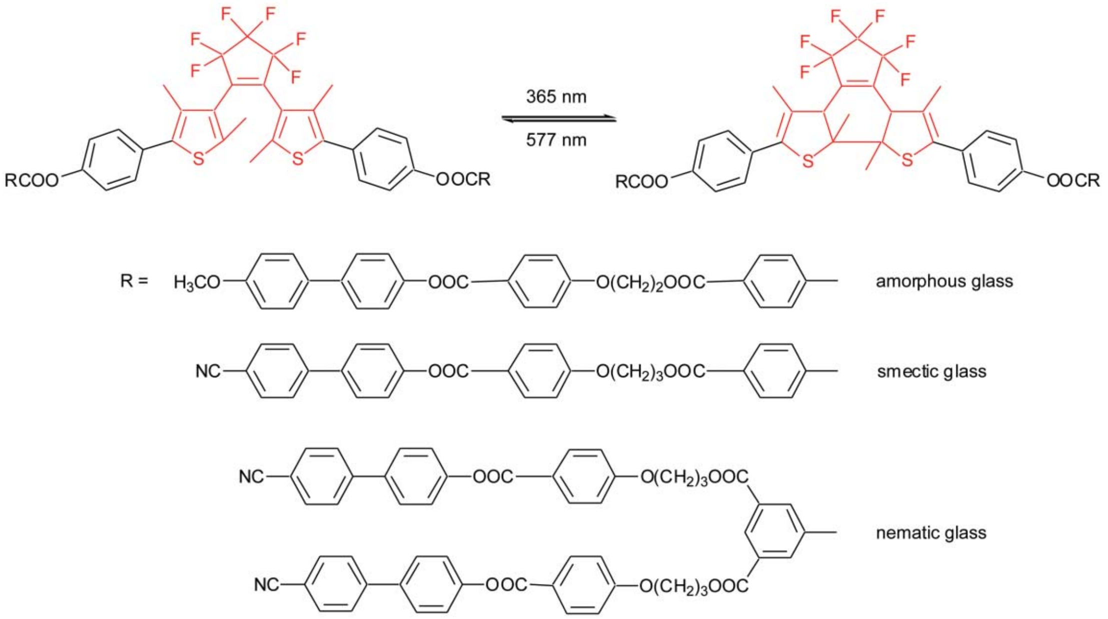


Fig. 13 Diarylethene liquid crystalline glassy materials.

treatment enhances the molecular orientation along the photo-cross-linked anchors parallel to the polarization direction of the linearly polarised light. This was achieved by controlling the orientation direction of the mesogenic groups in the recorded area using plural laser diode light exposures and by adjusting the polarization of the laser diode light.

Summary

Optical data storage is a widely reviewed field, of which holography may provide some of the answers for our much needed quest for media capable of handling high volumes of information. Holography is a 3-D volumetric approach to storage capable of storing 1 TB of information. Many materials have been tried and tested, in particular photoaddressable polymers, which comprise a photoresponsive unit and a mesogen unit. Liquid crystals play an active role in such materials as they serve to increase anisotropy *via* a co-operative mechanism. Liquid crystals also stabilise resultant anisotropy, which in some cases, may be difficult to erase. Photo-modulation of the N–I transition has been used to good effect to create high anisotropy with minimal surface relief formation. The latter arises due to molecular motions and movement on a macroscopic scale. Surface relief formation can be controlled using semi-fluorinated liquid crystal polymers. Liquid crystal ordering at the surface prevents surface relief formation. Photoresponsive cholesteric liquid crystals can serve as dual-purpose materials. Depending of the nature of the side groups, photoreversible changes in helicity, unwinding and winding, can be induced. Liquid crystals that form glasses on cooling produce optically transparent films. Induced anisotropy in such materials is expected to be both high and stable.

Acknowledgements

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