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Holographic Data Storage

From the Surface to Volume: Concepts for the Next Generation of Optical–Holographic Data-Storage Materials

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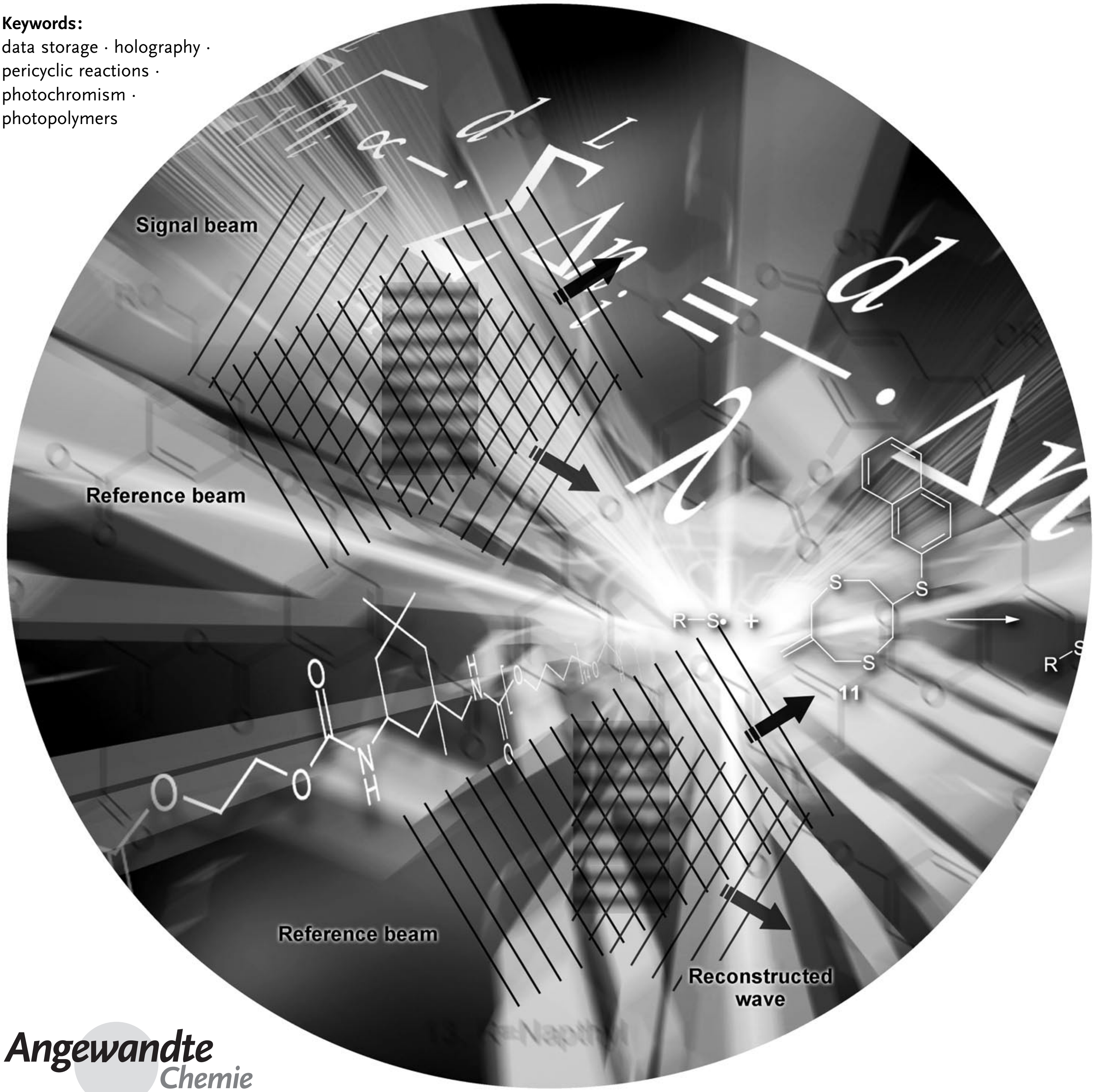

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Optical data storage has had a major impact on daily life since its introduction to the market in 1982. Compact discs (CDs), digital versatile discs (DVDs), and Blu-ray discs (BDs) are universal data-storage formats with the advantage that the reading and writing of the digital data does not require contact and is therefore wear-free. These formats allow convenient and fast data access, high transfer rates, and electricity-free data storage with low overall archiving costs. The driving force for development in this area is the constant need for increased data-storage capacity and transfer rate. The use of holographic principles for optical data storage is an elegant way to increase the storage capacity and the transfer rate, because by this technique the data can be stored in the volume of the storage material and, moreover, it can be optically processed in parallel. This Review describes the fundamental requirements for holographic data-storage materials and compares the general concepts for the materials used. An overview of the performance of current read–write devices shows how far holographic data storage has already been developed.

From the Contents

1. Optical Data Storage: An Introduction

The success story of digital optical data storage (ODS) began in 1982, with the launch of the compact disc (CD). Their 650 MB memory capacity and the superior quality of the sound were clear advantages over the vinyl record, thereby leading to an almost complete replacement of the record. Unlike records, the discs do not deteriorate because the signal transfer takes place without mechanical contact. Mass reproduction of the information can be performed very cheaply by injection molding or compression molding with a polycarbonate disc. In 1996, additional improvements and modification of the product led to the introduction of the digital versatile disc (DVD), which has a capacity between 4.7 GByte and 17 GByte. A DVD is able to store an entire movie with multiple language audio tracks and provides excellent image quality. The storage of high-definition television (HDTV), however, requires even higher storage capacities. For this purpose, Blu-ray disc (BD) and high density DVD (HD DVD) have been developed, which allow for storage capacities between 15 GByte and 50 GByte on a disk with a diameter of 12 cm. At the beginning of 2008, the BD was established as the standard format for the third generation of optical media at the expense of HD DVD.

The family of formats containing CD, DVD, and BD consists of pre-recorded (read only memory = "ROM"), write-once (recordable = R or write once read many = WORM) and rewriteable (rewriteable = RW or recordable/erasable = RE) media. The specification of the various formats guarantees perfect compatibility between media content and drives and allows the music, film, and software industries, which are the suppliers of the information content, to plan its business for decades, because of this backwards compatibility. As with all ODS the medium and the drive are always physically separate entities; therefore, the storage capacity required for particular backup and archiving tasks can be conveniently increased in incremental steps.

The fundamental physical principles of the optical data-storage formats currently on the market are well understood.[1] An objective lens with a numerical aperture (NA) focuses a laser beam with wavelength λ through a transparent substrate or a transparent cover layer onto a highly reflective information layer. The radius s of the diffraction-limited focused laser spot in the plane of information is given by Equation (1).

$$s = \frac{\lambda}{2NA} \tag{1}$$

If the data disc rotates, the laser spot follows the spiral track of the embossed pits or of the written marks, which have different discrete lengths but the same widths. The reflectivity is locally modulated by the optical character of the pits or of the marks (phase or amplitude objects). The information itself is therefore digital in the lengths of the pits or of the coded marks. These lengths are measured between successive changes in the polarity of the readout signal. Because of its sequential nature, this method of data encoding is called "bit-wise".

2. Optical Data-Storage Roadmap

The optical data-storage formats that are currently on the market are based on the principles of far-field optics, in which the storage density can be increased by reducing λ and increasing the NA. The ODS roadmap (development plan) has therefore followed the far-field optics scaling law $(NA/\lambda)^2$

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with the formats CD, DVD, and BD. However, the density scaling factor for "bit-wise" and two-dimensional, that is, planar data storage, has already reached its upper limit for practical applications with the advent of BD. Therefore, research is now focused on technologies that are able to overcome the physical limits of traditional systems (Figure 1).

Systems that are based on near-field optics are currently under investigation; for example, solid-immersion lens recording (SIR), super-resolution near-field structure (Super RENS), or combinations thereof.[2–4] In these cases, the effective *NA* can be increased above the value of one, which represents the limit for the far field.

Attempts have been made to increase the number *n* of gray levels that are associated with each pit above the value of 2,[5–7] meaning that the data density can be increased along

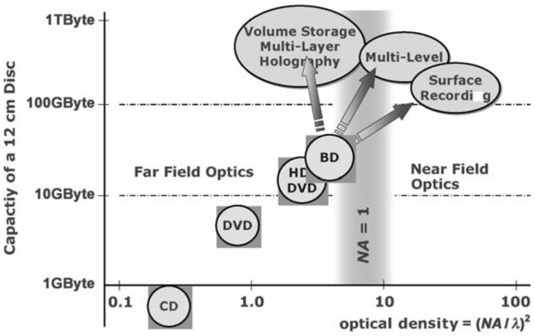
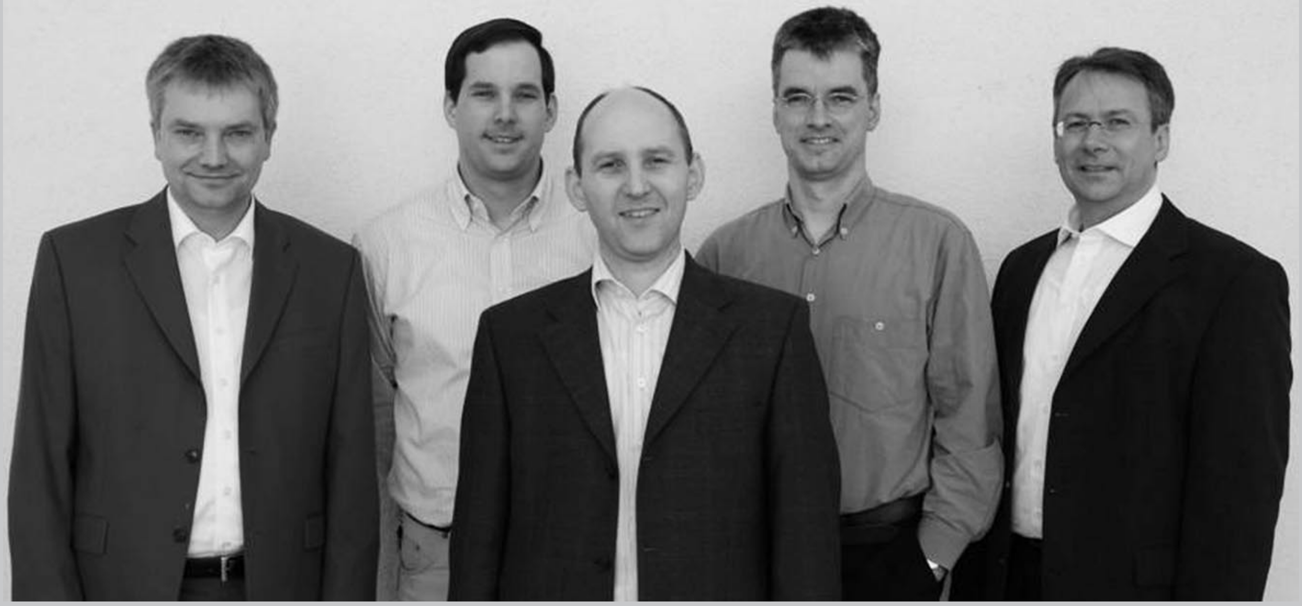


Figure 1. Roadmap for optical data storage. Various technologies are currently under research. In this representation, λ is given in μm.



Friedrich Bruder (right) studied physics and completed his PhD in 1992 at the University of Freiburg. He was then a polymer physics laboratory group leader in the central research center at Bayer AG at Krefeld-Uerdingen. Bruder has since worked in various research projects at Bayer AG, Bayer Polymers AG, and Bayer MaterialScience AG. In 2007 wurde Bruder was made an Advanced Fellow of Bayer MaterialScience AG. His work at Bayer MaterialScience currently involves the physical aspects of the development of materials for holographic photopolymer.

Rainer Hagen (middle) studied physics and completed his PhD in 1998 at the University of Bayreuth. In the subsequent years he carried out research in a leading role at the central research center at Bayer AG (Leverkusen); thereafter he worked at Bayer MaterialScience AG as an Innovation Manager and Technology Scout for Light&Optics, Security Technology, and E&E in Automobiles. In 2006 he was a Hagen founder of a Genesis Project, from which the Competence Center for Holography arose. He currently leads a customer project in this group with the goal to form new global applications for photopolymer films.

Thomas Rölle (2nd from right) studied chemistry in Marburg and Bologna. After completing his PhD in Marburg, he was then a Feodor Lynen scholar with Robert H. Grubbs at CalTech. In 1999 he was made laboratory group leader at the central research center at Bayer AG; there he investigated the design and synthesis of privileged structures as peptide-mimetic inhibitors for protein families and thereafter in medicinal chemistry at Bayer Healthcare AG. Since moving to Innovation Management at Bayer MaterialScience AG (2005), he has developed photopolymers as functional films for holographic applications.

Marc-Stephan Weiser (2nd from left) studied chemistry in Bayreuth and Edinburgh and completed his PhD in 2006 at the University of Freiburg. His thesis was awarded with the Arthur Lüttringhaus prize. He then worked as a post-doctoral fellow at Mitsui Chemicals, Inc. in Sodegaura (Japan) on the synthesis of polyolefin block copolymers. In 2007 he was made a laboratory group leader at Bayer MaterialScience AG. There he is currently involved in the development and product integration of a new photopolymer material for holographic applications.

Thomas Fäcke (left) studied chemistry and completed his PhD in 1995 in Marburg. He was then made laboratory group leader at the central research center at Bayer AG in Leverkusen. In 2000 he moved to the coatings raw materials section. From 2002 he worked in Pittsburgh (USA) and in 2004 he took over technical marketing for powder coating binders in North America. Back in Leverkusen, since 2006 he has led technical marketing for polyurethane-dispersion-based synthetic coating binders. In 2007 he assisted the development of an innovation unit for holographic photopolymers. Today he leads the Competence Center for Holography at Bayer MaterialScience AG.

a track by a factor $\log_2(n)$. This can also be referred to as multilevel recordings.

To use the entire volume of the storage medium, the data can be arranged in multiple information layers. The two-photon absorption technique may represent one possibility for the realization of such multilayer recordings.[8] Purely organic materials, such as diaryl ethers, dye-doped poly(methyl methacrylate) (PMMA) and other polymers, or doped sapphire crystals have been studied for this approach.[9–12] An additional method for volume storage is clearly holographic optical data storage.

3. Holography and Holographic Data Storage

Optical holography enables the capturing of the entire information (phase and amplitude) contained in the light reflected from an object. In addition to the intensity of the reflected light, the phase length of the light stemming from various points of the object is also recognized with this technique. Because the phase is a measure of the distance of different points on the object to the viewer, by means of holography the entire three-dimensional information from an object, not just the information concerning the light intensity, is captured. Such information capture is achieved by storing the interference field of the emitted object waves and a coherent reference wave in a photoactive medium. This storage takes place preferentially as a modulation of the refractive index in the medium, which is proportional to the interference field, and is called a hologram. If we consider the simplest case of the interference of a plane-wave signal—in this case all the light emitted from the object has the same phase—with a standardized reference plane wave, the interference field consists of striped patterns of light and dark areas (a grating). The stripe spacing depends on the angle between the signal and the reference wave, and the intensity difference between light and dark areas is determined by the ratio of the amplitudes of the signal and the reference wave. Stored as a corresponding modulation of the refractive index in a photoactive medium, the original signal wave is reconstructed upon irradiation with the standardized reference wave by light diffraction under the Bragg condition (Figure 2).

The simplest case discussed above of a hologram from the interference of two plane waves has found many applications in holographic optical data storage. The active data bits in a holographic optical data-storage media are always stored as such individual gratings or a suitable combination of such individual gratings. Those bits are then read by reconstruction of the corresponding signal wave through irradiation with the reference wave under the correct angle (Bragg condition).[21] It is possible to take advantage of the fact that the angular acceptance range that is responsible for the reconstruction becomes smaller with increasing thickness d of the medium, that is, the Bragg selectivity increases with increasing thickness d of the medium. In a medium with high thickness (typically over 200 μm), it is possible to write many gratings ("multiplexing") in the same volume, which can be reconstructed individually without crosstalk, because, for example, the angle of the reference wave can be varied in a large number of discrete steps. In holographic data storage, it is also crucial for a high storage capacity to have the possibility of producing thick media (ca. 1 mm) to act as a real volume reservoir. In addition, it is possible by using suitable optics (Fourier holograms), to save an entire data "page", for example, for each angle of the reference beam. In these data pages, the data bits are arranged, for example, as a grid pattern made of light (on-pixels) and dark rectangles (off-pixels); this is called "page-wise" storage. The data pages are then simultaneously reconstructed on an area detector, such as a CCD chip, and the rates of data transfer may be greatly increased by parallel processing.

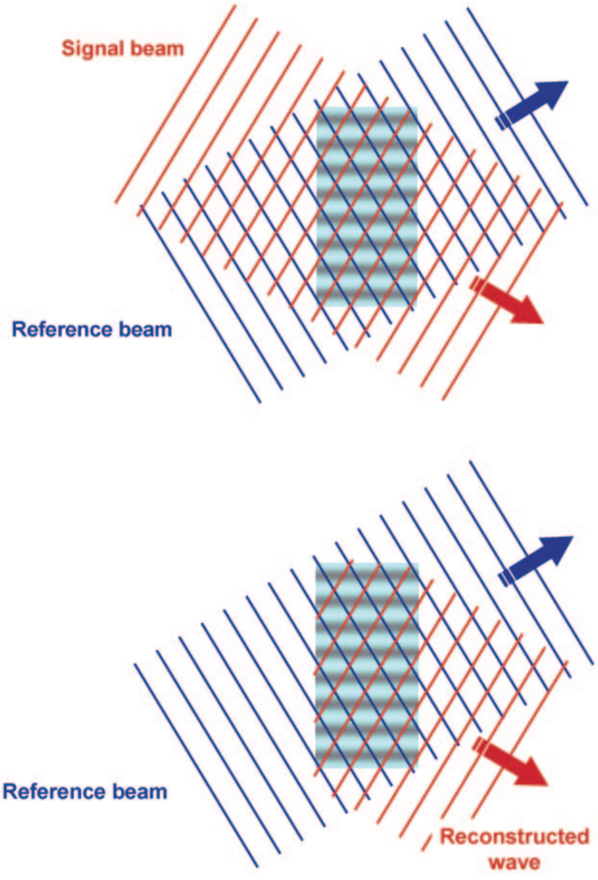


Figure 2. Left: The interference from a plane signal wave and a plane reference wave leads to a striped intensity pattern. In a photoactive medium, this pattern is translated into a modulation of the refractive index, which is proportional to the intensity, thereby resulting in the hologram. Right: The reference wave is diffracted at the modulation of the refractive index such that the original signal wave is reconstructed.

3.1. Implementing Holographic Data Storage

In this Section, a brief discussion of the current research on implementing holographic optical data storage is given and put into perspective with the roadmap discussed above. In Section 4 the requirements for the photoactive medium necessary for the realization of holographic optical data-storage are discussed.

As already explained in Section 3, holographic data storage offers the possibility to arrange the information in data pages, that is, at least one data page that contains N bits can be stored in each volume element of the medium ("page-wise"). Furthermore, multiple data pages can be stored in the same volume element of the medium ("multiplexing"). For multiplexing photopolymers are currently preferred as the photoactive material for WORM or R media.[13] Integrated solutions of drive and disc are close to commercialization.[14] Attempts have been made to realize rewriteable and erasable holographic optical data storage. The main focus of such investigations is on the use of photorefractive crystals and the first work dealing with this approach has been published.[15] A recent book on photorefractive materials and on the physical mechanisms underlying the holographic recording has been written by Frejlich.[16] The middle and right panels of Figure 3 show different schemes proposed in some current investigations on page-wise holographic data storage, which make use of angle or shift-multiplexing.

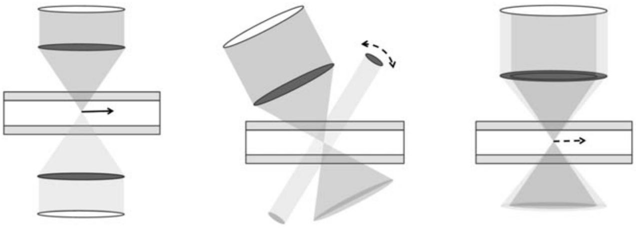


Figure 3. Left: Holographic recording of "micro mirrors". The signal and the reference waves are counter-propagating spherical waves with a common focus. The intensity of the beams is pulsed so that "micro mirrors" of different lengths can be written. Layers of information outside the focal plane can not be reconstructed through the Bragg condition and are therefore invisible. Center: Two-beam angle multiplexing. The incidence angle of the reference beam (plane wave) is changed in discrete steps relative to the signal beam. In each step, a full data page is written in the overlapping volume of the medium. Right: Two-beam collinear (coaxial) shift multiplexing. The reference beam is focused in the medium through the same objective lens as the signal beam. Reference beam and signal beam employ different areas of the objective lens aperture. Through the rotation of the disc into discrete steps, a full data page is written in the partially overlapping volume elements of the medium.

For several years, the use of holographic techniques for the "bit-wise" principle has also been investigated. In this approach, diffraction-limited large reflection holograms, known as "micro-mirrors", can be written by two counter-propagating, coherent light beams in their common focus in a photoactive medium. In this case, the hologram is written only within the focusing depth of the objective lens, that is, in the beam waist (Figure 3, left). The "micro-mirrors" act as the optical equivalent of (virtual) pits. The potential advantage is the possibility of having many layers of information without having to use reflection layers.[17,18] This scheme is part of the "multilayer" approach. This approach can use established data encoding and error correction and may allow a similar optic as today's BDs. However, in this case the data-transfer rate per layer will not be higher than that of the current BDs. Prototypes have been reported with photopolymers and photochromic dyes doped into thermoplastics.[19,20]

4. Material Requirements for Holographic Data Storage

Holographic data-storage gratings are always designed such that the resulting modulation of the refractive index Δn_i is sufficiently small for the physical problem to be considered as a linear approximation. In this case, the modulation index of the grating that arises from the interference field takes the form of a simple sine or cosine function. The amplitude of the modulation index is exactly Δn_i. The maximum diffraction efficiency of the grating η_i in reaching the Bragg condition is then given by Equation (2)[21] where d is the thickness of the medium, λ the wavelength of light in vacuum, α_0 and β_0 are the angle of the reference beam and the angle of the signal beam in the medium relative to the surface normal of the medium.

$$\eta_i = \left(\pi \cdot \frac{\Delta n_i \cdot d}{\lambda \cdot \sqrt{\cos(\alpha_0)\cdot\cos(\beta_0)}}\right)^2 \tag{2}$$

For the generation of a hologram with modulation index Δn a part of the dynamic range of the medium is consumed. The dynamic range of the medium is often denoted as $M\#$ ("M-number") and is formally described as the number of simple holographic gratings that can be written in the same volume of media by multiplexing to create a diffraction efficiency η of 100% (or 1).[22] In practice, $M\#$ is determined by subtracting similar but smaller diffraction efficiencies η_i from the multiplexing of L simple holographic gratings. This gives in Equation (3).

$$M\# = \sum_{i=1}^{L}\sqrt{\eta_i} \propto \frac{d}{\lambda}\sum_{i=1}^{L}\Delta n_i \equiv \frac{d}{\lambda}\Delta n \tag{3}$$

Thus, $M\#$ is a suitable measure of the possible storage capacity of a given medium, and is proportional to the thickness d and the index contrast Δn of the medium. $M\#$ determines the number of index gratings, L, that can be written in the holographic medium, and whose individual diffraction efficiencies η_i can be clearly distinguished from the noise level.

Equation (3) clearly shows that it is advantageous to minimize λ in order to maximize $M\#$. Therefore, the holographic medium, should, if possible, be sensitive to the blue-violet spectrum.

Media having a large $M\#$ value, which for example, can be achieved by a high index contrast Δn, can only be used optimally for high-storage capacities when at the same time a large thickness d of the medium is realized; otherwise, owing to lack of Bragg selectivity, the "multiplexing" of many data pages in the same volume is not possible. Therefore, the absorption of the medium at the wavelength used should not be too large, because otherwise optimal interference conditions when writing the grating cannot be achieved over the entire thickness of the medium. In addition, the media should have very low parasitic light scattering ("scatter") as this scatter increases the noise level, which enforces a higher minimum diffraction efficiency η_i on the individual index gratings, resulting, at a given $M\#$, in a reduction of L and thus a reduction of the storage capacity. In the case of volume scattering, this is proportional to d, and thus a compromise between the size of $M\#$ and d must be found.

A high sensitivity (or: how much Δn is produced per photon?) is crucial for high data transfer rates. The available laser power is limited, especially when one looks to the blue-violet spectral range (ca. 405 nm) and considering practical applications with which the form factor of the drive must be compatible, for example, a desktop computer. Since a high photosensitivity implies a given absorption, the need also arises to optimize d in terms of $M\#$.

Furthermore, shrinkage of the photoactive medium during the writing of the holograms might occur. This means that written index gratings no longer match in position and period to the interference fields with which they were formed. When reading out the data in this case, the Bragg condition is violated and the maximum diffraction efficiency according to Equation (2) is no longer achieved. The signal can in fact be lost completely. Since the Bragg selectivity increases with increasing the d value, the signal decay at a fixed shrinkage also becomes greater. Again, an optimal compromise between $M\#$ and tolerable shrinkage in a given thickness d must be achieved.

The holograms in the photoactive media must have long-term stability, especially for archiving applications, and multiple readouts must not lead to modification or even accidental erasure of the holograms. This is a particular issue when working with rewritable holographic optical data storage. In general, the process of writing with holographic media is purely photonic, thus resulting in no threshold behavior. The same is true of the corresponding deletion process, that is, repeated data access can easily lead to unintended overwriting. Fixation of the holograms after the data is written mitigates or prevents this accidental erasure.

4.1. Photorefractive Materials

In the search for suitable media for holographic data storage one comes to the chemically diverse and scientifically interesting photorefractive materials. The photorefractive effect is a light-induced change in the refractive index in a material and was demonstrated for the first time in 1966 in iron-doped lithium niobate ($LiNbO_3$) crystals.[23] In subsequent years, in a very visionary approach, the importance of these crystals for holographic data storage was recognized and holographic methods were successfully adapted.[24,25] A second thrust was the development of holographic storage media and methods in the early 1990s through successes in material development: new organic photorefractive materials were developed. The first organic crystals were 2-cyclooctylamino-5-nitropyridine (COANP), doped with 7,7,8,8-tetracyanoquinodimethane (TCNQ) as transport molecule for the charge carrier.[26] The first photorefractive polymer was the electrically polarized epoxy polymer bisphenol-A-diglycidylether 4-nitro-1,2-phenylenediamine.[27] The photo-conductivity was achieved by doping with the hole transport molecule *N*,*N*-diethylaminobenzaldehyde diphenylhydrazone. The then revolutionary data densities of 4 Gbit cm^{-2}, achieved using lithium niobate in 1997[28] showed that the potential of well-known inorganic crystals was yet to be realized. In 1997, the DVD had just been launched onto the market, with a data density of 0.4 Gbit cm^{-2}. Advances in laser and digital processor technology and new knowledge of the appropriate processing of the crystals made this success possible.

The conditions that must be met by a photorefractive material are:

1) Light-induced production of electron-hole pairs (a one-electron defect is commonly referred to as a "photohole"),
2) Sufficient mobility of one charge carrier, normally of the photoholes,
3) The presence of trapping states to immobilize the charge carriers,
4) Optical nonlinearity to form the linear electro-optic effect (the $\chi^{(2)}$ effect, also known as the Pockels effect).

In crystals, the operating principle is similar to that of polymers. Instead of the electron-hole pairs, charged (fixed) ions and free carriers are generated with opposite polarity. To summarize, photorefractive materials must be both photoconductive (Figure 4 (b) and (c)) and optically nonlinear (electro-optically active, Figure 4 (d)) to diffract the light and thus form the basis for holographic data storage.

Clearly, the advantage of using functional polymers comes into play in the optimization of both material properties and their successive tuning: one can select specific functional groups, each responsible for the formation of one of the

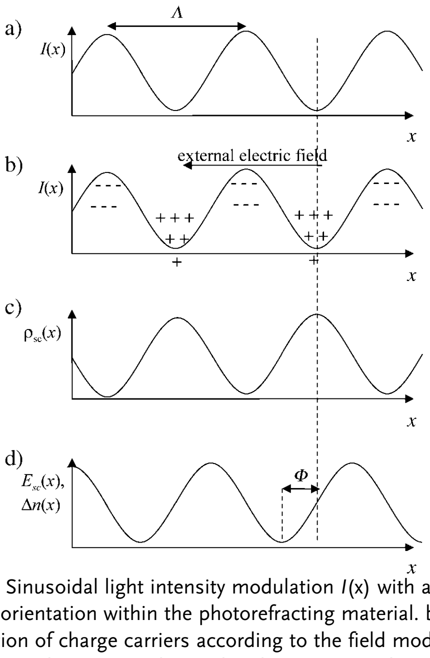


Figure 4. a) Sinusoidal light intensity modulation $I(x)$ with a period Λ in a spatial orientation within the photorefracting material. b) Creation and separation of charge carriers according to the field modulation of the light. c) Resulting space-charge distribution $\rho_{sc}(x)$; d) Space-charge field $E_{sc}(x)$ and refractive index modulation $\Delta n(x)$, phase-shifted in intensity by Φ.

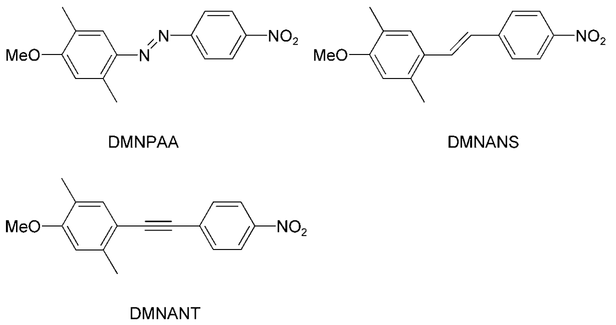
macroscopic effects, nonlinearity and photoconductivity, and build them in the correct mixing ratio in the polymer. The result is customized photorefractive polymers. This can be considered theoretically as follows:

In the static case, the light-induced charge distribution in the interference field of the writing light, for example a sinusoidal interference grid, is phased shifted by 90° with respect to the refractive index pattern. The refractive index modulation is given by [Eq. (4)]:

$$\Delta n = -\frac{1}{2} n^3 r E_{sc} \tag{4}$$

where n is the refractive index, r is the effective linear electro-optic coefficient and E_{sc} the field strength of the electric space charge field.[29] The conditions for high Δn values are, in the static case (this is the situation in which the holographic grating is fully formed after the write operation and in equilibrium) known to be given by strong electro-active dyes, such as azobenzene, stilbene, or tolane derivates, and high space charge field amplitude.

The synthesis of the corresponding dyes, and their implementation in high macroscopic nonlinearities was long a key route for the development of photorefractive materials. Very good model molecules are, for example, DMNPAA (4-methoxy-2,5-dimethyl-4′-nitroazobenzene), DMNANS (4-methoxy-2,5-dimethyl-4′-nitrostilbene), and DMNANT (4-methoxy-2,5-dimethyl-4′-nitrotolane; Scheme 1).[30] Dyes of this type have been installed in host-guest systems, as well as bifunctional polymers and low molecular weight glass formers. Today, other materials are known to have similar properties to DMNPAA.[31]



Scheme 1. Dyes used in photorefractive materials.

From parameter r to the second relevant parameter E_{sc}: The conditions for a strong space charge field, and therefore for a strong holographic grating, can be phenomenologically captured relatively easy, but are more difficult to implement in practice. We do not want to discuss them without considering the speed of the field buildup, which is indeed the holographic light sensitivity of a photorefractive material.

For small polarity fields, E_{sc} approaches the value of the diffusion field E_D, which depends on efficient charge carrier transport, in other words, which is produced by efficient hole-transporting molecules. 2,4,6-trinitrofluoroenone (TNF), for example, is a good sensitizer for photoconductors, such as polysiloxane (PSX), or polyvinylcarbazole (PVK), with which it forms charge-transfer complexes. For strong polarity fields, growth velocity and height of the space–charge field are limited by the number of defects in the material or by the actual trap density. According to the standard model of photorefractive polymers, the parameters of mobility and photohole lifetime are the ones to be optimized.

Now, how quickly does an organic photorefractive material respond to a light exposure? It is believed that, in general, the process of carrier generation by absorption of a photon is very fast ($t_{\mathrm{abs}} < 10^{-9}$ s), especially in comparison to the subsequent processes. Typically, the generation of free photoholes saturates quickly, because the lifetime of the photoholes is short ($t_h \approx 10^{-4}$ s). In crystals, for example, the production rate of mobile ions converges towards the recombination rate with immobile, stationary anions during the subsequent processes. Fast writing and even massive multiplexing is possible in crystals: Staebler et al. recorded 500 angle-multiplexes volume phase holograms in iron-doped $LiNbO_3$. Each hologram showed a diffraction efficiency of greater than 2.5%, with writing and fixing occurring simultaneously at 160°C.[23] The fastest photorefractive materials show response times of around 5 ms at an incident power of $1\,\mathrm{W\,cm^{-2}}$.[32]

In polymers, the refractive index modulation Δn can be enhanced significantly by field-induced orientation of optically nonlinear but polar molecules. Diffraction efficiencies of 20% have been demonstrated.[33] Fast writing is not possible in this case, because the chromophore dynamics is on the order of seconds, even in systems with low glass transition T_G, while the photohole mobility, which can be determined by time-of-flight (TOF) measurements or holographic time-of-flight (HTOF), shows significantly shorter transit times ($t_{\mathrm{TOF}} < 10^{-5}$ s).[34]

In photorefractive polymers, the proof of high $M\#$ value and therefore of their suitability for industrially feasible data storage is yet to be demonstrated. High polarity field strength and charge trapping in nearby electrodes reduces the reproducibility of the efficiencies.

4.2. Chemistry of Photopolymers

The class of photopolymeric materials is characterized, particularly in comparison to inorganic crystals such as lithium niobate, through more accessible raw materials. Holographic photopolymers were first described in 1969 as a mixture of acrylic monomers (barium and lead acrylate and acrylamide) and a photoinitiator.[35] Typically, photopolymers are, however, composed of a total of three components: the photoinitiator, one or more monomers, and a polymeric binder. The binder provides mechanical stability and ensures a suitable formulation with compatible starting materials and good optical properties. In addition, plasticizers, inhibitors, and stabilizers are added.

4.2.1. *Model of Hologram Formation in Diffusion-Based Photopolymers*

The term “photopolymer” is sometimes in a broader sense for organic material that is suitable as holographic recording media. In this section, this term will only be used for materials, in which a diffusion process contributes significantly to the formation of the phase holograms. Figure 5 illustrates the common model of hologram formation in photopolymers.

Figure 5, panel a shows the essential components of a photopolymer medium: monomer, initiator, and binder. In the holographic interference experiment of two intersecting laser beams (Figure 5, panel b) the polymerization in the areas of greatest constructive interference proceeds most quickly, and consequently the monomers are consumed most quickly in these areas (Figure 5, panel c). In the areas of destructive interference little or no polymerization takes place. The increasing consumption of monomer in the bright regions forms a concentration gradient. This means that monomer diffuses from the dark areas to the light.[36,37] Therefore a photoinduced mass transport takes place (Figure 5, panel d). This ends when all monomer is consumed or when no more monomers can reach the macroradicals due to vitrification of the photopolymer in the progress of the polymerization (Figure 5, panel e). If the material-dependent refractive indices of the binder and monomer differ from each other, the mass transport, at the same time, leads to the formation of a refractive index patterns: a phase hologram.

For effective phase hologram formation, the diffusion of monomer should be faster than its consumption by polymerization, as otherwise the refractive index modulation Δn is reduced. This holds true particularly for large diffusion lengths, i.e., large grating periods Λ. Furthermore, studies have shown that short polymer chains or radicals diffuse in the opposite direction, which is reflected in a reduction of the refractive index modulation shortly after exposure.[38]

One of the most studied systems is acrylamide molecule dissolved in a binder of polyvinyl alcohol.[39] In particular, it is found in this system that the holographic grating index contrast Δn decreases with smaller grating period Λ. Such small grating periods, for example, are used in reflection holograms.[40] The forming polymer chains (macro radicals) with their active chain ends grow out of the region of highest intensity of light into the dark areas: the area of polymerization changes with the macroradicals growth and the hologram formation is described by a non-local reaction-diffusion model - the forming phase hologram is 'smeared' and the resolution decreases.[41,42] Alternatively, these systems can also be described by a local reaction-diffusion model or analytical procedures.[36,37,40,43,44]

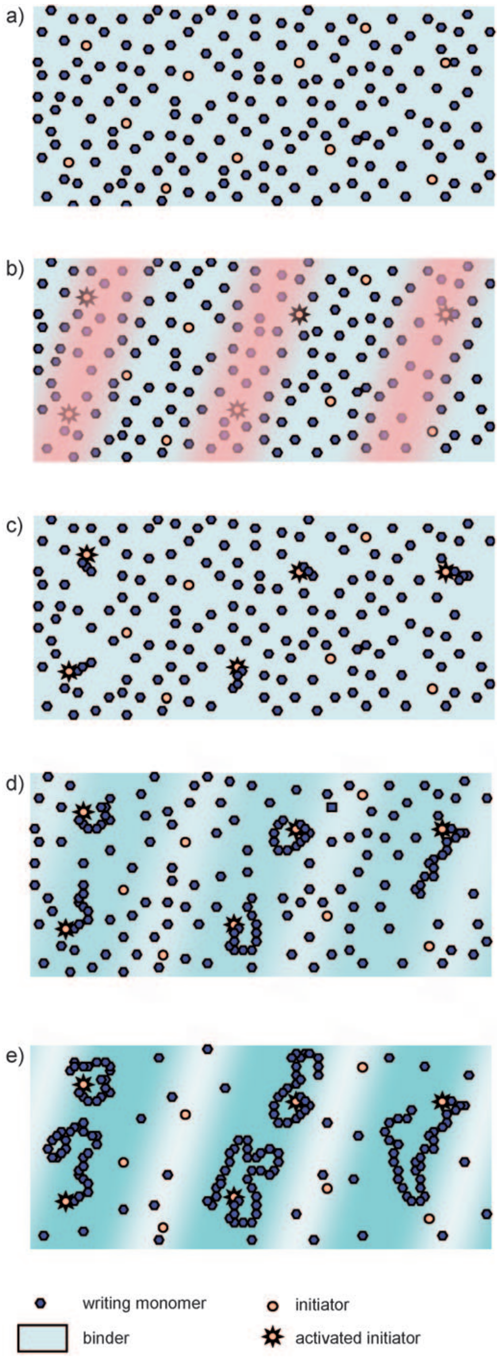
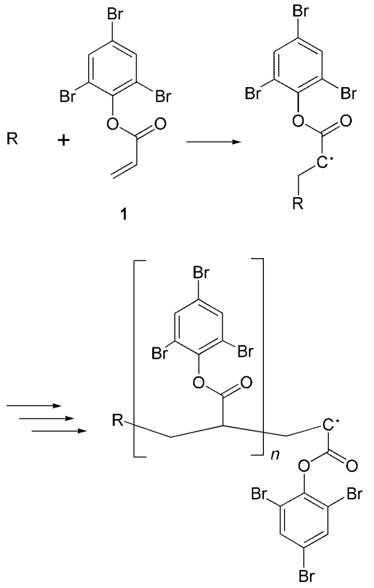


Figure 5. Reaction diffusion model describing photopolymer hologram formation. a) The photopolymer consists of monomers and initiators, both dissolved in a binder. b) Overlap of two laser beams leads to an interference pattern and, in the case of constructive interference, excites the initiator. c)–e) Propagating polymerization leads to the diffusion of monomers to the macroradicals and therefore to an accumulation of monomer units in the lighter areas.

4.2.2. *Chemical Amplification: The Key to the Use of Low-Cost Lasers*

A fundamental problem with organic materials for holography is their low sensitivity to light, especially when one compares them with silver halide based photographic materials. In general, the low quantum yield of photochemical reactions can be compensated for by chemical amplification. For holographic data-storage materials based on photopolymers three different amplification processes have been described. By far the most important method is the free-radical polymerization (see Scheme 2) of acrylic acid esters and amides, N-vinyl compounds and allyl esters. Mixtures of

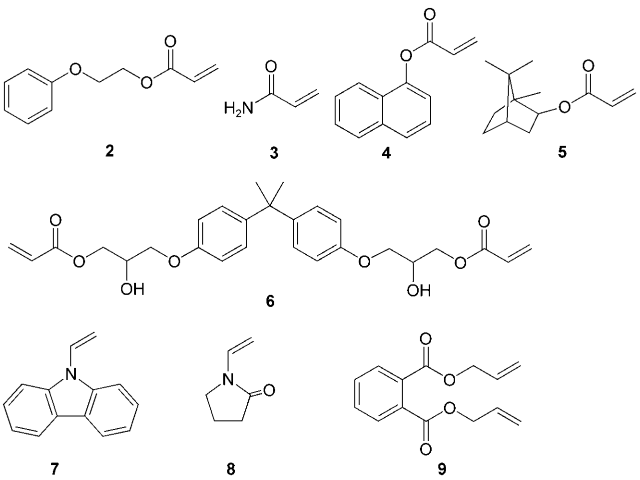


Scheme 2. Chemical amplification through radical polymerization of 2,4,6-tribromophenylacrylate (**1**) as an example.[46] For recent findings on acrylate polymerization, see Ref. [47].

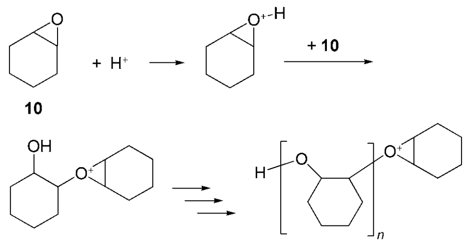
different reactive monomers have been described and can increase the achievable index modulation.[45]

Free radical polymerization has many advantages since it proceeds quickly, free-radical initiators are well developed, and there is a wide raw material base for the monomers. At standard temperatures, the reaction is irreversible, so that write-once media (WORM - Write Once Read Many) can be prepared, which are particularly suitable for long-term archiving. Scheme 3 shows a selection of the monomers described in the literature.[48]

The main problem is the relatively large volume shrinkage of the medium that occurs during free radical polymerization. This complicates reconstruction of the hologram and the Bragg angle used during the writing step must be corrected and adjusted for the volume shrinkage during the reading process. In data-storage medium constructions, the shrinkage is anisotropic, so that a simple correction of Bragg angle or the laser wavelength is of limited use. For all writing chemistries, it is therefore crucial to minimize the amount of writing monomers used, which as a result reduces the achievable storage capacity. All material developments, therefore, ultimately optimize the balance between capacity and readability. Ring-opening cationic polymerization shows much lower volume shrinkage, as for each newly formed bond between the monomers a strained ring is opened. Therefore, overall the chemical bond density will not increase. For collinear drive design (Figure 3, left) cyclohexene oxide **10** based monomers that can be polymerized by proton-forming photoinitiators with low shrinkage (Scheme 4) have been approved conceptionally.[49] The polymerization is also not inhibited by atmospheric oxygen, as is the case with conventional acrylate based monomer systems. Recently, sensitizers for blue lasers based on 1,4-bis (phenylalkinyl)-naphthalene have been described.[51]



Scheme 3. Radically polymerizable monomers of holographic photopolymers.



Scheme 4. Cationic ring-opening polymerization for media with low shrinkage.

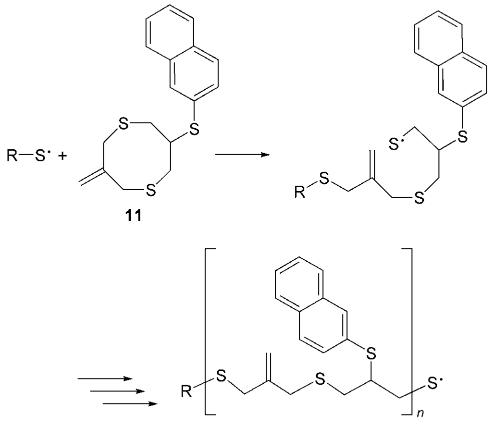
The disadvantage is that the generated acid affects the long-term stability of the holograms and triggers dark reactions that make it difficult to write a holographic disc successively. That only a few different monomers have been prepared reflects the limit on the development potential of this class of materials.

The ring-opening, free radical polymerization of cyclic allylsulfide **11** combines the advantages of low volume shrinkage ring opening polymerization and low dark reactivity with the wide range of available free radical photoinitiators (Scheme 5).[51] The polymerization is relatively slow, but this is not necessarily a disadvantage, since a balance between diffusion and polymerization must be set. However, this aspect will gain in importance in the future as the ever-present demand for higher data transfer rates continues.

The use of allylsulfide in holographic data storage has been described only recently, and to date only basic test have been reported.

4.2.3. Monomers Alone do not Make a Medium: The Role of the Binder

In the late nineties, various institutes and companies built functional holographic read–write demonstrators for the first time.[52–54] Since then, attention has turned away from hitherto standard media systems such as lithium niobate. From then on, high-viscous acrylate mixtures were provided with addi-



Scheme 5. Radical ring-opening polymerization for media with low shrinkage.

tives to obtain the desired properties of high refractive index modulation, good light sensitivity, low shrinkage, and appropriate manufacturing processes of the media. Figure 6 shows an overview of the concepts concerning the writing components monomer and binder, which are discussed below.

Dry or solid photopolymers, that is, materials that are dimensionally stable before exposure and in which the registered holograms do not blur, are therefore the main targets of materials development. Starting from solutions of monomeric acrylates, compatible thermoplastics have been incorporated, such as polyvinylalcohol (PVA), in order to obtain paste-like, non-flowing materials. However, these PVA materials are very sensitive to humidity and have a short shelf life, requiring them to be continuously modified and tested.[55,56]

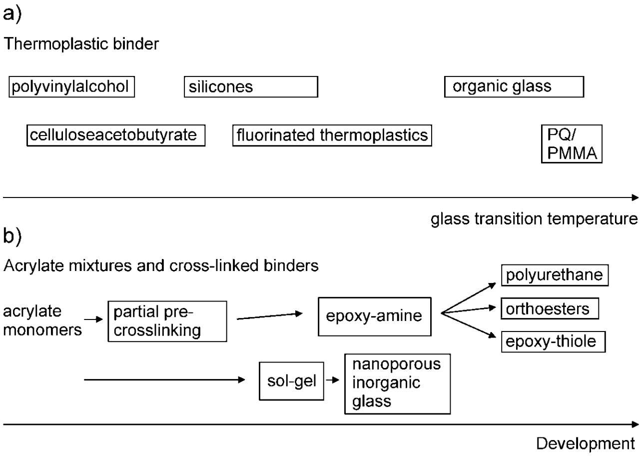


Figure 6. a) Various thermoplastic materials for the preparation of photopolymers have been described. The relative glass transition temperatures (T_g) of the thermoplastics play an important role in the production and stability of the holographic data-storage media: A high T_g is necessary to form stable discs but also reduces the sensitivity of the photopolymer and vice versa. b) Organic and inorganic cross-linked binder constitutes the latest generation of photopolymer materials and are superior to those of (a). Organic, cross-linked photopolymers based on epoxy-amine, polyurethane, epoxy, and orthoester-thiol chemistry show the best quality profiles. Acrylate monomers are commonly used as writing monomers. Sol–gel networks have been described, but have long hardening times.

For other holographic applications, materials from Fa. E. I. DuPont de Nemours & Co. are already well-known, which, among others, contain a mixture of phenoxyethyl acrylate in cellulose aceto butyrate (CAB).[57] Hexaaryl bisimidazoles with mercapto benoxazole were used as initiators;[58] however, a high shrinkage of 3–10% and insufficiently low thickness resulted in unsatisfactory results.[59] Improvements to CAB-based photopolymers using new writing monomers and the addition of dendrimers to enhance the diffusion have also been described.[60,61]

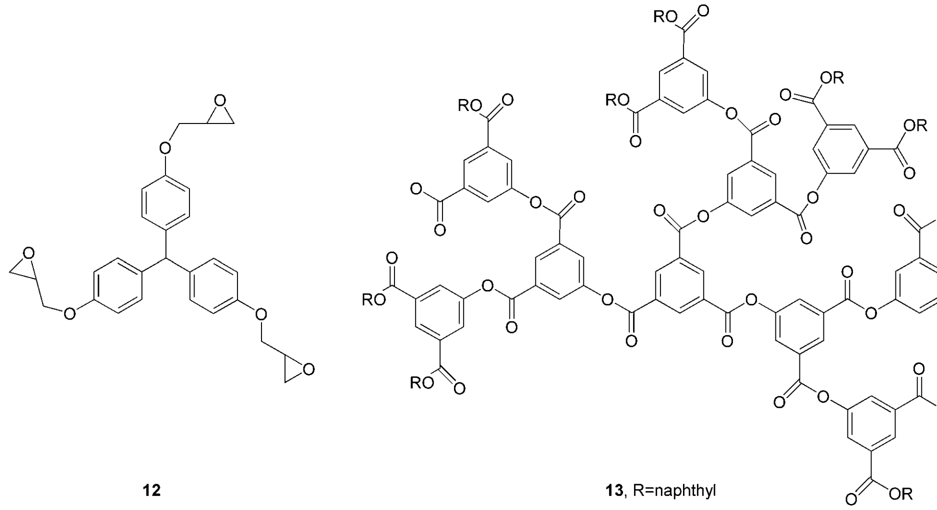
Waldman et al. have developed formulations specifically for data-storage applications with the aforementioned ring-opening cyclohexene oxides, in which bi- and higher functionality writing monomers were used that contained a silicon bridge.[62] Short-chain silicone was used as a binder, due to its compatibility with the monomer. In general, the compatibility of the binder with the writing monomer and the photoinitiator poses a major challenge to meeting the required optical quality of the overall formulation. The refractive index difference between binder and monomer should be high, as this directly determines the data-storage capacity of the medium. Fluorinated compounds are particularly low refractive species. Inoue et al. showed that modified poly-perfluorooctylethylacrylat can still be sufficiently compatible.[63]

4.2.4. *Thermoplastic Media with High Glass-Transition Temperature*

For holographic storage media, simple media manufacturing is desirable. Based on the injection molding technique employed for CD, DVD, and BD media, it is technically obvious to use this approach for holographic materials. For this purpose, however, PVA and CAB do not show sufficient form stability. A holographic medium based on such materials must be poured into a mold, which typically consists of optically transparent, non-birefringent double-diffracting thermoplastics with high glass-transition temperature. Bisphenol-A polycarbonate is almost exclusively used as the thermoplastic in this case.

The design of media would be much simpler if the holographic materials itself could fulfill these requirements so that they could be injection molded directly. Castagna et al. have proposed a triarylmethane **12** that as an organic glass material inherently provides stable properties (Scheme 6).[64] Dipentaerythrit-penta/hexaacrylate is used as the monomer, which undergoes very little shrinkage during holographic writing. However, relatively long exposure times and exposure doses are required.

Conceptually similar is the formulation of Kou et al., who propose a dendritic organic glass **13** with methyl methacrylate as the writing monomer.[65] Dichloromethane is used as a solvent for production and after removal a dry, thermally stable film with good light sensitivity is obtained. For industrial applications, however, the dimensional stability must be optimized still further.



Scheme 6. Organic glass former to create stable photopolymers according to Ref. [64,65].

4.2.5. *Poly(methyl methacrylate) Formulations: A Special Case*

Highly transparent thermoplastics, which are widespread in industrial use, are suitable for the production of dimensionally stable media. Doped poly(methyl methacrylate) (PMMA) has been intensively investigated, which is prepared using an in situ method: methyl methacrylate is mixed with phenanthrene quinone (PQ) and a thermal initiator and then is processed into a dimensionally stable thermoplastic medium.[66] This media technology is characterized by very low shrinkage and high refractive index modulation.

Franke et al.[67] have investigated the mechanism of Benzyl Dimethyl Ketal doped PMMA, which is assumed to hold for all doped PMMA photopolymers (see Scheme 7). Under 366 nm irradiation the ketal **14** splits homolytically, starting the polymerization of still available methacrylates or adding to the PMMA itself. During the several hours following exposure, Benzyl Dimethyl Ketal diffuses out of the dark into the bright areas. In the subsequent lengthy thermal processing residual benzyl dimethyl ketal continues to migrate from the dark into the bright areas, thus further increasing the refractive index modulation.

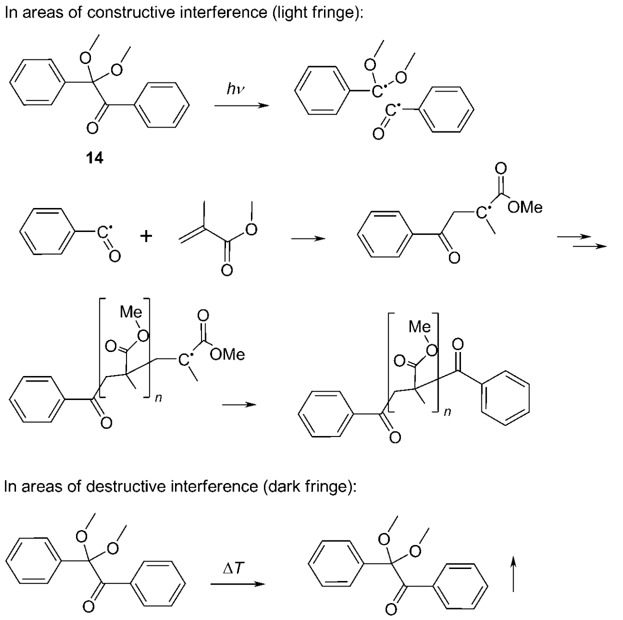
Napthoquinon (NQ) was recently proposed as an alternative to PQ, since it has a higher diffusion rate. NQ/PMMA with a spectral operating range of 488–530 nm has been described and offers a higher modulation index than PQ/PMMA.[68,69]

4.2.6. *Nanoporous Glasses as Structural Stabilizers*

Porous glasses are an apparently elegant solution for the most stable matrices.[70] Nanoporous glasses are produced by selective hydrolysis of special glass mixtures, followed by soaking in an a mixture of acrylates and photoinitiators, and stabilization by partial photochemical cross-linking.[71] The media show very low shrinkage. The problems here are the complex manufacturing process, the adjustment of the refractive indices to the matrix, and the size uniformity of the nanopores in order to obtain perfectly clear media.

4.2.7. *On the Way to Rugged, Light-Sensitive Media with High Data-Storage Capacity*

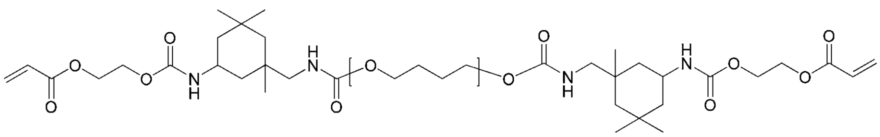
For a new optical medium to be acceptable, the capacity needs to be at least ten times that of BD media. New media for consumer applications should therefore have a capacity of 500 GB–1 TB. To achieve this, one needs media with thickness of $>100\,\mu m$.[72] Schilling et al. mixed common acrylic acid ester and vinyl amines as the writing monomer with a urethane acrylate resin **15** (Scheme 8).[73] After mixing and media preparation partial cross-linking was performed with UV radiation. A major advantage of this production method is the low viscosity of the photopolymer. The reproducable partial cross linking of those materials during media manufacturing still pose a major challenge.



Scheme 7. Writing mechanism of poly(methyl methacrylate) (PMMA) doped with benzyl dimethyl ketal. Benzyl dimethyl ketal is cleaved homolytically in the areas of constructive interference and polymerizes residual monomers. In areas of destructive interference, no reaction occurs and the unreacted initiator escapes in the subsequent baking process.

4.2.8. *Orthogonalizing of Matrix and Writing Chemistry*

The above-discussed use of an acrylate-containing oligomer indicates a way to extend this concept through orthogonalization of the binder chemistry and the writing chemistry. Conceptually, this is the logical further development of



15

Scheme 8. In situ binder **15** on the basis of a C_4-polyether isophorondiisocyanat urethanacrylate according to Ref. [73].

nanoporous glasses (see Section 4.2.6.). The crosslinked binder is the matrix in which the writing chemistry is (dimensionally) stabilized.

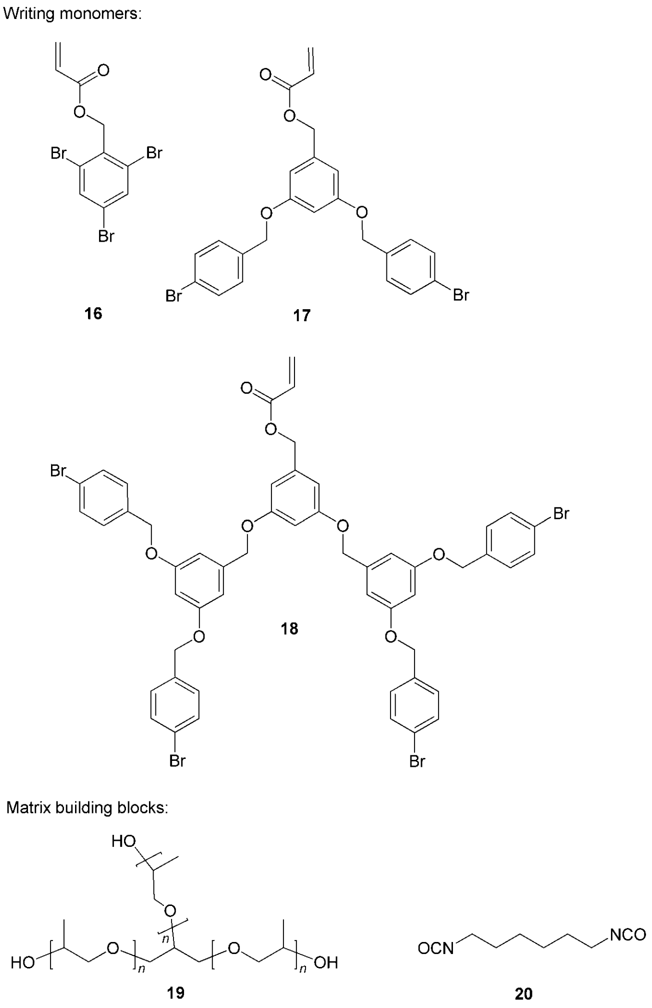
When a radical polymerization is used for writing, and an epoxy/amine reaction (such as butanediol diglycidic ether with ethylene diamine) for the cross-linking of the matrix,[74–77] these reactions do not interfere. The advantages of such a system were further exploited at Bell Laboratories (and later at InPhase Technologies) and various combinations of polymerization chemistry and matrix crosslinking chemistry were proposed (Scheme 9).[78] A high dynamic range can be achieved by properly designing the matrix components on one side and the monomers on the other to yield refractive indices that are far apart. The higher the refractive index difference between the two chemistries, the higher the data-storage capacity.[79] However, for good media it is crucial to optimize the compatibility not only of the raw components themselves, but also of the polymerized monomers with the crosslinked matrix.[80] Another important advantage is the in situ production of the media, when the photo polymer is immobilized between two substrates, so that optically flat and sufficiently thick media are obtained. The media are rugged, dimensionally stable, and the total refractive index of the photopolymer changes only slightly when writing. Thus a holographic data-storage medium that works well, and is easy to prepare is obtained. It has also been shown that initiators for red, green, and, especially important, blue lasers are available.[81] The suitability of media for long-term storage was also shown.[82]

In addition to isocyanate-alcohol[83] and epoxy/amine crosslinking, also orthoester-anhydride crosslinking, polypropylene diglycidyl ether polyethylene imine crosslinking, and epoxy-thiol cross-linking have been described.[51,84,85] Such media show a very balanced property profile with good light sensitivity, high data-storage capacity, good optical properties and long lifetimes.

4.2.9. *From Sol–Gel Chemistry to Nanoparticles*

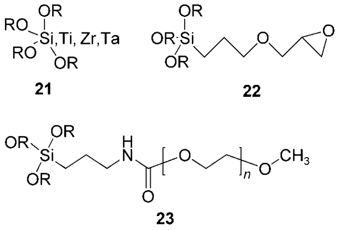
In addition to the use of organic matrices, crosslinked material concepts using inorganic–organic hybrid materials are also possible. To this end, sol–gel chemistry is especially promising for holographic applications, as hydrophilic monomers can be easily processed and sufficiently thick media can be obtained.[86,87] The refractive index of the matrix can be increased through the addition of titanium and zirconium alcoholates. By careful selection of silicon and alkyl silicon alcoholates, the reactivity of alcoholates can be adjusted.[88] For such formulations low refractive, common aliphatic acrylic monomers, for example, acrylic acid esters of aliphatic alcohols, are used.

Improved compatibility of the mixtures was achieved by introducing alkyl groups to the silicon alcoholate **21**.[89] Organic monomers can be introduced into the corresponding photopolymer through the use of triethoxy silylpropyl polyethylene glycol-carbamate **23** (see Scheme 10).[90]



Scheme 9. Components of a photopolymer based on dendritically constructed acrylate monomers. The crosslinking binder is composed of a polyurethane matrix, which has been constructed from a trifunctional polyether and hexamethylene diisocyanate according to Ref. [83].

Controlled hydrolysis and subsequent condensation allow for a high optical quality, even if the necessary production times of several hours are relatively long and open surfaces are required for the removal of the condensation products.[91] On the other hand, metal chelates (zirconium isopropoxide/methacrylate) can be used as monomers, which form high refractive metal oxide nanoparticles with particularly low turbidity.[92] This class of materials shows generally good



Scheme 10. Precursors for sol–gel-based photopolymer; longer side chains support the compatibility of the formulation. $R = C_1$–C_3.[89,90]

holographic properties, but due to their lengthy preparation process are less suitable for industrial applications.

The advantages of inorganic materials can also be used in another way to prepare specialized optical materials. For example, titanium dioxide exhibits a high refractive index and, as a nano particle, can be transparent to visible light. A mixture of pentaerythritol, isooctyl acrylate, and 4 nm nanotitanium dioxide shows a index modulation of 0.015.[93] The highly functional acrylate polymerizes rapidly, so that the remaining components are displaced at the location of polymerization. The nanoparticles accumulate in the unexposed, dark areas. If one uses SiO_2 instead of TiO_2, a lower refractive index is obtained in the dark areas, while with TiO_2 a higher refractive index can be detected by an optical phase shift of 180°.[94] In general, nanoparticles are a useful addition to the formulation of photopolymers. The optical quality and the minimization of light scattering is strongly influenced by the absolute particle size and distribution as well as by the dispersion efficiency.

4.2.10. *Liquid Crystals as Components in Photopolymers*

Finally, photopolymers that contain liquid crystals as an additive (H-PDLC = holographic polymer dispersed liquid crystal) are discussed. A typical formulation consists of a highly functional acrylate, *N*-vinylpyrrolidone as a chain extender, the initiator system, and the liquid crystals. *N*-vinylpyrrolidone is used to react with immobile macroradicals and then to increase the double bond conversion with further acrylate molecules. It also affects the rate of formation of the nematic phase and its particle size.

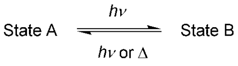
Similar to formulations containing nanoparticles, the liquid crystals diffuse to the dark areas during exposure.[95] High refractive index modulations can be achieved if the hologram is written above the nematic–isotropic phase transition temperature. After cooling, the liquid crystals reorganize themselves in the dark areas of holographic imaging, so that high light scattering in the medium is inhibited. If one writes, on the other hand, below the nematic–isotropic phase transition temperature, the transparency decreases with the progress of the lattice formation, because in this case nucleation and growth of the nematic phase droplets occurs.

The most important application of the H-PDLC is found in a structure consisting of two conductively coated glasses and the H-PDLC in between. Depending on the laser geometry, diffractive gratings can be generated parallel or perpendicular to the glasses, which can be switched by means of electric fields. The applicability as a data-storage material with good light sensitivity and high resolution has been shown.[96]

4.3. *Photochrome and Other Materials*

A third principle for optical data storage is based on the photochromic effect, which consists of a reversible phototransformation (Scheme 11).[97]

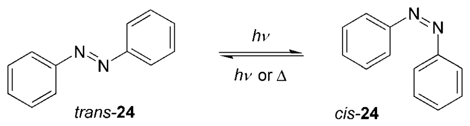
The state A, which defines the usual conformation or constitution of a part of a molecule, changes after the interaction with electromagnetic radiation *hν*. Obviously, during this process the absorption spectra, as well as a number of other physico-chemical properties (refractive index, dielectric constant, redox potential and the molecular geometry) change. This effect was described for the first time 1867 by Fritsche in the reaction of tetracene with air and light.[98] Initially, such reactions were described as “phototropic”; it was only in the 1950s that Hirshberg coined the term photochromism,[99] which has been used ever since. Dyes are among the first organic substances for which the photochromic effect has been observed and described. In these substances, obviously, the excitation is induced by visible light, leading to the name “photochromic effect”, as the spectral absorption of state A and B is different. In addition to this feature, photochromes must have the already discussed general characteristics required for optical data storage. For photochromic compounds, this is, in particular, the thermal stability of the two states A and B, which is not always given. Obviously, the intrinsic advantages of holographic optical storage devices such as, for example, high write/read speed, high spatial resolution and multiplex recording also have to be met by photochromic materials.[100] From the variety of possible organic components relevant to data storage, the photochemically induced *cis*/*trans* isomerization of the azo bond is especially prominent and presented first.



Scheme 11. Photochromic effect.

4.3.1. *Photo-Addressable Polymers: Photochromism with Orientation*

Azobenzene **24** is a representative of a well-known and widely characterized group of photochromic molecules. The photoeffect is based on molecular isomerization, which, in this special case, is a *trans*–*cis* isomerization (Scheme 12). This leads to a temporary conformational change with a different spatial arrangement of the molecule. This isomerization is also observed in polymers, when the azobenzene side-chain molecules are bound to one side of the main chain.



Scheme 12. Azobenzene and the spatial arrangement of its isomers.

At the molecular level the *trans-cis-trans*-cycles lead to a cooperative rearrangement of the side groups away from the polarization direction of the photophysically active light. This effect can be macroscopically observed through a dichroism and an anisotropy of the refractive index. In early studies on the application of azo compounds in polymers for optical data storage, the azo dyes Methyl Red and Methyl Orange were dispersed in poly(vinyl alcohol). In this way, the above-mentioned optical dichroism was demonstrated.[101,102]

The fact that the photoinduced orientation anisotropy can be erased by irradiation with circularly polarized or unpolarized light is of great relevance to the technical usability of photo-addressable polymers (PAP). In conjunction with the second phenomenon that the side chain orientation can be "overwritten" through a rotation of the polarization direction of the light, preferably by 90°, write/erase/write concepts become available for data storage. This finding enables PAP materials to be used besides so-called holographic WORM media (Write Once Read Many), for which they are suitable thanks to their good volume stability, but furthermore also as a re-writable (R/W) data storage.[103] In summary, in contrast to photopolymers, in PAPs no reaction with bond opening or bond breaking takes place upon light irradiation, but only a reorientation of the side chains, which, under certain conditions, can be even reversible.

In the production of azopolymers it is possible to distinguish between unstable and stable groups; their synthesis, characterization, and fields of application have been described in detail.[104] In principle, the azobenzene units can be installed in the polymer in three different ways: from an historical point of view, the first polymers were host-guest systems, in which the azobenzene molecules were dissolved in the polymer matrix. Later, fully functionalized polymers followed, in which the azobenzene groups were chemically bonded as side chains or as part of the main chain, the backbone of the polymer.[105,106] The functionalization allowed significantly higher degrees of doping and thus stronger, more efficient, and long-term stable photo orientations.

The dynamics of the side chain depends on the strength of the coupling to the main chain or by the degrees of freedom of the azo groups, as shown through investigations using different spacer lengths between the azo group and the main chain.[107–109] Researchers continually sought the optimum balance between high stability in dark storage and high sensitivity when exposed to linearly polarized light.

The isomerization of azobenzene units in polymer side chains was described for the first time in 1972. The presumed mechanism was an inversion at one of the two nitrogen atoms. For most azobenzene compounds, the *trans* form ("*E* Form") is thermodynamically more stable than the *cis* form ("*Z* form"). For azobenzene itself the difference is 50 kJ mol^{-1}.[110] The *cis* form is, however, the photochemically favored conformation. Usually, the photochemical conversion takes place with high quantum yields; on the other hand, the reverse isomerization, which follows a first order kinetics, is usually also a fast process.[111] The azobenzene unit acts as a chromophore that absorbs the incident light. The absorption spectrum contains a π–π* band (often in the UV range) and an n–π* band (often weaker in intensity and in the visible range). To obtain a stable isomerization product, the distance between the two bands should be sufficiently large and the π–π* band should be in the region of shorter wavelengths.[110]

In the isomerization of the nitrogen–nitrogen double bond from *trans* to *cis*, the rod-shaped azobenzene is converted into a bent form. It must be noted that as a steric requirement for the rearrangement of the double bond a free volume of about 10^{-1} nm^3 must be available.[112] Assuming a rotation as the prevalent mechanism for the isomerization, the required free volume would be significantly larger, approximately 3.8×10^{-1} nm^3.[113] Below the glass transition of the polymer matrix, the isomerization proceeds significantly slower, thus requiring a sufficiently flexible matrix.[114] A crosslinked matrix decreases the speed of isomerization.[115] Similarly, the isomerization is slowed as the main chain of the polymer or the spacer in the side chain becomes more rigid.[111,116]

For some of the azobenzene units, an abnormally rapid isomerization reaction can be observed above the glass transition, which was interpreted as an evidence for a non-uniform distribution of free volume in the polymer.[117] In contrast, a part of the azobenzene units isomerized much slower than expected from the kinetics in solution. This percentage correlates with the difference of the isomerization temperature and the temperature of the glass transition.[113]

The optical properties of the PAP are influenced crucially by substitution at the azobenzene unit. Through the selection of suitable substituents both the absorption spectrum of the chromophore and the kinetics of the isomerization reaction can be tailored. In addition, the refractive index of the material changes in the exposed areas through the isomerization of the azo bonds.[118] To achieve a high refractive index difference Δn in the exposure, long, rod-like substituents are preferred.

Often, the conformational changes that result from the described rearrangement of the double bond are not stable over a sufficiently long time. This instability can have both thermodynamic and photochemical reasons. The thermodynamic reason is represented by the slow relaxation of an anisotropic amorphous state back in the more favorable entropically disordered state. This phenomenon is often referred to as "physical aging". In mode theory, it is assumed that the β and γ relaxations of the side chain molecules of the polymer are still weakly active in the glass state. The volume theory explains "physical aging" with the presence of free non-equilibrium volume, without conflicting with the prior model. Azo groups that are located in the vicinity of such a cavity can arrange themselves in a thermodynamically favorable fashion. Azo groups, which have enough local free volume are "hooked" in the polymer and therefore stable in terms of orientation.

Therefore, the conformational changes of individual azo groups are not important for optical data storage, but rather the steric cooperative rearrangement of the azobenzene units during exposure to linearly polarized light.[119] The photophysical effect can be explained as follows: during the light stimulus a rearrangement between the stretched *trans* and the bent *cis* form occurs. However, only those azobenzene units can be excited by the polarization of the incident light for which the orientation of the molecular axis (in the *trans* form) in the matrix has a parallel component to the polarization direction of the excitation light. All the azobenzene units that are completely perpendicular to the polarization direction of the excitation light are almost invisible to the excitation light. This effect can be explained by looking at the relevant molecular parameter: the dipole moment of the transition. In push-π-pull substituted azocompounds, the transition moment is, in a first approximation, a vector that is parallel to the molecular axis. As the excitation probability is proportional to the square of the angle between the polarization vector and the molecular axis, only molecules "correctly" oriented will be excited.

For the *trans-cis* back isomerization all the directions are equal, but only the azobenzene units lying in the polarization direction are further excited; this leads, as depicted in Figure 7, to an accumulation of azobenzene units perpendicularly aligned to the polarization direction of the excitation light over the exposure time.[120] An anisotropically oriented preferred orientation is created from the initially isotropic distribution of the azobenzenes, whose optical properties are correspondingly different. This process is known as orientation hole burning, as during its course less and less chromophores can be addressed by the light.

The orientation of the azobenzene units and the thus generated patterns are largely stable at temperatures below the glass transition temperature of the polymer, T_G, the limitations have been mentioned previously. The orientation is basically "frozen" as long as no circularly polarized light is allowed to interact or the polymer is heated to temperatures close to T_G.[116]

The described change in the orientation of the azobenzene units can be amplified and stabilized when mesogenic side chains are inserted in the polymer matrix in addition to azobenzene units. These side chains are supposed to strengthen the steric effect by stabilizing the new orientation of the chromophore by means of spontaneous spatial arrangement of the non-photo active mesogenic units.[121] This effect also occurs with a pure *trans–cis* isomerization in the presence of other mesogenic groups.[119,122–124] For this to occur, the substituents at the mesogenic units have to be adjusted to the azobenzene side chains to create steric or dipolar interactions. Investigations have shown that this so-called "neighboring" effect occurs only for groups of the same polymer backbone. The interaction of groups of different polymer chains is therefore negligible.[125] Careful selection of the substituents and an optimized ratio between mesogenic and chromophoric side chains allows a Δn value of 0.5 to be reached for these copolymers.[126] It has been found that the optimal ratio between mesogenic and chromophoric side chains in the copolymer appears to be just on the edge of the formation of a liquid-crystal from the amorphous phase content.

In 1987, several years after the first publications on the *cis–trans* phenomenon, the requirements for the reversible storage of data were satisfied using PAP. At the same time, a liquid crystalline copolymer, made out of a combination of photo active and photo inactive side chains has been described.[127]

When tailoring a suitable data-storage material, a balance has to be found between the necessary flexibility to allow the isomerization of the nitrogen double bond and the stability of the written data (i.e. the aligned domains). To improve the stability of the alignment, several aspects can be advantageous: high glass transition temperatures of the matrix, a suitable design of the co-monomers, short spacer units as well as liquid crystallinity very precisely adjusted in its strength, which allows a stable orientation of amorphized PAP at room temperature.[108,109,128]

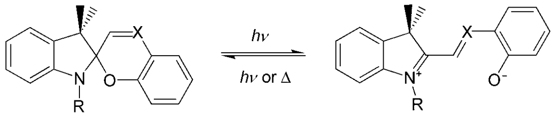
Figure 7. Polymerized azobenzenes. Gray ellipses: side chain groups based on azobenzenes. light Ellipses: mesogen side chain groups, which follow to photoorientation of the azobenzenes and stabilize them. The main chain of the polymer is shown as a gray line as are the short $(CH_2)_2$ spacers, which make the link between side chain and main chain flexible. Large circle: Light field, in this case linear (horizontal) polarized monochromatic light, that leads to an ordered photoorientation of the side chains.

In addition to the above-described change of the absorption properties, changes in the viscosity, in the solubility, in the mechanical properties, the surface energy, weathering, and other parameters of photo-addressable polymers can occur as well.[111,129–136]

The rewritability of the material is achieved through irradiation with circularly polarized light; in this way the anisotropically oriented azobenzene units are statistically realigned over a new *trans-cis-trans* isomerization cycle. In the literature, over 300 cycles of rewritability are reported.[137] However, the complete deletion of all data is not a trivial step and is usually not practical to achieve.[116]

4.3.2. Light-Induced Electrocyclic Reactions and Their Application in Holographic Data Storage

Pericyclic reactions of selected highly functionalized classes of compounds have also proven to be significant for optical data storage (Scheme 13).[138]

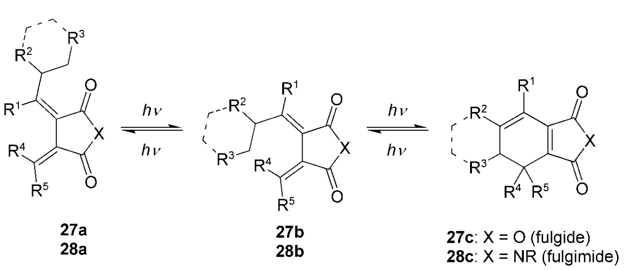


25: X = CH (spiropyran)
26: X = N (spirooxazine)

Scheme 13. Cycloreversion of spiro(benz)pyrans **25** and spirooxazines **26** under irradiation.

Specifically, selected spiro(benzo)pyrans **25** and spirooxazines **26** show the tendency to undergo a cycloreversion upon irradiation.[139] However, in the transition from the colorless spiro form into the colored merocyanine the charges are formally separated so that even low thermal stress or long-wave radiation can lead again to electrocyclic ring closure.[140] The relatively low stability of the ring-open form can be increased by electron-withdrawing substituents such as nitro or CF_3 groups, but the reverse reaction is never completely suppressed.[141] The absorption maximum can be shifted by other substituents. Another feature of the ionic merocyanine form is a strong tendency to aggregate, both in solution and as film. This reveals an intrinsic weakness of this class of compounds that has prevented the construction of stable data-storage media based on this approach because only a few read/write cycles can be performed.[142]

However, the above-mentioned spiro compounds have opened the field, and fulgides have recently been investigated intensively, as they should have the necessary prerequisites for optical data storage (Scheme 14).[143] The relatively easy accessibility of these derivatives of 1,3-butadiene-2,3-dicarboxylic acid and their corresponding anhydrides obtained through the Stobbe condensation has resulted in a wide variations of this structural class over the last 100 years.[144]



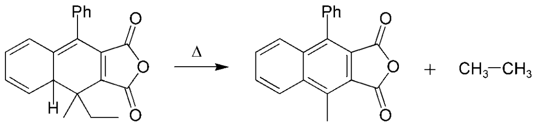
27a
28a

27b
28b

27c: X = O (fulgide)
28c: X = NR (fulgimide)

Scheme 14. Photochemistry of fulgides and fulgimides.

The transition of the colorless ring-open form into the cyclic form takes place in two stages: The thermodynamic product **27a** is first converted into the intermediate **27b** through a double bond isomerization, and a further light absorption leads to the closed form **27c**, following a 6π-electrocyclization reaction. The cyclic form **27c** is thermodynamically stable, but according to some reported anomalies, in selected sterically very hindered molecules such as **29**, prolonged heating can lead to the cleavage of ethane, which results in the formation of compound **30** upon aromatization (Scheme 15).[145]

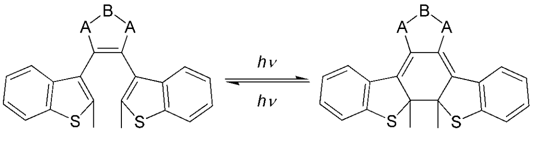


29 **30**

Scheme 15. Elimination of ethane from fulgide **29**.

The recent synthesis of a variety of heteroatom-substituted fulgides led to examples with very short response time (in the nano-to pico-second range), high reversibility of photochromism, very good thermal stability and high quantum yield, for which up to 105 read/write cycles have been reported.[146] The announcement of the Fluorescent Multilayer Disc (FMD) by Constellation 3D Inc., with a capacity of approximately 140 Giga-byte and a data rate of 1 GB sec^{-1}, whose technological concept was based on fulgidas, however, was not a commercial success, mainly because of the lack of long-term stability.[147]

Diaryl ethylenes **31**–**32** have proved very promising for optical data storage. They consist of *cis*-configured diarylethenes, usually electron withdrawing substituted internal olefins (Scheme 16).[148]



31a: A = CO; B = O
32a: A = B = CF_2

31b
32b

Scheme 16. Photochemistry of diaryl ethenes.

The lack of long-term stability often observed in these classes of compounds can probably be attributed to the relatively large underlying negative entropy of activation of the cyclization and its slightly positive activation enthalpy. Another difficulty stems from the fact that the electrocyclic reactions leads, as expected, to the formation of by-products. If a selectivity of 99.9:0.1 is assumed, a 10-fold reaction from state A to B (write/read cycle) leads to the formation of approximately one % of by-product. Based on these considerations as of today, rewritable optical data storage based on electrocyclic reactions does not appear very promising.

Among the other exploratory approaches for holographic data storage, anthracene or bacterioorhodopsin-based approaches should be mentioned.[149–151]

Table 1: Qualitative assessment of material concepts for holographic data storage.

Property	Photorefractive	Photopolymer	Photochrome Photo-addressable	Electrocyclic
volume shrinkage during writing	+	−	+	+
light-sensitivity	−−	++	−	○
data capacity	++	++	○	○
optical quality	++ LiNbO$_3$/−	++	++	++
reproducibility	−	++	+	○
processing suitability of the medium	−−	+	+	+
long term stability of the holograms	−−	+	○	−
other	large electrical voltage; rewriteable	write once	polarization holography possible; limited adsorption media thickness limited, rewriteable	rewriteable

4.4. A Comparison of the Material Concepts

In Table 1, the material concepts are compared qualitatively. For a long time, photorefractive media such as crystals of lithium niobate have been the only high-quality model systems available. They are characterized by their high optical quality and the absence of shrinkage during the writing of the hologram. However, industrial-scale, economic production is not yet possible. Photopolymers, on the other hand, show very good general properties; however, the material shrinkage has to be taken into account and compensated for. Photo-addressable polymers (PAP) and photochromic materials are very good with regards to manufacturing and in their optical quality, but cannot convince with their data capacity due to self-absorption. Another disadvantage is their low light sensitivity. For write-once media, photopolymers are the preferred class of materials, on which research focuses on today. For rewritable media different classes of materials have been developed, which show interesting features; still, for industrial use further improvements are necessary.

5. Prototype Holographic Optical Data-Storage Systems

In addition to the development of photoactive, holographic materials and media there is also the need to adjust the drive technology to the material performance, and conversely to adjust the material performance to the drive technology. In traditional and established optical data-storage material, media and drive developers do not necessarily work in the same companies or institutions. Because holographic optical data storage is still in the pre-commercial phase, often the core competencies are all concentrated on a focus point or there are very close collaborations between various centers of excellence.

Drive development takes place predominantly along the above described "page-wise" or "bit-wise" technologies. For the next generation of optical data storage after BD, a potential capacity of 1 TByte is regarded as a minimum requirement to achieve broad acceptance in the consumer market. In addition, a rate of data transfer is required such that a medium can be completely written in around 2 hours. In view of this requirement, "bit-wise" seems to be a very challenging approach, because the data transfer rate can hardly be increased beyond that of a single layer. Currently, with the fastest Blu-ray recorders (12x write speed), 25 GB can be written in approximately 10 minutes. That would still mean six hours and 40 minutes of writing time at 1 TByte of capacity, i.e., 40 layers. Furthermore, the photosensitivity of the materials that are currently being considered for "bit-wise" is far from that needed today for already existing optical data storage. Therefore, "page-wise" appears as a promising way to satisfy the data rate requirements with the used materials. This, however, comes at the expense of compatibility and synergy losses with already existing ODS technologies, concerning optical pickup, data coding, and data processing.

In the following, the status of the best and most advanced system demonstrations is described, first the "bit-wise", and then the "page-wise" technology.

5.1. "Bit-Wise" Prototypes

For this technology, a photoactive, holographic material with a threshold behavior with respect to the laser power is preferable. Nevertheless, the hitherto most advanced system demonstrations have been realized with traditional photopolymers. Only GE Global Research claims to having developed a photochromic material that shows a threshold behavior with respect to the laser power. The quality of the data presented varies from a simple demonstration of the possibility to write quasi-statically a virtual Pit and then to extrapolate to the capacity of a 12 cm disc, in which under certain conditions an increase in the *NA* of the objective lens might proof necessary from the demonstration to the drive, to have quasi-dynamic writing of several superimposed layers, to the fully controlled system demonstration with tracking and focusing servo.

In 2008, GE Global Research published the first data on polymer discs doped with photochromic dyes, which showed a threshold behavior with the energy dose.[152] These experiments were conducted with two counter propagating focused laser beams with wavelength in vacuum of 532 nm. With an *NA* valueof 0.2, pits 1.5 microns apart could be resolved along the track in a quasi-static experiment. The depth of the pits was reported as approximately 12.9 micron FWHM and the minimum dose required to write was 0.5 μJ. In 2009, the same group announced a 100-fold higher reflectivity of such microholograms, which are supposed to be readable by Blu-ray optics.[153] The materials were written at a wavelength of 405 nm. A possible data capacity of 500 GB on a 12 cm disc has been extrapolated.

Furthermore, in 2008 Orlic et al. demonstrated in a quasi-dynamic writing experiment (without servo-control) pit dimensions of up to 200-300 nm in a photopolymer by Aprilis.[18] The laser wavelengths used were 532 nm or 405 nm. The track pitch was reduced to 500 nm and the distance between the information layers was only 2 microns.

The most advanced system demonstration with a view to a practical drive originates from Sony.[154] The setup works with a 405 nm laser and two beams in opposite direction for recording the information. A track servo and an auto focus servo guarantee dynamic control during the recording and readout process. The *NA* value of the objective lens is 0.51, the realized track pitch is 1.1 microns and 1.9 GB/layer was achieved. The linear speed along the track is $0.15\,\mathrm{m\,s}^{-1}$, which is still very small (Blu-ray 1x uses ca. $5\,\mathrm{m\,s}^{-1}$). The distance between the layers, 25 microns, is still very large, but it is possible to realize 10 layers. Interestingly, less than 10 % jitter is observed in the read signal, which is very close to commercial optical discs. The jitter describes the fuzziness of the pit lengths and thus the accuracy of the information. The holographic medium used was a photopolymer from Nippon Paint.

A major simplification in the optics can be achieved if for writing the holograms the opposing beam can be generated through an integrated mirror in the medium (Lippmann construction). The requirements of the coherence length of light would be drastically reduced as well. However, when reading the information, this mirror generates a high-level direct current (DC) signal that masks the small signal changes through the pits completely. It has been successfully demonstrated how this DC contribution can be suppressed through a balanced homodyne detection.[155]

5.2. *"Page-Wise" Prototypes*

The "page-wise" approach is the classic method used by holographic optic data-storage systems to save the data within the entire volume of the record carrier. As previously mentioned, a thick storage unit is essential to achieve high storage capacity. The resulting high Bragg selectivity requires both the carrier and the drive components to have high macroscopic dimensional stability, because slight changes in the thickness of the medium or in the adjustment of the optical drive lead to a violation of the Bragg conditions. Therefore, for the development of a feasible system, it is not sufficient to consider the data capacity and data transfer rate alone; the flexibility of the system, the carrier, and the drive to dimensional changes resulting from thermal expansion, vibration, and misalignment of the optical components must also be taken into account.

5.2.1. *Coaxial Shift multiplexing*

As for two-beam multiplexing (see Section 3), a test bed for holographic discs was built by the PRISM and the HDDs consortiums with a beam configuration following the principle of coaxial shift multiplexing. In this case the investigation and demonstration of various aspects of system architecture and media was of prime interest. Here, green laser sources were applied. The data, however, was still read out in transmission through the disc on the opposite side of the writing head. The first complete disk-drive solution, able to write and read from the same side, used a disc based on green-sensitive photopolymers introduced by Optware.[156] This solution led to the definition of HVD (Holographic Versatile Disc) standards, which, in their initial versions, defined a recordable disc with a 200 GB capacity and the pre-recorded discs with a 100 GB capacity.[157] Sony refined this principle with the application of a blue-violet laser with a wavelength of 405 nm and an objective lens with an NA value of 0.85. They demonstrated data densities of 270-415 Gbit/in^2 on a photopolymer-based system, which corresponded to a 12 cm disc of approximately 500 GB data capacity.[158,159] Further methods to increase the data density, also based on this coaxial drive technology, have been proposed, using phase modulation of the pixels in the data page of the spatial light modulators (SLM). This allows the coding of gray-scale, that is, "multi-level" data, in the data page. The potential feasibility of this approach has been recently demonstrated in the MEXT project.[160]

5.2.2. *Coaxial Phase Multiplexing*

A coaxial beam with the ability to write and read the data from the same side has been demonstrated in card media.[161] For this purpose, a thin polymer film based on liquid crystalline side-chain polymers of azobenzene was used as the medium. As in this case polarization holography (with two lasers) can be used, phase multiplexing of the data pages becomes possible. A laser with a wavelength that overlaps with the absorption band of the azobenzene molecule writes the data and a laser with a higher wavelength, which operates outside the absorption band, reads the data. In a prototype, data densities of 0.65 $\mathrm{Gbit\,in^{-2}}$ and a data transfer rate of 1.6 Mbits per second have been demonstrated.

5.2.3. Two-Beam Angle Multiplexing

In the 1990s, the PRISM tester, which was one of the first test beds, was developed to investigate various aspects of system architecture and media.[162] The PRISM tester worked with a 0°/90° geometry between the beam axis of the signal and of the reference, and used angle multiplexing. A laser with a wavelength of 532 nm was employed. Variations of this concept have also been implemented as DEMON I and II at IBM. These designs had been created to accommodate $LiNbO_3$ crystals as the medium. Read-only memory (ROM) with the data stored in photorefractive crystals was developed as a prototype in a 19-inch industrial rack from the University of Cologne, and presented by OPTOSTOR AG at the CeBit '99 in Hannover.[163]

Complete drive–media systems based on two-beam angle multiplexing have been developed by the company InPhase Technologies. In a system designed for professional archival storage, up to 300 GB of user data can be stored, with data transfer rates of 160 Mbits per second.[14] A laser with a wavelength of 405 nm is employed to achieve the maximum possible data capacity. Fourier optics are used for the signal beam and a plane wave is used as the reference beam. The angle of the reference beam is adjusted with a galvanic mirror. The data readout is done in reflection from a phase conjugate mirror (i.e., double passage through the medium) to compensate as far as possible for the optical interference of the wave front through the medium itself. The medium is a disc with a diameter of 13 cm based on the photopolymer Tapestry 300 HR. Hitachi, and InPhase Technologies have presented a further simplification of this optical system, in which the reference and signal beams pass through different areas of the objective lens of a blu-ray disc with a *NA* value of 0.85.[164] The phase-conjugating mirror is implemented as an impressed groove structure in one of the polymer substrates, very similar to the pre-groove structure in a CD-R or DVD-R. With this system the data densities are equivalent to those corresponding to a data capacity of 500 GB on a 12 cm disc.

6. Conclusions and Outlook

We have reported on basic optical design as well as the corresponding system demonstrations of holographic read–write devices and have given an overview on photorefractive, photochromic materials, as well as on photopolymers. The latter show a balanced performance profile and are therefore ideal to develop the fourth generation of optical media.

The needs of society for digital mass storage devices will continue to grow in the same breathtaking pace, which has been unanimously observed from the beginning of the "digital revolution". The introduction of the compact disc was preceded by a wave of innovation, which converted optical digital data storage into a product suitable for everyday use. Optical data-storage technology is very inexpensive, provides users with medium-speed access, is robust, and has a long lifetime. The separation between medium and reading devices allows for easy scaling of the capacity, so that this technique can be used for backup solutions, that is, medium-term backup and archiving appropriate for the long-term storage of data.

Solid-state memory systems, magnetic hard drives, and online storage continue to compete for the attention of customers. Solid state memories are ideal for mobile applications, as they contain no mechanical parts and are built in a compact way. Since they will remain relatively expensive, they are especially suitable for temporary data storage. In terms of storage capacity, hard discs are very inexpensive. Because of the fast data access and high capacity, they are suitable for applications with direct availability in a stationary environment. However, their disadvantages are high energy consumption in continuous operation and a very limited lifetime.

We have summarized the various approaches in the field of holographic optical data storage and we see that some of these approaches are close to launch as a fourth-generation optical media. This raises the question which of these technologies offers the best price-to-performance ratio for which market segment. Holographic data storage has the best prospect for long-term archiving in a professional environment, for which not only the initial price, but also operating costs and conversion costs play a key role. Users would still have to replace the currently used magnetic tapes. The development of consumer products is a logical step, but requires standardized low-cost read–write devices that have yet to be developed.

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