

# Holographic Recording Medium

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**Abstract:** The requirement for diverse applications such as digital video, interactive media etc. demands high storage densities, rapid data transfer rates, random access to data and removability of the storage media. The complete technology involves suitable recording medium and the processes for recording, post treatment and reading. The challenge in the development of holographic storage system is the availability of appropriate recording medium which shows maximum refractive index change on irradiation.

In this article, attempt has been made to discuss the important disclosure of patents made during rapid development of the holographic recording medium. Silver halide emulsions to variety of photopolymers are developed to achieve minimum polymer film shrinkage, minimum post processing and multiple writing. All types of polymer based mediums are incorporated in this article. Few discussions are divided into subsections. It has generally been observed that acrylates, acrylamide, carbazolyl-, fluorenyl-, anthracenyl- containing monomers are common monomers and polymethyl methacrylates, polyvinyl alcohols, epoxy resin, sol-gel to polyelectrolytes are the common matrix resin. A recent addition is the nanoparticles in the composition to improve the diffraction efficiency and hologram stability. A different class of photopolymer called photorefractive polymer is also reported. Liquid crystalline polymer is photopolymer which provides erasable holographic media. Claims chosen are mostly from US patents. Some other literatures are also included as demanded by the discussion. The important features of the medium used in patents are highlighted. The details about performance, as claimed in certain patents, are incorporated. Rapid developments are observed in the subject.

**Keywords:** Holography, holographic recording medium, optical storage, reference beam, diffraction efficiency, optical, polymer, monomer, photochromism, nanocomposite, photorefractive polymer, photoactive liquid crystalline polymer, polyelectrolyte, epoxy resin, sol-gel matrix.

## 1. INTRODUCTION

Holography is a form of optical information storage. The continuous challenges and demands related to optical storage come from many directions. The next generations of data archiving, digital video, interactive multimedia, security and game products etc. demand increasing storage densities and data transfer rates in addition to other application features. In general, optical holography, upon which holographic storage is based, is a method that can record the complete characteristics of a light wave. It is a method of recording three dimensional images of an object. Holographic image differs from photographic image as it has perspective and depth and can be viewed from various angles.

In 1948, Denis Gabor invented the technique of recording phase information by means of a background wave, which converts phase differences into intensity differences. The general principles are described by Leith *et al.* [1]. A hologram is basically a recording of the optical interference pattern formed at the intersection of two coherent optical beams. Typically, light from a single laser is split into two beams, the signal beam and the reference beam. The beam that propagates along the signal path carries information, whereas the reference beam is designed to be simple to reproduce. A common reference beam is a plane wave i.e., a

light beam that propagates without converging or diverging. The two paths are overlapped on the holographic medium and the interference pattern between the two beams is recorded. Each point on the object reflects light to the entire recording medium, and each point on the medium receives light from the entire object. The intensity profile of the pattern is determined by both the phases and amplitudes of the interfering light waves. The hologram can be played back by illuminating with a coherent light identical to the reference beam. While passing through the hologram this beam collects the phase and amplitude modulations and reconstructs the wave front that matches with that of the object image.

There are many types of holograms, and various ways are adopted for classifying them [2-4]. In simple terms it can be divided into two types: reflection holograms and transmission holograms.

### 1.1. Types of Hologram

#### Reflection Hologram

The reflection hologram, in which a truly three-dimensional image is seen near its surface, is the most common type. The hologram is illuminated by white light at a specific angle and distance and located on the viewer's side of the hologram. The image consists of light reflected by the hologram.

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### Transmission Hologram

The typical transmission hologram is viewed with laser, usually of the same type used to make the recording. This light is directed from behind the hologram and the image is transmitted to the observer's side.

### Hybrid Holograms

Between the reflection and transmission types of holograms, many variations can be made such as:

### Embossed Holograms

To mass produce cheap holograms for security application such as the eagle on VISA cards, a two-dimensional interference pattern is pressed onto thin plastic foils.

### Integral Holograms

A transmission or reflection hologram can be generated from photographs (usually transparencies) of an object. Usually, the object is "scanned" by a camera, recording many discrete views. Each view is shown on an LCD screen illuminated with laser light and is used as the object beam to record a hologram on a narrow vertical strip of holographic plate. The next view is similarly recorded on an adjacent strip and so on. When viewing the finished composite hologram, a stereoscopic image is observed.

### Holographic Interferometry

Microscopic changes on an object can be quantitatively recorded and measured by making two exposures on a changing object. The two images interfere with each other and fringes can be seen on the object that reveals the vector displacement.

### Multichannel Holograms

When the angle of the viewing light on the same hologram is changed, completely different scenes can be observed. This phenomenon has enormous potential for massive computer memories.

### Computer-Generated Holograms

There are three basic elements in holography: the light source, the hologram, and the image. If any two of the elements are known, the third can be computed. For example, if there is parallel beam of light of certain wavelength and a "double-slit" system (a simple "hologram"), the diffraction pattern can be calculated. Also, from diffraction pattern and the details of the double-slit system, the wavelength of the light can be calculated.

Although holography was conceived in the late 1940s, it was not considered a potential storage technology until the development of the laser in the 1960s. The resulting rapid development of holography for displaying 3-D images led researchers to realize that holograms could also store data at a volumetric density of as much as  $1/\lambda^3$  [5,6].

Despite the huge potential and substantial progress [7-13] the development in the area slowed down after mid-1970s. This was probably due to non-availability of compatible devices for the holographic recording and reproducing. During early 1990s, volume-holographic data storage research got re-look by the researchers [14-20] mostly due to the

availability of suitable devices. With various devices available for use the holographic-storage research began to thrive [21-35].

The interference fringes, produced due to optical interference between the object beam and reference beam, are recorded if the two beams interact in a suitable photo-sensitive media. The media falls in various categories such as a photopolymer [36-45], inorganic crystal [46-48], photographic film [49] etc. The bright and dark zones of the interference pattern create chemical and/or physical changes in the media. This, in turn, creates a replica of the interference pattern as a change in absorption, refractive index or thickness. When the recorded matrix is illuminated by a readout beam similar to the original reference beam, some of the light is diffracted to reconstruct a copy of the object beam. If the recording is done by using an object beam which came from a 3-D object, then the reconstructed hologram makes the object appear in 3-D mode [50].

## 1.2. Hologram Writing and Reading

### Write-Once Read-Many (WORM)

A material that permanently stores volume holograms must undergo some kind of irreversible photochemical reaction, triggered by the bright regions of the optical interference pattern leading to changes in index of refraction or absorption. For example, a photopolymer material polymerizes in response to optical illumination [51-64].

### Read-Write

In contrast to the organic WORM media, most erasable holographic materials are inorganic photorefractive crystals doped with transition metals or rare-earth ions [65,66] or photorefractive polymers [67-72]. The information can be written and erased as required.

## 2. HOLOGRAPHIC RECORDING MEDIUM

A great number of patents were filed during development of holographic writing methods and the writing medium. Fig. (1) shows the approximate number of total patents filed during the development till date.

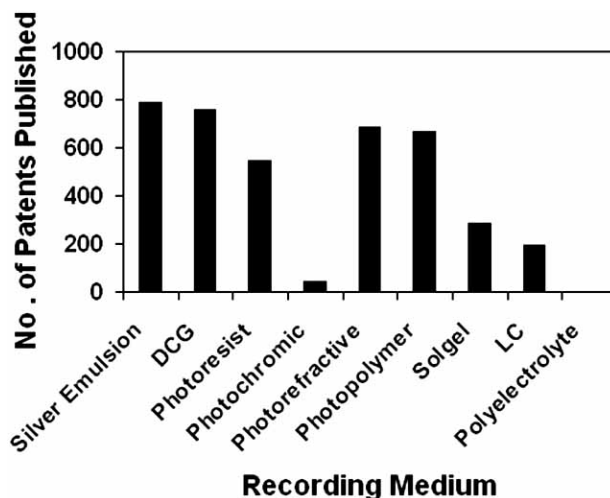


Fig. (1). Patents published on various recording media.

## 2.1. Silver Halide Emulsion

Silver-halide recording materials for holography are interesting for many reasons. Silver halide is the first material used for recording holograms. It is also the most important material for holography for its high sensitivity and numerous applications. It can be coated on both film and glass up to very large formats. Both amplitude and phase holograms can be recorded in it. High resolving power and easily availability are other common features. But it has some drawbacks such as high absorption characteristics, inherent noise and limited linear response, irreversible recording, wet processing requirement, printout problems in phase holograms etc.

The holographic plates are coated with an emulsion of gelatin containing suspended grains of silver halide crystals. Silver chloride and silver bromide are normally used. Silver

iodide is never used alone and usually employed in a mixture along with silver bromide. These silver halide grains are sensitive to light. The photochemistry of total process is shown in Fig. (2). When a plate is exposed to light, photons from the light source pass through the emulsion. There is every possibility that a photon bumps into a silver grain. If a certain number of photons hit a grain, a small site of metallic silver is formed on that grain. The site can be considered as being a mark on a silver halide grain [73].

Silver halide emulsion is being used over hundred years as photographic plate. Initial attempt was made to use the silver halide coating as holographic recording layer. The first patent on silver halide emulsion, used for holography, is available in literature in 1972. The modifications on initial developments are attempted with newer techniques of preparation, processing, post processing. This has enabled the user to make choice from wider varieties.

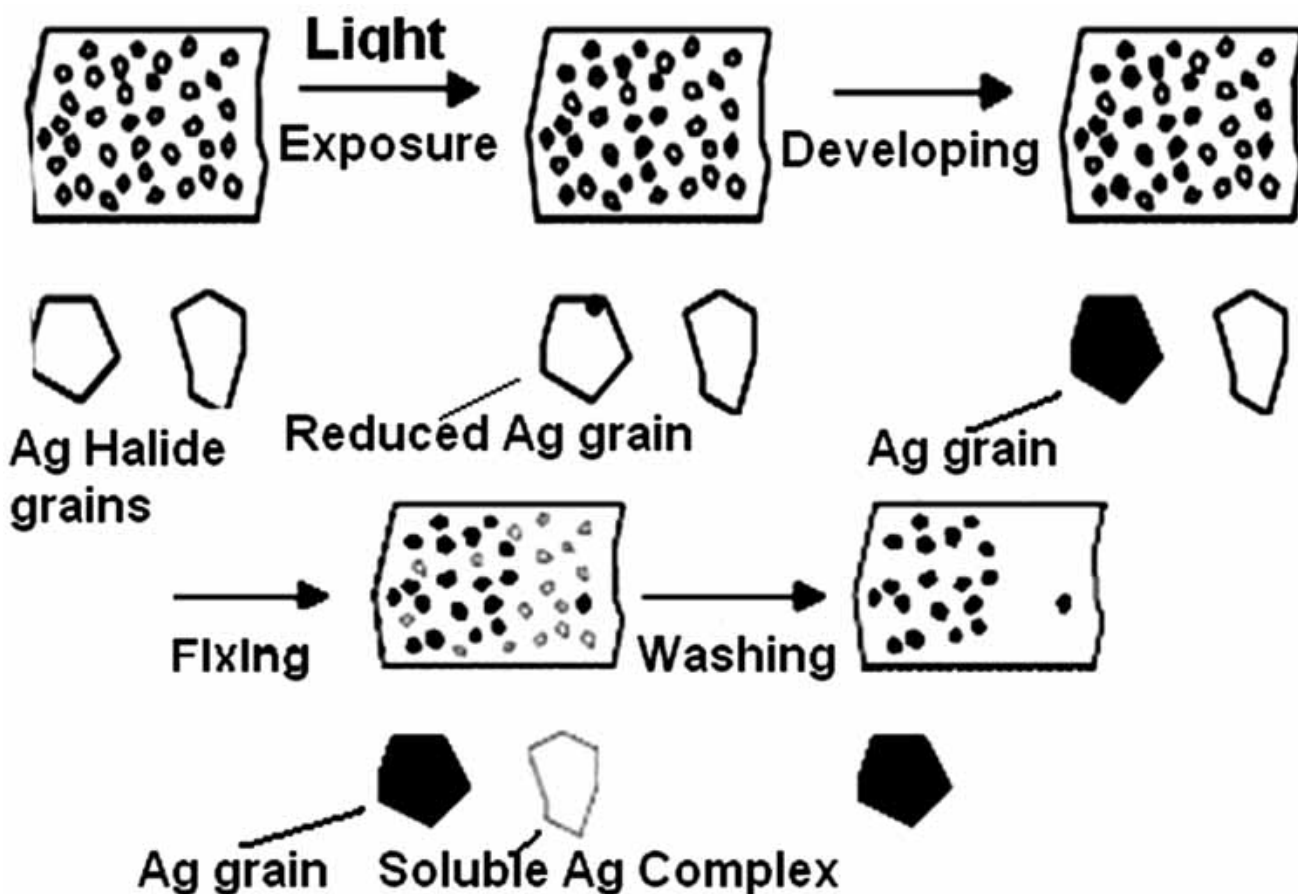


Fig. (2). Holographic photochemistry for silver halide emulsion: developing, fixing and bleaching.

### 2.1.1. Sensitized Silver Halide Emulsion

Silver compounds are sensitive to light to various extents. Silver chloride is only sensitive to violet and UV light, silver bromide absorbs up to about 490 nm, and silver iodide/silver bromide mixture up to about 520 nm. Therefore, sensitizers (dyes) are added to the emulsion to make it sensitive to other parts of the spectrum. The patents published in 1972 consists of making silver emulsion having an average grain-size of about 50-100 nm for the preparation of photographic plates or films with high resolution, for use in microphotography and in astrophotography, for recording nucleo-physical phenomenon, for the preparation of masks in the production of microelectronic integrated circuits, for use in holography, etc. Silver halide is incorporated into aqueous gelatin, into which the silver halide is precipitated in presence of sensitizer compounds such as substituted imidazole, benzoimidazole or naphthoimidazole [74]; substituted pyridine, thiazole, selenazole, benzothiazole etc [75].

Further work on sensitizers are continued to address the related limitations. Many of the dyes known for spectrally sensitizing photographic silver halide emulsions for the red wavelength range of 600 to 690 nm have the disadvantage of having a low solubility in water so that they usually are dispersed in emulsions or added in the form of an alcoholic solution. Consequently, they are not removed adequately during the processing. As a result, a considerable residual magenta to blue hue is left in the dried material which is disturbing in photographic material. In one embodiment the emulsion was sensitized with trinuclear merocyanine dye which in addition to providing a desired spectral sensitivity range of 600 - 690 nm, satisfactory speed and gradation to the silver halide emulsion, are sufficiently soluble in water so that after development and fixing of the photo-exposed silver halide emulsion they are rinsed away for the greater part [76].

Invention was directed to produce a holographic silver halide photosensitive material having higher sensitivity and image quality than was previously possible. The photosensitive material produced is stable and reproducible [77]. The medium responds to every usage of laser, including the use of lasers in a single color or multi colors, stationary-light lasers and pulsed-light lasers. The invention enables concurrent use of gold-chalcogen sensitization and reduction sensitization, which has been generally forbidden at the same time. According to this invention, gold-chalcogen sensitization and reduction sensitization can be concurrently carried out during chemical sensitization to result in achievement of both high sensitivity and high image quality.

Silver halide based hologram material having high sensitivity and diffraction efficiency, providing an excellent image and having less color residue is recently reported [78]. A hologram silver halide photographic material having at least one silver halide emulsion layer formed on a support, wherein an average particle diameter of silver halide particles in a silver halide emulsion is 0.03  $\mu\text{m}$  to 0.07  $\mu\text{m}$ ; a film thickness of the silver halide emulsion layer is 4 - 9  $\mu\text{m}$ ; a silver/gelatin ratio of the silver halide emulsion layer is 0.3 to 0.6.

### 2.1.2. Processing

After the selection of medium composition the processing comes as next important consideration. Phase holograms prepared by conversion of the metallic silver image of a conventionally processed photographic plate to a transparent compound having refractive index different from that of the gelatin matrix are known. The photodecomposition of the silver halide, when exposed to high intensity radiation, to silver metal results in print-out darkening of the plate. To avoid the print-out darkening characteristics of the bleached silver halide process for making holograms, a process using hardened dichromated gelatin has been used [79,80]. A similar method is described in European patent [81]. The plates are sensitized by soaking in an ammonium dichromate solution, dried and then exposed. After exposure the plates are washed in running water to remove the remaining dichromate sensitizer and dehydrated in isopropanol baths. The phase holograms formed consist of cross linked or tanned gelatin in a gelatin matrix. Diffraction efficiency of 77% is seen near the exposure of 30  $\mu\text{J}/\text{cm}^2$ . (at 632.8 nm) [81]. Another patent reports the post-exposure treatment method of a silver halide emulsion layer which involves chromium (III) potassium sulfate,  $\text{Cr}^{3+}$ -containing salts, and  $\text{Al}^{3+}$ -containing salts as the hardening agent in the concentration range of 1-8% [82].

### 2.1.3. Processing on Plastic Substrate

Producer of hologram generally does the recording and processing by placing the medium on glass substrate and later transfers to glass substrate for transporting and displaying. This process is time consuming and can affect the integrity of the hologram. One process describes the direct coupling of recording layer on plastic substrate and carrying out the recording and processing [83]. Holographic recording material layer includes a first side which is coated with barrier layer made of polyvinyl alcohol. The second side is fixed to the plastic substrate. When the exposed holographic recording material layer coupled to the plastic substrate is exposed in a liquid bath formation of gas bubbles between the plastic substrate and the exposed holographic recording material layer is minimized.

### 2.1.4. Fine Grain Silver Halide Emulsion

Factors determining the sharpness of a silver halide photographic material obtained by coating and drying of silver halide emulsions are light scattering and granularity. Light scattering depends clearly on grain size. Insufficiency in fineness of the silver halide grains causes insufficient sharpness in the images and the quality.

Various methods are adopted to get fine grain silver emulsion such as using a stabilizing agent in the form of bulky organic molecules [84].

In one invention, an increase in grain size (Approx. 0.05  $\mu\text{m}$ ) is prevented by the instantaneous expulsion of the superfine grains from the mixing vessel in which they are just formed [ 85, 86 ].

### 2.1.5. Silver Halide Sensitive Gelatin (SHSG) Technique

Silver halide sensitized gelatin (SHSG) is an interesting technique for the production of holographic optical elements.

It combines the high sensitivity of photographic emulsions with the well-known low scattering and high diffraction efficiency corresponding to dichromated gelatin [87].

Recent development of ultra-fine grain silver halide emulsion has increased an interest in the Silver Halide sensitive gelatin (SHSG) technique. SHSG technique is expected to provide comparable effects with the DCG when applied to an ultra-fine grain silver halide emulsion.

Briefly, the SHSG technique involves exposing and locally tanning a silver halide emulsion layer. Then, silver salt or silver in the emulsion layer diffuses out due to fixing and leaving behind only pure gelatin. In the last step, the remaining gelatin is dehydrogenated using a hydrophilic organic solvent. The dried SHSG hologram includes only gelatin and micro voids of air [88]. The gelatin has a refractive index of 1.5, and the air filling the micro voids has a refractive index of 1.0. This difference of refractive index can maintain excellent diffraction grating efficiency. A diffraction efficiency of 96% is reported.

## 2.2. Dichromated Gelatin

Dichromated gelatin finds use in holography due to its excellent holographic properties, including low scattering and high index modulation [89]. The drawbacks of dichromated gelatin include the raw material's variability, complex wet processing, poor shelf-life, and environmental instability requiring hermetic sealing. Besides being a valuable material in the field of holography, dichromated gelatin is able to provide holographic plane gratings of almost theoretical spectroscopic resolving power. In common with other non-silver halide materials, dichromated gelatin is usually sensitive only to UV and blue light. The efficacy of dichromated gelatin system is based on the difference in swelling between exposed and unexposed gelatin. By photochemically cross-linking the gelatin through photolytic decomposition products of the dichromate sensitizer difference in swelling is induced. Fig. (3) shows the crosslinked structure of dichromated gelatin. The resultant image is developed by removing gelatin which remains uncrosslinked.

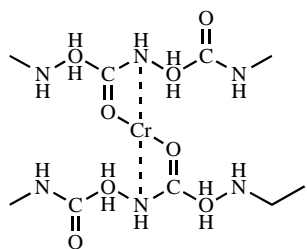


Fig. (3). Crosslinked Structure of Dichromated Gelatin.

An important limitation on the use of dichromated gelatin as a phase hologram material has been the inability of developed holograms to resist high relative humidity. A method for the passivation of dichromated gelatin holograms to high relative humidity ambient is described in one invention [90]. The method involves a developing process wherein an exposed hologram is initially treated with an ammonia neutralized photographic fixing solution containing  $\text{CrO}_3$ . Chromium oxide complex is introduced in the photographically fixed hologram. The chromium trioxide is

thermally activated after the permanent development of the hologram and reacts with the hydrophilic groups responsible for moisture absorption in the gelatin film, thus passivating the recorded holograms to high relative humidity.

### 2.2.1. Spectral Sensitivity

Although dichromated gelatin systems have been proven to be satisfactory for use as a holographic material, such systems suffer certain drawbacks because their spectral sensitivity is limited to wavelengths below 520 nm. It has been observed that addition of a dye sensitization material extends spectral sensitivity to greater degree [91].

A method for increasing the sensitivity comprises the steps of casting aqueous solution of gelatin and ammonium dichromate to form film which is dried and later sensitized by immersing it into a solution containing a spectrally sensitive acid fast violet dye selected from the group consisting of the thiazine and triphenylmethane dyes and ammonium dichromate [92].

An experimental study to ascertain the combinative action of zinc chloride and triethanolamine (TEA) on improving the photosensitivity of red-sensitized dichromated gelatin (RSDCG) has been carried out [93].

### 2.2.2. Processing

At ordinary room atmosphere conditions, it is found that dichromated gelatin holograms are relatively stable. Excessive rate of dehydration can create a high-stress condition and cause a milky-white appearance in the gelatin plate which produce heavy light scattering. The use of a combination of water and alcohol bath is found to be effective for preventing excessive rate of dehydration. In mass production, the use of a highly flammable isopropyl alcohol can be dangerous, particularly at elevated temperatures.

A good number of patents and literature are available in which various methods are reported on improvement of processing to achieve greater stability and minimum light scattering. A method for making high diffraction efficiency holograms from dichromated gelatin (DCG) including the steps of curing the DCG under controlled time, temperature and humidity conditions is described [94].

In another invention, the exposed hologram after usual hydration is dehydrated by contacting the hydrated gelatin with a mixture of isopropyl alcohol and an inert anhydrous fluid, such as a liquid fluorinated hydrocarbon solution [95]. The preferred inert liquid is a liquid fluorinated hydrocarbon solution such as Freon (1, 1, 2 -trichloro - 1, 2, and 2 -trifluoroethane). The dehydrated hologram pattern is then stabilized by baking. The efficiency reported is around 94%.

The invention also aimed at improving optical image properties of gelatin holograms by reducing uneven shrinkage during chemical development [96]. This is accomplished by introducing from 2 to 10 weight percent of a water soluble sizing agent into the gelatin. Suitable sizing agents used are polyvinylpyrrolidone homopolymer and polyvinylpyrrolidone-vinyl acetate copolymers. In this invention, the polymer is homogeneously mixed with dichromated gelatin prior to the gelatin's application to a substrate to form a holographic plate. The added polymer interacts with the

dichromated gelatin to give a gelatin of increased structural strength. This improved dichromated gelatin is then used to coat a substrate to form a holographic plate.

Further work keeps on appearing from time to time due to the possibility of attaining high diffraction efficiency of dichromated gelatin. Overview of its importance for holography, difficulties with its treatment, possibilities of its utilization, optical properties are given [97]. Chemical processes being under way in gelatin from its exposure to fixing, the experience with the formation of holographic optical elements into dichromated gelatin is mentioned.

The formulation of holographic recording medium, containing poly(vinyl alcohol) and chromium, is an innovative approach [98]. This approach combines the monitoring of the structural modification of the polymeric matrix and the fate of the various chromium species. For the first time, it has been established that chromium(V) not only is an indicator of the hologram quality, as previously assessed, but also appears to be responsible for the crosslinking implied in the hologram formation. Actually, the crosslinking has been proved to proceed through coordination bonds around chromium(V), which acts as a bridge between the polymeric chains. The role played by the ammonium cations in the hologram quality has also been elucidated. The improvement brought by ammonium dichromate with respect to potassium dichromate involves amide groups resulting from poly(vinyl alcohol) phototransformation. These groups provide additional chelating sites for chromium(V), leading to an increase in the matrix crosslinking.

### 2.3. Photopolymer

Silver halide based materials were quite suitable for making both hologram originals and hologram copies. However, the disadvantages are that they are expensive as the original materials cost and processing costs are very high. Further, immediate access to the finished product is not there. Dichromated gelatin and conventional photoresist materials, which are less expensive, have been tried. It is observed that they also require wet processing steps to develop and fix the image and consequently involve delayed availability. Relatively inexpensive copies can be made by a diazo film process. But, the exposure time is relatively long, the spatial frequency capability and the image intensity are low as compared to the original. Electrostatic imaging

processes offer high speed and quick access, but are restricted to low spatial frequencies because of the size of toner particles.

Photopolymer materials can be used for recording phase holograms, where applications in mass-production of display holograms and optical elements are of main interest. Normally, the material has a short shelf-life and a rather limited refractive index change. The exposure for transmission holograms is about  $5 \text{ mJ/cm}^2$  and about  $30 \text{ mJ/cm}^2$  for reflection holograms. Diffraction efficiency can be as high as 60 % for a transmission hologram and 85 % for a reflection hologram, and the signal-to-noise ratio is about 90:1 for exposures which give the highest diffraction efficiency.

Spatially non-uniform illumination during holographic recording produces free radicals by initiator decomposition. Subsequent reaction of free radicals with monomer molecules leads to vinyl polymerization of monomer in the bright regions. This polymerization process lowers the chemical potential of monomers in these regions, leading to their migration (diffusion) from the dark to the bright regions. Photopolymer materials are practical materials for use as holographic recording media, as they are inexpensive and self-processing (dry processed). Understanding the photochemical mechanisms present during recording in these materials is crucial to enable further development [99]. There are many reports on various monomers, hosts and techniques employed for holographic recording [100-103]. Fig. (4) shows the mechanism of hologram formation in photopolymer systems [104]. During holographic recording, the optical interference pattern initiates polymerization in the photo-reactive system; polymerization occurs in the light-intensity maxima of the interference pattern, while no polymerization occurs in the nulls.

Report on photopolymer based holographic recording was available during early 70's [105,106]. A photopolymerizable layer containing a polymeric binder, an addition-polymerizable monomer, a photoinitiator system, a chain transfer agent, and a plasticizer was used. Exposure of this layer to radiation bearing holographic information results in photopolymerization with accompanying changes in various physical properties in the exposed areas. The use of photopolymerizable compositions for holograms permits the recording of very high spatial frequencies free of any particle

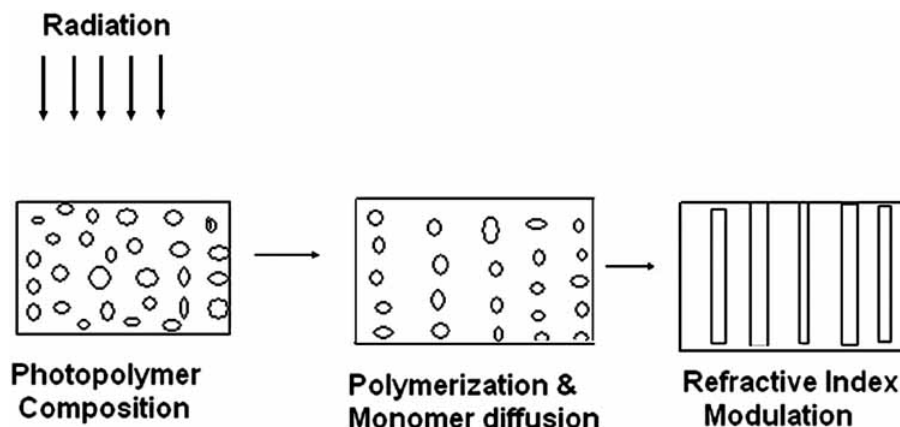


Fig. (4). Holographic recording mechanism of photopolymer film.

size limitation, since the photosensitive compositions used does not contain any particulate material. The single step of exposure alone produces a useful and stable finished hologram. The inventors reported the recording in the range of 200 to 2,000 l/mm. Similar composition reported a refractive index modulation of at least 0.005 and spatial line frequency of about 1000 lines per mm [107].

### 2.3.1. High Sensitivity

A photopolymerizable composition which is capable of successfully ensuring both high sensitivity and excellent storage stability is claimed by another inventors [108]. A photopolymerizable composition comprising a polymer having a radical polymerizable alpha-hetero-substituted methacrylate, a photopolymerization initiator and a polymer binder having carboxyl group, a phenoxy group, or a sulfamoyl group has been developed and claimed to be stable matrix with enhanced performance [109].

Holographic photopolymer compositions having fluorinated binders are provided that produce excellent reflection holograms [110]. Refractive index modulation values higher than 0.01 are achieved, with typical values observed is higher than 0.04 with specific compositions. Reflection efficiencies in the order of 70% to 99% are achieved at film thickness of 10 to 100  $\mu\text{m}$  that are particularly useful in the fabrication.

Security and identity cards including hologram are invented. Holographic methods and materials developed to detect and prevent forgery in identity cards such as credit cards and access cards to security areas are already developed. This invention employs microholograms that are recorded in very small areas on the card and are not readily visible to the bearer. Special recording materials for high efficiency holograms are used to allow the confinement of the recording in about 10-100  $\mu\text{m}$  size area. Photopolymerizable composition consists of free radical ethylene monomer whose polymerization is initiated by a combination of polyethyleneimine and lithium acrylate [111]. Apparatus for the recording and reading of the holograms are also disclosed.

Index contrasting-photoactive polymerizable material is reported for using as holographic recording medium [112]. The invention provides an article comprising a holographic storage medium which consists of a support matrix and one index-contrasting photoactive polymerizable material, wherein the polymerizable material comprises at least one reactive functional group and at least one index-contrasting group, wherein the index-contrasting group is substantially absent from the support matrix. The polymerizable material is designed to have the properties such as: (1) distance between at least one reactive group and at least one index-contrasting group is at least the average radius of the index-contrasting group; (2) two or more reactive groups per molecule of photoactive polymerizable material; (3) an index-contrasting group having a strong chromophore absorption at a wavelength shorter than the recording wavelength, or (4) the photoactive polymerizable material comprises a reactive nanoparticle. Further, the photoactive polymerizable material has an average index contrast of

greater than about 0.1, a molecular size of at least about 1 nm in at least one spatial dimension.

Recording material, for making hologram that has high sensitivity, gives a large refractive index difference, and has excellent storage stability after recording, is claimed [113]. The hologram recording material comprises of a polymer matrix having a three-dimensional crosslinking structure, a polymerizable monomer, and a tertiary amine compound, the polymer matrix being formed in the presence of the polymerizable monomer by a polymerization reaction that is different from a polymerization reaction of the polymerizable monomer.

Inventions aiming at providing a hologram recording material, which attains compatibility of high refractive index change, flexibility and high sensitivity with small recording shrinkage, and suitable for volume hologram recording, are recently reported [114,115]. Organometallic compound are used which contains at least two kinds of metals, oxygen, and an aromatic group; aromatic groups being bonded directly to one metal. Other ingredients are metal oxide fine particles having size in the range of 1 to 50 nm and a photopolymerizable compound. Fine particles are selected from silica, alumina, titania and zirconia.

Holographic recording materials, comprising a binder substantially free of exudation having high refractive index and are diffusible and compatible with Cationic Ring Opening Polymerization (CROP) and miscible with the monomer(s) and/or oligomer(s) used in the CROP holographic recording materials, are developed [116]. It has also been found that these said binders maintain a favorable thermodynamic enthalpy of mixing during the holographic recording process so that spatial and chemical segregation is primarily driven by molecular weight build-up during polymerization and so that segregated domains remain thermodynamically stable throughout the recording process and throughout the anticipated life time of the media. It has been found that recording materials comprising the binders of the present invention remain substantially free of exudation of said binders when the materials are heated to temperatures between 25  $^{\circ}\text{C}$  and 110 $^{\circ}\text{C}$ .

### 2.3.2. Sensitizers

The photopolymerization-initiating capacities of the conventional photopolymerization initiators in the visible region longer than 400 nm are far lower than those in the ultraviolet region shorter than 400 nm. Therefore, the application of the photopolymerizable compositions, containing conventional photopolymerization initiator, is very limited. Rose Bengal, Eosin and Erythrosine, hexaarylbiimidazole with *p*-dialkylaminobenzylidene ketone etc. are found to possess high sensitivity. Although these techniques are effective for improving sensitivity to the visible rays, the sensitization velocities are still unsatisfactory. In one invention a photopolymerizable composition having high sensitivity to visible light of 400 nm or longer and comprising a photopolymerization initiator consists of: (a) a salt of an organic boron anionic compound with an organic and cationic dye such as cyanine and xanthene dye or a combination of an organic and cationic dye with a salt of an organic boron anionic compound [117]. Another composition claims the

use of spectral sensitizers for photopolymerizable systems which not only extend the spectral response but also increases both the speed and resolution of the system, improves the thermal stability of the system by increasing the polymerization temperature and improves the processing characteristics of the resulting image. A new class of sensitizers for photopolymerizable compositions is derived from cyclic ketones and tricyclic aminoaldehydes. A preferred compound is cyclopentanone, 2,5-bis[(2,3,6,7-tetrahydro-1H, 5H-benzo [i,j]quinolizin-9-yl)methylene] [118]. The sensitizers belonging to a class of materials such as chloro, fluoro, cyano and alkoxy substituted hexaarylbiimidazole are also disclosed [119]. Similarly a photopolymerizable composition comprising (i) a polymerizable compound; (ii) a methine compound; (iii) at least one compound selected from the group consisting of: (a) compounds having carbon-halogen bonds, (b) aromatic onium salts, (c) organic peroxides, (d) thio compounds, (e) hexaaryl-biimidazoles, (f) ketoxime esters, is claimed to have high sensitivity to a wide range of actinic light rays ranging from ultraviolet to visible light [120]. High sensitivity and improved storage stability is claimed in the invention using photopolymerizable compound along with amide of an aliphatic polyhydric amine etc. and an oxime ether compound [121]. One similar composition is claimed to have high sensitivity to actinic rays in the range of ultraviolet to visible light and provides film having improved strength in exposed areas [122].

Photopolymerizable compositions are colored depending on a dye present in it. These compositions can not be used in the field where clear transparency is required such as hologram. Another disadvantage is the inferior storage stability. A photopolymerizable composition comprising a polymerizable compound, a photopolymerization initiating composition such as diaryliodonium salt and a dye molecule having carboxyl, sulfonyl groups is invented [123]. The color of the dye can be removed by light irradiation. Accordingly, the composition is claimed to be used for producing a hologram where transparency, high quality diffraction grating are required.

### 2.3.3. Matrix and Processing

In this section, the mechanical and thermal stability, ageing degradation of hologram and the processing involved are discussed. A method for processing exposed holograms to enhance their thermal stability and enable them to withstand a windshield lamination process is invented [124]. The secondary processing procedure entails an optional step of applying a moisture barrier to the hologram, followed by heat stabilizing the hologram up to 135°C, cooling and storing it in a relatively low humidity environment. Moisture barrier to the exposed photosensitive material is provided by immersing it in a solution of a volatile solvent comprising freon and a solute comprising a fluorocarbon powder such as polychlorotrifluoroethylene.

### 2.3.4. Lower Shrinkage

A latent-imaging photopolymer system for recording thick refractive index patterns is disclosed [125]. The system utilizes a porous matrix (porous silica glass matrix.) which has been sensitized by chemisorption of a photosensitive polymerization initiator (benzoin). According to the

invention porous silica glass plate was sensitized with a photosensitive compound which is a polymerization initiator. It was then illuminated with a light pattern corresponding to the desired image. After this photoreaction, the exposed compound is no longer useful as a polymerization initiator. Thus, a negative image is recorded in the substrate by deactivating portions of the photosensitive initiator at points corresponding to the incident light pattern. The image is then developed by filling the pores of the matrix with a monomer composition. The photosensitive initiator compound which remains in the rigid body is activated by a uniform application of light energy. This selective initiation of polymerization throughout the matrix leads to a corresponding modulation of the refractive index of the final polymer. Another invention addressing the dimensional stability also uses non-light scattering porous material [126]. A glassy hybrid inorganic-organic crosslinked matrix is also claimed, in which a photoimageable system comprising of one or more photoactive organic monomers are distributed [127]. The medium is fabricated by mixing the matrix precursor with the photoimageable components and curing the precursor to form the matrix. The matrix and photoimageable system exhibit independent reactivities, such that the step of matrix formation does not substantially affect the photoimageable system. The hybrid matrix precursor is typically an oligomer derived from a compound represented by  $R_n M(OR')_{4-n}$ , where M is a metallic element having a valence of three or higher, such as silicon, titanium, germanium, zirconium, vanadium, or aluminum, R is an alkyl or aryl, R' is a lower alkyl, and n ranges from 1 to 2. The hybrid nature of the matrix material provides several advantages. The inorganic character offers thermal, mechanical, and chemical stability, and also reduces both the bulk viscoelastic creep and the bulk polymerization-induced shrinkage. The organic character provides compatibility between the matrix precursor and the photoactive monomer, allowing homogeneous mixing during fabrication of the medium. Another concept to take care of the dimensional stability is the use of expansion agent in the holographic composition. Spiro compounds have been reported to exhibit relatively small shrinkage or even expansion upon polymerization due to opening of two rings per polymerized monomer functional group [128]. However, the shrinkage compensating ability of the spiro compounds is not as great as has been claimed or desired, primarily because the measured results are due, at least partly, to a phase change [129].

The invention relates to use of an expansion agent having a cleaving moiety with the capacity to be cleaved or fragmented by a catalytic reaction, e.g., acid catalysis [130,131]. The cleavage, by increasing the number of molecules in the material, causes expansion that compensates, at least in part, for shrinkage induced by polymerization of the monomer or oligomer. The expansion agent is capable of providing compensation in the range of 0.2-0.4% volume shrinkage per molar concentration of polymerized monomer functional groups. Such compensation is performed at relatively low temperatures around 40°C. However, low diffraction efficiency is reported.

A new type of photopolymerizable composition is invented to address the curing induced contraction problem [132]. The recording layer in the holographic recording

medium according to the invention comprises a matrix formed of a cured product of a spiroorthoester of an epoxy compound, a radical-polymerizable compound and a photoinitiator. A spiroorthoester of an epoxy compound has a high density since it has high intermolecular interaction before polymerization, and thus, it is known that the cured product thereof experiences small change in the intermolecular distance or may expand when cured through ring-opening polymerization. Moreover, even if a part of the matrix materials is left unreacted and gradually reacts with time, change in recording sensitivity with time may be suppressed because it is believed that any influence will not be given to a diffusion rate of the radical-polymerizable compound if the density change of the matrix is small.

### 2.3.5. High Thickness

Deposition of the pre-formed matrix material containing the photoimageable system requires use of solvent and therefore the thickness of the material is limited to about 150  $\mu\text{m}$ . so that the evaporation of the solvent does not create any flaw in the matrix. In holographic processes requiring three-dimensional space of a medium, the storage capacity is proportional to a medium's thickness. Thus, the solvent removal process inhibits the storage capacity of a medium [133]. The process in which little or no solvent is required for deposition of matrix of greater thicknesses e.g., 200  $\mu\text{m}$ , the possibility of reaction between the precursors to the matrix polymer and the photoactive monomer can not be eliminated. Such reactions are likely to reduce the refractive index contrast between the matrix and the polymerized photoactive monomer affecting the strength of the stored hologram.

Holographic recording medium or polymeric waveguide is formed by mixing a matrix precursor and a photoactive monomer, and curing the mixture to form the matrix *in situ* [134]. The reaction by which the matrix precursor is polymerized during the cure is independent of the reaction by which the photoactive monomer is polymerized during writing of data. In addition, the matrix polymer and the polymer resulting from polymerization of the photoactive monomer are compatible with each other. Use of a matrix precursor and photoactive monomer that polymerize by independent reactions substantially prevents cross-reaction between the photoactive monomer and the matrix precursor during the cure and inhibits of subsequent monomer polymerization. Use of a matrix precursor and photoactive monomer that result in compatible polymers substantially avoids phase separation and *in situ* formation allows fabrication of articles with desirable thicknesses. Epoxy polymerization, hydrosilylation, urethane formation, urea formation etc. were used as matrix polymer. Aryl acrylates were used as photoactive monomer and Ciba CGI-784 was used as photoinitiator. Similarly one other invention claims improved chemical and structural integrity along with the simplicity of the process [135]. The invention includes cationic epoxy polymerization, cationic vinyl ether polymerization, epoxy-amine step polymerization, epoxy-mercaptan step polymerization, unsaturated ester-mercaptan step polymerization, hydrosilylation, urethane formation and urea formation for making matrix. A similar approach was used in which both types of initiators are used [136].

New photosensitive acrylic material compositions comprised of polymerizable acrylic monomers and light absorbing dyes when polymerized forms thermally stable, light sensitive, hard matrix and inert to common chemicals [137]. The invention describes about photopolymer composition having at least two distinctive acrylate materials (mono-, di- or triacrylic), initiators (AIBN/BPO) and a light harvesting dye. When exposed the acrylate materials are polymerized and the dye (9,10-phenanthrenequinone) reactively bonds with the polymerized acrylate material upon photoexcitation.

### 2.3.6. Improved Shelf-Life

A technique is developed for improving the shelf life of polymer holographic storage media [138]. The prepolymer materials, typically 50-2000 nm in thickness, are coated onto a base glass plate and encapsulated with a counter glass plate. The prepolymer is then polymerized *in situ*, in an optically flat configuration, to form the matrix of the recording medium. This can be either thermally or photochemically initiated. Prior to encapsulation and polymerization, each glass plate is provided with a flexible edge tab that extends around the periphery of the plate. The tabs are sealed together with a suitable adhesive or bonding material, or alternatively mechanically crimped together, to produce a moisture proof package. This approach not only retards moisture intrusion into the polymer, but also prevents distortion of the glass substrate caused by stresses due to differential thermal expansion of the polymer and sealant during temperature variation in the use environment. An important advantage of this technique is that it allows the use of relatively high temperatures, i.e. temperatures that are potentially harmful to the polymer medium. This sealing technique also accommodates the shrinkage induced by polymerization of the matrix material. A similar problem may originate from absorption of moisture by photopolymer when exposed to environment. It may cause the photopolymer to swell and undergo refractive index changes in a spatially non-uniform fashion. When the photopolymer film is sandwiched between glass or plastic substrates, the non-uniform swelling and/or refractive index change in the polymer may diminish the optical quality of the holographic recording medium. A holographic recording medium positioned between two plastic such that the holographic recording medium has at least one exposed area; and an environmental barrier seal protecting the exposed area from environmental degradants [139].

The conventional photoimageable polyurethane holographic media having a crosslinked matrix is formed by the reaction of stoichiometric amounts of polyisocyanates to polyols. However, it was unexpectedly found that a cross-linked matrix formed by the reaction of a composition containing an excess amount (i.e. non-stoichiometric amount) of polyisocyanates to polyols, once formed into holographic recording articles, exhibits high optical clarity, and low scattering. The holographic articles are formed by the reaction of a composition containing an excess amount (i.e. non-stoichiometric amount) of polyisocyanates as compared to polyols [140]. The excess NCO available in the matrix after polyurethane formation reacts with moisture to form polyurea which improves moisture resistance. Substituted

phenylacrylate and Irgacure-784 was used as monomer and dye.

A new polymer architecture, called dendrimers, are used in many applications due to its additional advantages such as easier processing and quicker response as compared to linear analogues. A polymerizable composition comprising of a dendrimer having at least two polymerizable groups within a molecule; a radical initiator; and an alkali-soluble polymer is developed. It can be used for image-forming materials such as three-dimensional stereolithography, holography, lithographic printing plate, color proof, photoresist and color filter etc [141].

A novel liquid photoreactive asymmetric acrylate compound containing sulfur, aromatic moieties, and optionally bromine, and having high dynamic range sensitivity is disclosed [142]. The acrylate compound is a monomer for a photoimageable system. In one embodiment, when about 2-8% by weight of the acrylate compound is dissolved in a two-component urethane matrix system and incorporated in an optical article formed by reacting the two-component urethane matrix system. The photoinitiators used are from Irgacure brand and photoactive monomers selected from styrene, bromostyrene, divinyl benzene, and 4-methylthio-1-vinylnaphthalene. Polyols belong to the class of diols and triols of polytetramethylene glycol, polycaprolactone, polypropylene oxide. Preferred aromatic diisocyanates selected are diphenylmethane diisocyanate (MDI) and toluene diisocyanate (TDI).

### 2.3.7. Anti-Reflection and Other Coatings

The conventional manner to suppress Fresnel reflections is through the use of thin-film coatings. These anti-reflection (AR) coatings are typically multi-layer and can be designed for a general material interface, angles of incidence, polarizations, and spectral bandwidth. AR coatings are difficult to apply when such substrates of the media are of plastic, such as polycarbonate. Anti-reflection structured (ARS) surfaces have been developed. However, they have not been incorporated into holographic data storage media. When data are three-dimensionally recorded in the holographic recording medium, data recording and data reproducing are greatly affected by the reflection of the laser beams by the surface of the substrate. It is, therefore, necessary in the holographic recording medium to suppress the reflection of the laser beams by the surface of the substrate by providing an antireflection film on the surface of the recording film

Holographic media for storing and reading holographic data has been developed which has one or more external or internal surfaces having structures to minimize reflections from illumination incident on the surface and to enhance adhesion between surfaces within the media [143]. Structures for minimizing reflections constitute a grating pattern of sub wavelength structures which provide low reflectivity at the operating characteristics of holographic optical systems. Adhesion promotion may be provided by such structured surface with or without providing low reflectivity at the operating characteristics of holographic optical systems. The structures may be same or similar to one-, two-, or three-dimensional sinusoidal, triangular, staircase, moth eye, pyramidal, lamellar, or binary structures, or their com-

binations and periodic or random in nature. Another invention with similar claim disclosed that the holographic recording medium is sandwiched between two light transmittable substrates [144]. First antireflection film (inorganic, multilayer) was formed on the surface of the first light transmittable substrate and a second antireflection film formed on the surface of the second light transmittable substrate.

Usually, during recording on a hologram recording medium, a diffraction grating layer and a recording layer cannot be separated, resulting in an increase in manufacturing costs and resulting in a security problem due to the ease in reproduction of data by unauthorized person. The input of a reference beam to an area to which data is not to be recorded in a recording layer is prevented while recording data to the hologram recording medium [145]. Also, the amount of noise, while reproducing the data, from the hologram recording medium is reduced. The hologram recording medium includes a light velocity restriction member restricting an incidence area of a hologram recording layer. This restricts the incidence of a reference beam onto the hologram recording layer, preventing its incidence onto an area to which data is not to be recorded of the hologram recording layer during recording of data. The dyes used were eosin, rose bengal, erythrosine, and methylene blue, along with suitable hydrogen donors such as tertiary amines. Photoactive polymerizable materials include acrylates, methacrylates, acrylamides, methacrylamides, styrene, substituted styrenes, vinyl naphthalene, substituted vinyl naphthalenes etc.

### 2.3.8. Initiator

The common photopolymerization initiators used in the polymerizable composition are benzyl, benzoin ether, Michler's ketone, anthraquinone, acridine, phenazine or benzophenone. However, these initiators are low in the sensitization rate and extremely poor in the photopolymerization ability to visible light at 400 nm or more as compared with the photopolymerization ability to the light in an ultraviolet wavelength region of less than 400 nm. Accordingly, the photopolymerizable compositions comprising an initiator from above group are strictly limited to the specific application range. One invention describing a photopolymerizable composition comprises a photopolymerization initiation system capable of exhibiting excellent light sensitivity to visible light [146]. Photoinitiators are selected from substituted thio group, substituted oxo group, substituted amino group etc. containing compounds.

### 2.3.9. Multiple Initiator

Multiple initiators are used in the photopolymerizable compositions where it is intended to first form the matrix by one kind of polymerization. Further, holographic writing is conducted using another radiation.

One invention describes a photosensitive composition for volume hologram recording consisting of a cationic polymerizable compound which is liquid at ambient temperature; a radical polymerizable compound, radical photopolymerization initiator and a cationic photopolymerization initiator [147]. The photosensitive solution was applied on a glass sheet and cationic polymerization conducted to make a film

containing other ingredients. The film was exposed to laser for recording/writing hologram. Diffraction efficiency reported is around 30%. Another invention claims composition using radical polymerization initiator along with a cationic polymerization photo initiator [148]. It is capable of generating a Bronsted acid or Lewis acid that activates cationic polymerization upon exposure to actinic radiation. High thermal resistance, chemical stability and diffraction efficiency around 42% was reported.

### 2.3.10. Multiple Layer Hologram

For making holographic stacks and other applications, multiple layers of holographic exposures are done. Multiple layers or holographic exposures and methods for preparing multiple layers of holographic exposures are described in one invention [149]. The multiple layers of holographic exposure were combined to form holographic stacks and are fabricated from layers of exposed and processed photosensitive recording films, each of which has at least one independently recorded hologram. The holographic stacks are useful for providing wide bandwidth holograms and holograms having superimposed images.

### 2.3.11. Data Recording

Data are stored as microscopic pits on the surface of a substrate for read-only compact discs. Every bit of data has a specific physical location in the storage medium. The storage density of optical media is limited by physical constraints on the minimum size of a recording spot. Another limitation of conventional optical storage is that data are usually stored on the surface of the medium. Recording throughout the volume of a storage medium would enable the process to increase capacity. Another option is multi layer storage. However, it usually requires manufacture of special, heterogeneous, layered recording media, whose complexity increases with the number of layers. Usually, commercially-available multi-layer optical storage media offer two data layers, and come in pre-recorded format. All these limitations are addressed in the volume hologram recording technique. Unfortunately, volume holographic storage techniques require complex, specialized components. To ensure the reference and signal beams mutually coherent over the entire volume of the recording medium a light source with high coherence length, as well as stable mechanical system are required. This makes the process expensive and unstable.

In one invention, hologram writing and data writing mechanisms are made independent to allow optimization of data writing separately from hologram recording [150]. The system comprised of an optical medium having a photoactive material responsive to hologram recording condition and a second photo-active material responsive to a second data writing condition. The second one is dispersed or dissolved in the first photoactive material. The second photoactive material is usually in the form of micro particles, microdroplets or microcapsules which are dispersed throughout the first photoactive material. The first photoactive material contains photo-acid generator, active binder and cationic ring opening monomer in a polymer matrix and others whereas the second one belongs to the class of ferroelectric crystals such as vanadium oxide.

### 2.3.12. Mass Production

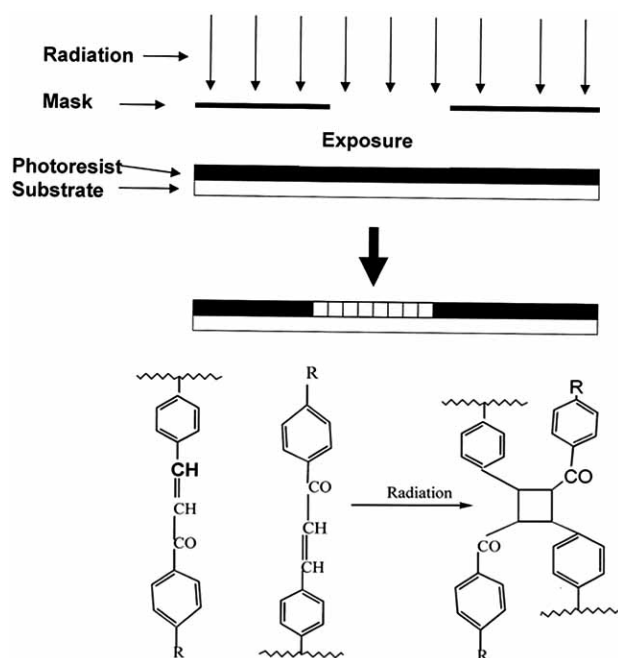
Mass production is required for any hologram to take it to the deliverable stage. One invention describes the mass production of the high performance holographic recording articles including the process and composition [151]. To prepare a high performance holographic recording article based on two-component urethane matrix system (polyols and isocyanates) deaeration must be carried out. The rapid mass production of this invention results in a high-volume production of the high performance holographic recording articles. Halogen substituted acrylates are used as monomer

### 2.4. Photoresist

For making embossed holograms, the recording medium is typically photoresist. Photoresist is a material which, after development, yields a surface profile whose depth is proportional to the intensity of the incident interference fringes. Photoresists are the ideal medium for making embossed hologram. An embossed hologram usually involves coating the surface of the photoresist of the hologram with a conducting metal like silver and immersing the coated hologram in an electroplating bath to plate a layer of nickel. The nickel plate layer is used as a hard master to emboss the interference pattern into plastic that has been softened by heat, pressure, solvents or some combination. The embossed plastic is finally coated with highly reflecting metal, like aluminum, to enhance the diffraction efficiency of the embossed hologram.

The work on photoresist materials have also started at the initial stage of development of holographic medium. One early invention describes the sensitivity improvement of organic volume phase holographic recording media comprising an alpha-diketone in an acrylic polyester polymer [152]. The host material is an acrylic polyester which is curable with free radical catalysts. During recording, a photochemical reaction occurs whereby the  $\alpha$ -diketone abstracts a hydrogen atom from the host resin, resulting in a change in the index of refraction of the medium and permanently storing a holographic grating in the medium. Fig. (5) shows the schematics of photoresist process and one representative chemistry

One problem appearing during use of these recording media is that during readout, when a coherent light reference beam is passed through the medium, a certain amount of spurious light scattering occurs. This results in distortion of the readout image which is due to interference of the readout beam with the different image beam. This light scattering cannot be erased as it originates from continuing irreversible photochemical reaction in the medium. Method of preventing further photochemical reaction in the recording medium after recording, particularly during readout, is highly desirable. To eliminate this limitation attempt has been made by introducing convenient post treatment method [153]. The invention disclosing use of organic volume phase holographic recording medium comprises an  $\alpha$ -diketone in an acrylic polyester polymer. The hologram is desensitized by exposing the medium to desensitizing light after



**Fig. (5).** Schematics of photoresist process and one representative chemistry.

recording is complete. This inactivates the  $\alpha$ -diketone and prevents damage to the medium during readout. The diffraction efficiency is reported to be around 15%.

Photosensitive composition for recording of holographic information in real time has been disclosed using photoresist [154]. It comprises of a polymeric sheet (2-cyanoacrylate polymers) containing a photosensitizer (*p*-benzoquinone) to bring about a change of the refractive index of the polymer upon irradiation in the visible or in the UV range. About 50% diffraction efficiency is reported.

A hologram is produced by causing a crosslinking reaction in accordance with an interference pattern in a recording carrier composed of a polymer containing in its unit structure an aromatic or hetero cyclic ring having a reactive position capable of being substituted by radical [155]. The polymer of a halogen-containing compound, when activated by radiation rays, generates radicals causing a cross-linking reaction among the polymer chains. This causes change in refractive index. Diffraction efficiency of 72% is reported. A similar invention claims spatial frequency of about 3000 lines/mm and diffraction efficiency around 90% [156].

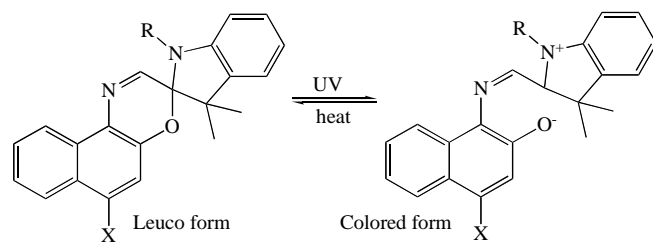
Volume phase reflection (VPR) holograms, which can be replicated without using an on-line laser exposure or subsequent chemical processing steps, is disclosed [157]. The resulting replicated hologram is dimensionally stable and is not affected by humidity, heat or other environmental factors. Diazo photoresist material is used in making hologram.

The properties and mechanism of relaxation processes of holographic gratings in amorphous chalcogenide semiconductor films have been studied by Teteris [158]. The possibilities of the practical applications of these materials as the photoresists for the production of the relief holograms and holographic optical elements are discussed. It is shown that the self-enhancement phenomenon of holographic recording in amorphous chalcogenide semiconductor films by light or thermal treatment can be used to increase the diffraction efficiency of the holograms.

The invention by Dausmann *et al.* [159] describes about the manufacture of CD master by exposing a hologram into a plate coated with photoresist with a reversed image by laser light. In this connection, different exposure techniques such as a 2D technique, a 3D technique, a dot matrix technique or a holomax technique can be used. The photoresist is then developed with an alkaline developer so that a holographic surface relief is created in the photoresist with a preferred depth of around 500 nm. The surface is then silver plated and an electroplated nickel casting is subsequently taken. The holographic image then appears right way round in the nickel matrix obtained and is raised over the nickel matrix. The nickel matrix then serves as the embossing matrix for a CD master from photoresist. The CD information is then produced in the surface of this photoresist in the usual photolithographic way in the form of pits and lands. The nickel matrix is embossed into the raised structures of the CD resist master carrying the CD information with a certain pressure, and indeed only down to a depth of 10 to 20 nm.

## 2.5. Photochromic Polymer

Because of various drawbacks of photorefractive and photopolymer materials, rewritable holographic recording materials based on photochromic conversion have attracted attention on three-dimensional optical recording [160]. Fig. (6) shows the isomer inter-conversion under exposure to radiation. Photochromic materials do not need any electric field to write or read the information. Further, the stored information can be either permanently stored or erased for repeated recordings. The photochromic nature enables these materials to record by UV irradiation and then erased with visible light or heat, or *vice versa*. To act as optical memory media the photochromic materials should possess thermal stability of both isomers, resistance to fatigue during cyclic write and erase processes, fast response, high sensitivity and nondestructive readout capability [161,162]



**Fig. (6).** Photochromic behavior: Isomer interconversion.

New azo-dye-doped polymer materials are used for recording dynamic holograms [163]. Dynamic holograms with high diffraction efficiency have been recorded at 468

nm, and study on efficiency of the Write, Read and Erase (WRE) cycle in these azo-dye-doped polymer materials is carried out. Significant observations in these materials are: (i) no need to change the polarization of the writing beam to erase the recorded holograms, (ii) WRE cycle is very fast (3–6 s) and (iii) recording of more than 250 WRE cycles completed without any fatigue.

PMMA matrix, doped in (*N*-4'-methoxy-2-methyl-5-phenyl)-3-pyrrol-ethylidene (isopropylidene) succinic anhydride fulgide, is seen to exhibit photochromic behavior [164]. No photodegradation is detected after more than 450 writing-erasing cycles. Optimal exposure for holographic recording media (10  $\mu\text{m}$  thick) and the diffraction efficiency is observed to be 1047  $\text{mJ}/\text{cm}^2$  and 2.26% respectively. Holographic grating with 1680 lines/mm at writing angle  $\theta=30^\circ$  is observed.

Photochromic diarylethene, 1, 2-bis [2-methyl-5-(3-fluorophenyl)-3-thienyl] perfluoro-cyclopentene has shown good photochromic reactions both in solution and in PMMA matrix by photo-irradiation [165]. Using the diarylethene/PMMA film as recording medium and a He-Ne laser for recording and readout, four types of polarization holographic optical recording are accomplished for the first time. The results show that the orthogonal circular polarization recording is the best method for holographic optical recording when the target photochromic diarylethene is used as recording material.

Phenanthrenequinone (PQ)-doped poly (methyl methacrylate) (PMMA) has been reported as holographic recording medium [166]. When the material is illuminated with an interference pattern, two gratings are formed. The first consists of PQ molecules that are attached to the polymer matrix via photochemical reaction and the second consists of unattached PQ molecules. Subsequent baking of the material causes acceleration in the diffusion rate of the unattached PQ molecules, which causes an overall amplification of the resulting diffraction efficiency.

Holographic recording in a new photopolymer system, created by copolymerization of an optically inert monomer, methyl methacrylate, and a second monomer that is optically sensitive, is demonstrated [167]. On exposure of the recording material to light, a portion of the optically sensitive component detaches from the polymer matrix and causes hologram amplification through diffusion of the free molecules. Post recording grating amplifications as high as 70% is observed.

Study on photochromic properties of diarylethene with 2, 5-dihydrothiophene bridging unit has shown excellent ring-open and ring-closed photochromism with UV/VIS light irradiation [168]. Holographic recording on thin film of PMMA-diarylethene as recording media is performed. Six different images are recorded in the same place on the sample with the dimension of  $64\ \mu\text{m} \times 42\ \mu\text{m}$  by the intersecting object beam and a reference beam with an intensity of  $15\ \text{mW}/\text{cm}^2$ , and the stored information is readout by the attenuated reference beam with an intensity of  $0.5\ \text{mW}/\text{cm}^2$ .

As most of the photochromic compounds used for holography exhibit poor thermal stability attempt has been made to enhance the thermal stability. One invention

discloses a holographic recording method and device in which the recording medium is a polymer such as polyester, cellulose acetate etc. in which photochromic material is incorporated [169]. Hologram is recorded by bleaching the photochromic material using a laser beam. The photochromic materials are a class of fulgides and fulgimides. The mechanism is to convert the photochromic materials, present in the medium, to colored cyclic form by using UV radiation. During holographic recording the cyclic form is bleached to non cyclic form. The action is in the molecular level ensuring high sensitivity of the medium.

One invention describing an optical recording medium of thermoplastic contains radiation-absorbing polymeric dye capable of selective radiation absorption in the wavelength range 300–1000 nm [170]. Thermoplastic deformation of the material is induced by a focused beam of radiation.

An optical storage system incorporating a compact optical storage means and an optical head is invented [171]. It relates to a holographic optical storage card able to store large amounts of data in a relatively small area and a read/write/erase head for use with the storage card. Photochromic crystals/polymer is used in some compositions.

A novel photochromic dithienylethene, [1-(2-methyl-5-formyl-3-thienyl)-2-(2-methyl-5-naphthyl-3-thienyl)]per-fluorocyclopentene (1a), is synthesized and its photochemical properties, such as photochromism in solution as well as in poly-methylmethacrylate (PMMA) amorphous film, fluorescence are investigated in detail [172]. Photon-mode holographic optical storage using dithienylethene as recording medium is performed successfully.

Holographic data storage materials based on dye-doped polycarbonate are described by Erben *et al.* [173]. The dyes are selected from the class of *o*-nitrostilbenes, which irreversibly bleach under exposure to light and show high thermal stability before and after exposure. The reduction in concentration of the dye in the host after exposure induces refractive index variations over a wide range of wavelengths and extends well away from the dye absorption peak conforming to the Kramers-Kronig relationship. The materials are injection moldable into the standard disc format and have negligible shrinkage during data storage. Samples were produced using different dyes and various concentrations in a polycarbonate host and processed on professional CD/DVD equipment. The refractive index change is as high as 0.04.

Azodye-doped  $\text{TiO}_2$ /ormosil hybrid materials for photonic applications are prepared by a low temperature sol-gel process from an organic-inorganic hybrid system [174]. Acid-catalyzed solutions of  $\gamma$ -glycidoxypropyltrimethoxysilane and methyltrimethoxysilane mixed with tetrapropyl orthotitanate were used as hybrid matrix precursors. The *trans-cis-trans* photoisomerization of azo-benzene small molecules in sol-gel hybrid organic-inorganic matrices are induced by a photoirradiation with UV light and subsequent visible light. The hybrid film doped with azodyes and heated at a lower temperature is suitable for applications in optical storage or optical switch. The planar waveguide properties of the hybrid films indicates that it is possible for the as prepared hybrid films to integrate directly on the same chip

of the optical storage or optical switch devices with the pump source.

## 2.6. Photorefractive Composition

The photorefractive effect is a nonlinear optical effect seen in certain crystals and other materials that respond to light by altering their refractive index. The effect can be utilized for storing temporary, erasable holograms and holographic data storage. On illumination of photorefractive material by coherent beams (signal and reference) of light interference between the beams results in a pattern of dark and light fringes throughout the matrix. In regions where a bright fringe is present, electrons can absorb the light and be photo-excited to the conduction band of the material, leaving an electron hole (net positive charge). Once in the conduction band, the electrons are free to move throughout the crystal. Since the electrons are being excited in the bright fringes, the net electron drift is towards the dark-fringe regions of the material. The refractive index of the crystal changes in the regions where the field is strongest. This causes a spatially varying refractive index grating throughout the crystal.

The major disadvantage of the monomer-polymer type recording medium is the possible distortions of the holograms due to shrinkage during polymerization. Photo-addressable--photochromic and photodichroic polymers that undergo a change in isomer state are reversible and relatively fast (msec). However, the disadvantages associated with these systems are fast dark relaxation, short dark storage time and the requirement of coherent light sources. Photorefractive polymers exhibit high dynamical range with low intensity illumination.

Energy transfer between two laser beams writing a volume hologram in a photorefractive polymer composite is utilized for video-rate optical processing applications [175]. A net increase in image intensity as high as a factor of 37 can be observed within one video frame time (33 ms) during application of total beam intensity of 1 W/cm<sup>2</sup> and 77 V/ $\mu$ m. Moving object detection (novelty filtering) is also demonstrated.

The photorefractive composition may be made by mixing the molecular components that provide the individual properties required into a host polymer matrix. Fig. (7) shows the representative chemical structure of photorefractive polymer. However, most compositions prepared in this way are not stable over time, because phase separation tends to occur as the components crystallize. Such type of compositions shows almost 100% diffraction efficiency. However, the response time is not satisfactory over 100 msec. Reasonable photorefractivity is attained when such materials are doped with large concentrations of chromophore, such as 25 wt % or more.

The carbazole-substituted polysiloxane sensitized by 2, 4, 7-trinitro-9-fluorenone is used as a photoconducting medium and 1-[4-(2-nitrovinyl) phenyl] piperidine is added as an optically nonlinear chromophore to record photorefractive effect [176]. The diffraction efficiency observed using a 100  $\mu$ m-thick film is 71% at the electric field of 70

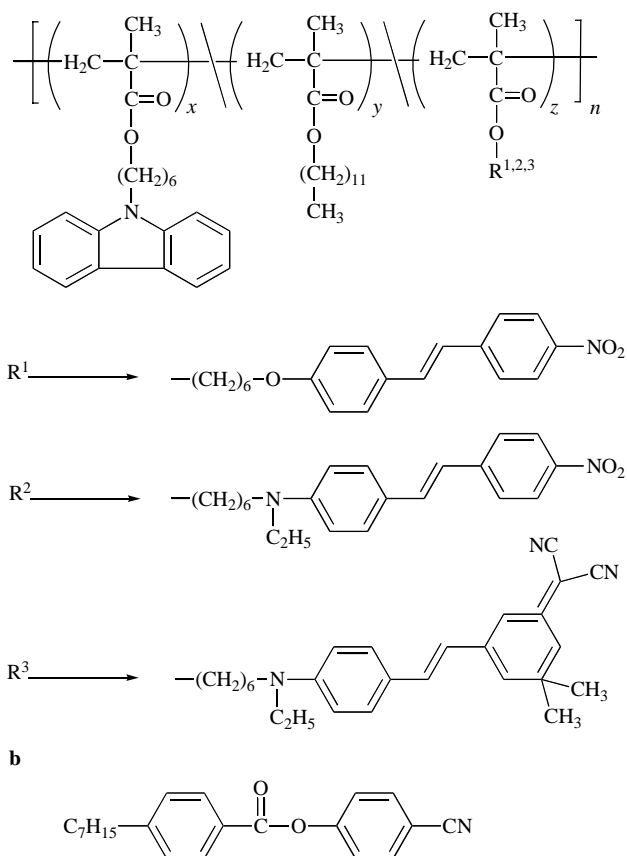


Fig. (7). Representative Chemical structure of photorefractive polymer.

V/ $\mu$ m. The potential of the current polymer material as a holographic recording medium is evaluated by the demonstration of holographic recording and subsequent reading of optical image.

In another invention a photorefractive (PR) device, comprising of a layer of a photorefractive polymer composite sandwiched in between two transparent electrodes, is fabricated [177]. The PR polymer composite composition is made of a photoconducting polymer, a photosensitizer, a second-order non-linear optical chromophore and a plasticizer. The PR polymer composite shows storing ability of image generated by interfering two coherent light beams inside the material. The diffraction efficiency of about 100% and high net two-coupling gain (>200/cm) are observed. The writing of information is reversible making it suitable for read/write holographic storage and real-time image processing applications.

A fundamental limitation of recorded space charge gratings in photorefractive crystals is the time dependent decay of even "fixed" gratings, which is accelerated at elevated temperatures. Substantial improvements in photorefractive device lifetimes are done by control of electron migration which causes decay of gratings in photorefractive materials due to diffusion and other effects. A new class of photorefractive devices using compensating electronic and ionic gratings having relatively low efficiency but usable gratings is developed by arranging the gratings to be

reflective in region outside the photo-excitation wavelength band of the photorefractive material [178]. Longer lifetimes in high efficiency gratings are achieved by constant or periodic illumination of photorefractive materials to attain uniform charged distribution of electrons.

One invention describes a holographic optical storage card which is able to store large amounts of data in a relatively small area having read/write/erase ability [179]. The erasable storage medium is a field-erasable photorefractive polymer material. Erasing is performed by applying a strong electric field to realign the chains of the polymer of the storage medium.

A photorefractive compositions includes a copolymer component that provides both photoconductive (charge transport) as well as non-linear optical ability and optionally sensitizer and plasticizer components [180]. Both the photoconductive and non-linear optical moieties are incorporated into the chemical structure of the copolymer mostly as side groups. The plasticizer, mostly linear or branched alkyl moiety, is also attached as side group. Photoconductive groups are usually phenyl amine derivatives, particularly carbazoles and di- and tri-phenyl diamine. Chromophore groups are aniline-type groups or dehydronaphthyl amine groups. Polymer backbone such as polyurethane, epoxy polymers, polystyrene, polyether, polyester, polyamide, polyimide, polysiloxane, and polyacrylate having appropriate side chains are used.

A chalcogenide glass comprising of sulphur and phosphorus, undergoes photostructural change in response to illumination with bandgap or sub-bandgap light resulting in a change of refractive index of the chalcogenide glass [181-182]. The invention relates generally to materials used for forming photorefractive holographic recording media usable as non-volatile WORM (write once read many) photorefractive holographic media.

Various photorefractive materials are used in another invention claiming advantages over shaping and wavelength control [183]. Inorganic photorefractive material used are ferroelectric crystal material such as barium titanate, lithium niobate and bismuth silicate. An organic photorefractive material is preferably used for various advantages over inorganic materials such as ease of shaping and control of sensitive wavelength. Another invention describes data writing and reading device capable of writing and reading data with respect to a holographic storage medium [184]. The storage medium has write-once read-many (WORM) memory and comprises of a photorefractive crystal and a photopolymer.

## 2.7. Nanoparticle Dispersed Composition

### 2.7.1. Holographic Assembly of Nanoparticles in Photopolymers

Holographic dry photopolymers are useful for data storage applications if both refractive index modulation ( $\delta n$ ) and dimensional stability are high. [185] However, it is difficult in conventional all-organic photopolymers due to limited refractive-index range of organic materials. Methods for holographic manipulation of nanoparticle assemblies in a photopolymer syrup and its use in photonic applications are

described by Suzuki et. al. and Tomita *et al.* [186-188]. Inorganic materials possess a wide variety of refractive indices. Therefore, use of inorganic nanoparticles as an optically mobile component in a photopolymer syrup offers the opportunity to attain larger  $\delta n$  compared with conventional all-organic photopolymers. The inclusion of nanoparticles also ensures appreciable suppression of polymerization related shrinkage leading to high dimensional stability.

Photo-insensitive nanoparticles are not consumed and undergo counter-diffusion from the bright to the dark regions. Their chemical potential increases in the bright regions due to consumption of the monomer. Thus the mutual diffusion process continues until photopolymerization is complete. Redistribution of nanoparticles under holographic exposure is thus accomplished resulting in compositional and density difference between the bright and the dark regions. Thus a refractive index grating is created. Fig. (8) shows the distribution of constituents (monomer and nanoparticles) before and after exposure. It is also demonstrated that volume holographic recording in ZrO<sub>2</sub> nanoparticle-dispersed acrylate photopolymer films have very low scattering loss [189]. More than thirty-times reduction in the scattering coefficient, as compared with those of previously reported TiO<sub>2</sub> nanoparticle-dispersed photopolymers, is achieved. It is shown that the refractive index modulation as high as  $5.3 \times 10^{-3}$ , together with substantive photopolymerization-shrinkage suppression, is obtained at the nanoparticle concentration of 15 vol.%. Dependences of nanoparticle concentration and grating spacing on the refractive index modulation are also investigated. Photopolymerization of aromatic methacrylate is investigated in organic-inorganic nanocomposite films for holographic writing [190]. High photoconversion leading to diffraction efficiency greater than 95% is achieved.

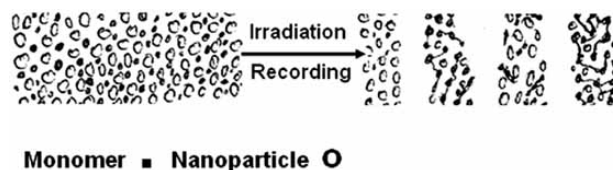


Fig. (8). Distribution of constituents (monomer molecules and nanoparticles) both (a) before and (b) during holographic exposure.

However, not much invention has been patented till date. A holographic recording material composition used for storing optical information as a spatial variation of refractive index have (a) a compound having at least one polymerizable

functional group; (b) a photopolymerization initiator; and (c) colloidal silica particles having an average particle diameter of from 4 to 30 nm [191]. Another invention relates to an optical storage medium using nanoparticles. According to the invention, the optical storage medium has two or more storage layers with nanoparticles, each storage layer being made of a dielectric material, wherein the dielectric materials of at least two storage layers have different dielectric permittivity [192].

## 2.8. Photoactive Liquid Crystalline Polymer

Azobenzene-containing polymers are among the most studied photoactive polymers.[193-195] The reversible photoisomerization between the rodlike trans and the bent cis isomers of the chromophore is effectively utilized in all studies. However, when azobenzene polymers are used for holographic recording, a simple grating formation due to a periodic modulation of refractive index between disordered trans-and cis-azobenzene creates only small refractive index change. Fig. (9) shows the cis-trans interconversion and Change of LC state through irradiation. On the other hand, liquid-crystalline azobenzene polymers have shown great promise [196]. The large modulation of refractive index arises from a photoinitiated phase transition between the nematic state and the isotropic state. Nematic state is compatible with the rod-like trans-azo-benzene and the disordered state is created due to disorganization of LC state by bend cis-azobenzene. Holographically formed Polymer Dispersed Liquid Crystals (H-PDLC) are phase-segregated liquid crystal / polymer composites which enable electrically switchable holographic recordings. They are formed using a holographic exposure apparatus to create an interference pattern, which is recorded through polymerization to produce

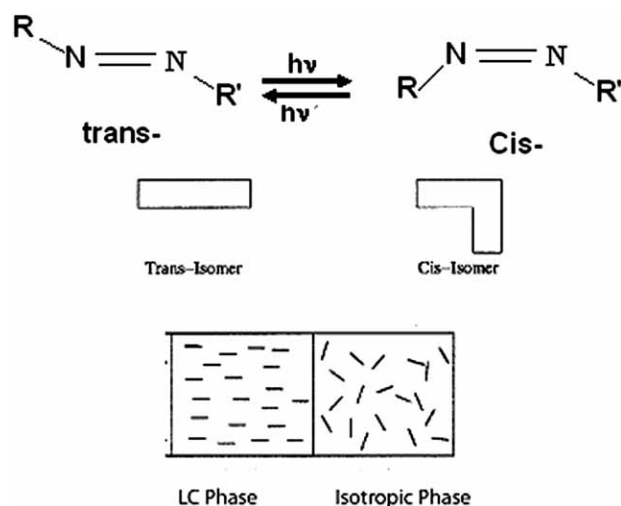


Fig. (9). Cis-trans interconversion and Change of LC state through irradiation.

Bragg-mode gratings. Application of an electric field eliminates the Bragg grating, and the material appears optically transparent.

Shibaev *et al.* reported a series of cholesteric copolymers containing combined chiral-photochromic side-groups which are characterized by selective light reflection in the visible and IR spectral regions [197]. The polymers are shown to be promising candidates for color data recording.

The action of light leads to the isomerization of both chiral photochromic groups and the photochromic group alone. Helical twisting power of the chiral moiety is effected. This process results in sharp changes in the helical structure and the optical properties of the polymer. By properly selecting the copolymer composition or preparing blends of LC polymers with low-molar-mass chiral and photochromic dopants, it is possible to obtain materials with different characters of the light-induced transformations [198]. The photochromic LC copolymers are considered as promising materials for reversible and irreversible black/white and color data recording for use in optoelectronics, data storage (in optical memory systems), holography, and color projection techniques etc.

Few inventions are patented by utilizing the isomerization phenomenon. It is claimed that a device to be used for reversible optical information storage, comprises polymeric liquid crystals as a storage medium [199]. The device contains a film comprised of a liquid crystal main chain polymer and the information is stored by means of a local variation of the molecular ordering. Accordingly to this reversible optical information storage does not depend on the polymer material being in a viscous region, storage is reliable and not subject to the influence of spurious fields. Information can be repeatedly stored and read without decomposition of the device. All the recorded information can be erased and the original state can be restored by increasing the temperature of the storage medium above  $T_i$  (isotropization temperature) and cooling in an electric or magnetic field.

One claim which proposes that the difficulties in high temperature recording related degradation can be avoided if certain polymeric side chain liquid crystals are used. It is then no longer necessary to keep the temperature below the  $T_g$  to store the device, but stable storage for many years should be possible with temperatures above  $T_g$  and below a temperature ( $T_i$ ) at which the polymeric material begins to become fluid. A device for reversible optical information storage without maintaining the polymer in a viscous region is described [200]. Polymeric liquid crystals, which contain photochromic groups as side chain, were used for the storage application. The storage and reading can be done on the solid film at room temperature. The information is erased by heating the sample above glass temperature ( $T_g$ ).

The pre-alignment procedures, as followed in earlier embodiments, may not be desirable in commercial storage devices as they tend to increase the complexity of the fabrication processes leading to increased chances of failure of the final product. Further, all the liquid-crystalline polymers, used earlier, appear to be of relatively low molecular mass, which results in poor mechanical properties. A macroscopic

pically isotropic side chain liquid crystal polymer, containing photochromic mesogenic groups, is synthesized [201]. By irradiation with light it can be permanently or substantially permanently converted into an optically anisotropic phase without any pre-orientation. The polymer is usually a polyester having mesogenic group. The holographic writing is demonstrated and the stored information density is about 5000-6000 lines/mm. Another invention relating to recording without pre-orientation is also described [202].

The films, used for holographic writing, are cast from an organic solvent and the films are irreversibly crosslinked. The invention addressing this problem, describes reversibly crosslinked, orientable liquid crystalline (LC) polymer films, comprising of an LC poly (methacrylate) PP and/or a mixture of PP with low molecular weight crosslinking components [203]. LC methacrylates form one comonomer whereas the crosslinking groups residing on other comonomer are -COOH or -CONH. A macroscopically isotropic side chain liquid crystal polymer containing photochromic mesogenic groups is used for permanently or substantially permanently converting into an optically anisotropic phase using suitable radiation without pre-orienting the LC. Grating strength increases with time of illumination and 15% grating efficiency is reported. Oligomeric siloxane compounds having liquid crystal properties (smectic liquid crystal phase) are also claimed to be used for optical data recording and storage applications [204].

Study on effect of molecular weight of polymer on the storage properties has also been carried out [205]. Side-group polymers (Mol. Wt. 5000 to 2,000,000) having permanently shape-anisotropic side groups are used for optical components which can be employed in optical data storage and transfer. Side-group polymers contain photochromic side groups (Azo) and permanently shape-anisotropic side groups (Benzoates) having high anisotropy of the molecular polarizability which can be converted easily into an optically isotropic, transparent, amorphous state which does not scatter light.

Holographic optical elements are formed from a polymer dispersed liquid crystal (PDLC) material comprising a monomer, a dispersed liquid crystal, a cross-linking monomer, a coinitiator and a photoinitiator dye [206]. These PDLC materials exhibit clear and orderly separation of the liquid crystal and cured polymer, whereby the PDLC material advantageously provides high quality optical elements. The PDLC materials used in the holographic optical elements may be formed in a single step. The holographic optical elements may also use a unique photopolymerizable prepolymer material that permits *in situ* control over characteristics of resulting gratings, such as domain size, shape, density, ordering and the like.

A hologram-recording material, including a photoresponsive molecule, a reactive molecule having an intrinsic birefringence, and a photopolymerization initiator that accelerates polymerization and/or crosslinking of the reactive molecule having an intrinsic birefringence is reported [207]. The concentration of the photopolymerization initiator is maintained in the range of less than about 0.1 wt % relative to the hologram-recording material, and that of the reactive molecule having an intrinsic birefringence is in a

range of about 30 to 80 wt % relative to the hologram-recording material.

## 2.9. Sol-gel Matrix

The problem of shrinkage during photopolymerization or crosslinking occurring during holographic writing needs sufficient attention to get good quality hologram with acceptable storage stability. Among various attempts the work on using sol-gel matrix needs special mention as the property enhancement and shrinkage minimization can be achieved simultaneously.

Correction of the shrinkage observed during UV post-recording curing in a holographic sol-gel material is shown by using various chemical formulations for the composition of hybrid supporting matrix [208]. A chemical modification of the matrix noticeably attenuates the shrinkage (from 1.3% to 0.4% of the material's initial thickness with the inclusion of just 20% tetramethylorthosilicate). Fig. (10) shows the chemical structure of tetraethoxy silane responsible for crosslinking. Material with improved stability for permanent data storage applications is achieved with different binders. In addition, a theoretical study has revealed the way by which to compensate for angular deviation in the Bragg condition during UV post-recording by tailoring the binder shrinkage ( $s$ ), maximizing the refractive-index modulation capability of the photosensitive mixture ( $\Delta n$ ) or both.

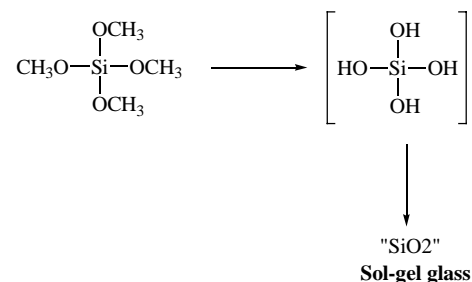


Fig. (10). Chemical structure of tetraethoxy silane responsible for crosslinking.

A recording material for holograms included a metal oxide porous body with an oxygen donor substance in the pores [209]. The production is done by a sol-gel process. A metal alkoxide (preferably tellurium alkoxide) precursor is dissolved or dispersed in a solvent. Water and acid are used for hydrolysis reaction of the precursor. The precursor undergoes partial polymerization by the hydrolysis reaction to form a partially polymerized oligomer as a stable sol. The sol was transferred to a substrate and allowed to stand in air. The gel obtained, by allowing the sol to stand in air, is then heated in a reducing atmosphere to form a metal oxide porous body having oxygen-deficient sites. In the case of separate addition of an oxygen-deficient material, it may be added during dissolution or dispersion of the precursor. Refractive index variation after holographic recording was around 0.2 which is considered to be very high.

## 2.10. Polyelectrolytes

Improvement of existing holographic recording medium, to keep pace with the demanding technologies, is always

being attempted. The latest invention is that a polyelectrolyte can be used as holographic recording medium with high diffraction efficiency by applying conventional lithography techniques and heating [210]. The main advantages of this material are that it is non-toxic, water soluble, less production time and less unit cost to replica holograms. Fig. (11) shows the typical polyelectrolyte structural units.

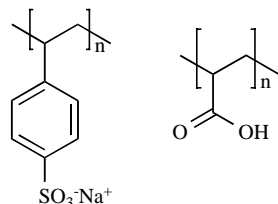


Fig. (11). Typical polyelectrolyte structural units.

Till now, no important claim has been made in the form of patent. Looking at various parameters, it is expected that the research work will be amplified and related technologies will be coming to the users in recent future.

### 3. CURRENT AND FUTURE DEVELOPMENTS

Holographic storage is very important to modern technologies concerned to communication and display. Hundreds of separate holograms, known as pages, can be recorded through the full depth of the storage medium. Nanomemories and nanodisk drives, which will soon be commercialized, will materialize quantum leaps in gigabytes at very nominal cost. It is also expected that improvements in screen display will be very rapid.

In this article, all possible polymer based compositions such as silver halide emulsion, dichromated gelatin, photopolymers, photoresists, photochromics, LC polymers, photorefractive polymers, polyelectrolytes and nanocomposites are discussed. All the important relevant developments are covered from both papers and mostly from patents. It has been observed that first few fields were ventured by researchers during early seventies. The developments are observed to be rapid during nineties. Every item has its advantages as well as disadvantages. Over the years attempts have been made to address the problems in all the types of recording medium. For example, silver halide emulsion is still being actively studied during 2007. A great number of patents and papers are available in literature. The combination of dichromated gelatin with silver halide is being tried with new techniques which are able to eliminate earlier associated problems. Photopolymers are the most active component in development of holographic recording medium. Various attempts are made to increase the diffraction efficiency, decrease the polymerization related shrinkage, minimize the degradation on storage, and minimize the post processing. In fact, present trend is to use multiple curing type monomers and oligomers so that one is polymerized (solidified to film) in presence of the other. The second one is not affected by this process. Later hologram is recorded with much superior properties as compared to the conventional one. This reduces the storage problem of holographic film before recording and minimizes the shrinkage. Hollow glass spheres, sol-gel methods are being tried to enhance the

performance and stability. Photoresist and photochromics also will remain subject of modification. Photorefractive polymer has just started showing its advantages over other systems. Slowly this will become a highly pursued material. For WORM technology LC polymers are always there. Although this is not a hot topic to developers till now, it is going to remain a topic of persistent interest. Polyelectrolyte work has just initiated. It has to go long way to prove its worth. Finally, looking at the mechanism of recording, using nanocomposites of photopolymers, it is certain that this will become a prominent future material.

Regarding future holographic recording, it is expected that the nanocomposite, polyelectrolytes and photorefractive polymers will remain most active materials of development. However, other materials can not be ruled out as further development will make it more competitive along with its existing strength. For example, The European Commission funded Silver Cross project in which NEWI is partner aims to develop a robust recording medium by developing a new ultra-fine-grain, high sensitivity (less than  $2 \text{ mJ cm}^{-2}$ ) low light-scattering, panchromatic silver halide emulsion for color holograms and HOEs.

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