INTRODUCTION

The history of optical recording can be traced back to 1970's with the invention of the first laser videodisk. Until that time, the recording of sound and images was done through the use of magnetic tape. But during 70's technologists had realized the fact that large amounts of data or informations could be stored and easily retrieved, by using a new technology called optical recording. Today, everything from CDs to CD-ROMs; from DTS (digital theatre system) to holograms, makes use of optical recording technique to record and store informations. Thus optical technology was established as a mainstream media supplier for audio, video and computer storage. Optical storage sales are exploding; billions of CDs are sold annually. The remarkable success of recordable and rewritable optical discs is based on their removability, compatibility standards and low cost mass production, and also on excellent lifetime [1-3].

The success of CD technology indicated the possibility of data storage based on optical phenomena as an alternative to magnetic storage. A key difference is the ease with which the optical media can be removable. Removability is an attractive feature, but makes standardizing efforts more complex compared with magnetic storage. Significant advances in the enabling technologies made
it possible to increase the capacity on the digital versatile disc (DVD) format that was introduced in 1995. The basic structure of DVD-ROM is similar to the conventional CD-ROM, storing the data as a 2-D pattern. The DVD stores 4.7 giga bytes (GBs), which is 7 times the capacity of CD. The implementation of blue-violet diode laser in DVD system will lead to a further increase of storage density by a factor 2.5. The blue DVD family is expected to penetrate the storage market with in the next five years [4-9]. Thus the optical data storage technology offers

- Very high storage density
- Low cost
- Direct access
- Very good performance
- Multiple user concurrent access
- Reduced physical requirements
- Rewritable or permanent media
- Very long archive
- Removable media.

In the future, optical data storage is expected to follow two directions to improve the capacity and performance of discs that are available currently. One-way predicts the further increase of the areal storage density that use only the surface of a medium for writing or reading. On the other hand, optical storage is based on laser material interaction so that an entire spectrum of different optical phenomena can be used to realize an optical memory. Developments of non-linear optical materials that exhibit strong laser induced changes of their optical properties enable various novel approaches to become realizable practically. Using non-linear optical
effects, advanced technological solutions for optical storage may take advantage of new spatial and spectral dimensions. Technologies like holographic storage\(^{10-11}\), two-photon or fluorescent memories etc are at the various stages of development. Opening a new dimension in addition to the 2-D surface of a storage medium, they have the potential to improve tremendously both capacity and data transfer rates of optical storage systems.

The simplest way to use the third dimension of a storage medium is multilayer storage. Using multiple data layers instead of one, the overall storage capacity will grow linearly with the number of layers. Data layers are separated by thin transparent spacers and addressed separately by a focused laser beam. The number of layer per side of the disc is limited strongly by higher optical power requirements and interlayer cross talk. The aberrations that appeared while focusing to several layers at different depth simultaneously combined with other recording techniques make the multiplayer approach more attractive. In the case of fluorescent memories that use transparent materials as storage media, the number of layers can become very large. Such quasi-3D optical memories use the volume of storage medium by recording the data as binary planes stacked in 3-D. The data is stored by discrete bits in the plane, but also through the volume\(^{12-15}\).

### 1.1. Holographic data storage

In holographic storage, the information is recorded through volume. One of the unique characteristics of optical volume storage is the very high bit density that can be achieved. A hologram is actually made of a complex system of fine lines, which form diffraction gratings. These diffract and
redirect light to form the 3-D image of the original object. These complex gratings are created during recording of a hologram. When the object and illuminating laser beams are arranged so that the light reflected off the object forms an interference pattern. When the film records the pattern a diffraction grating is formed. Consistent characteristics of holographic images are:

- The images are true 3-D images, showing depth and parallax and continually changing in aspect with the viewing angle.
- Any part of the hologram contains the whole image.
- The images are scalable. They can be made with one wavelength and viewed with another, with the possibility of magnification $^{[15-18]}$.

Holography is a two-step method. The first step is the recording of an interference pattern. In this step the object is illuminated with a coherent light wave. This wave is split into two beams. One beam hits the object directly and one beam (reference beam) hits the film. The object reflects some of the light (object wave). The object is recorded in the hologram superimposed with reference beam (see figure 1.1).

**Fig 1.1. Hologram recording**
In the second (the reconstruction) step the hologram (suitably processed) is illuminated with the reference wave (figure 1.2). The reference wave has to be the same as in the recording process. This reference wave called reconstructing wave is diffracted by the interference pattern of the hologram so that the object wave (virtual image) is reconstructed. Additionally a second image (real image) is also reconstructed.

**Fig.1. 2. Hologram Reconstruction**

Bragg-selectivity allows many holograms to be stored in the same plate by applying appropriate multiplexing methods [26]. Holographic memory [23-25] is a promising technology for data storage because it is a true 3-D system, data can be accessed, an entire page at a time instead of sequentially, and there are very few moving parts so that the limitations of mechanical motion are minimized. Combined with multiplexing, the inherent parallelism of holographic storage can provide a huge increase in both capacity and speed. For more than 30 years, holography has been considered as a storage approach that can change standards and prospects for optical storage media in a revolutionary manner. In the memory hierarchy, holographic memory lies somewhere between RAM and magnetic
storage (Table 1) in terms of data transfer rates, storage capacity and data accesses times\textsuperscript{[17,19-22]}

*Table 1. Comparison on the memory hierarchy of holography, RAM and magnetic storage.*

<table>
<thead>
<tr>
<th>Storage medium</th>
<th>Data Access time</th>
<th>Data transfer rate</th>
<th>Storage capacity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Holographic memory</td>
<td>2.4 $\mu$s</td>
<td>10 GB/s</td>
<td>400 Mbits/cm$^2$</td>
</tr>
<tr>
<td>Main memory (RAM)</td>
<td>10-40 ns</td>
<td>5 MB/s</td>
<td>4 Mbits/cm$^2$</td>
</tr>
<tr>
<td>Magnetic Disk</td>
<td>8.3 ms</td>
<td>5-20 MB/s</td>
<td>100 Mbits/cm$^2$</td>
</tr>
</tbody>
</table>

Depending on a number of supporting technologies, holographic memories became realizable with advances in photonics technology, particularly with improvement in liquid crystal modulators, charge coupled devices, semiconductor detectors and laser sources. On going research efforts have led to impressive advances.

Another approach to 3-D optical storage offers a compromise by combining bit-oriented storage of CD-DVD and holographic volume recording. Micro lithography expands surface storage into 3-D by storing the data as microscopic volume gratings instead of bits. A thin photopolymer layer is used as a storage medium. The optical system has many components in common with CD-DVD systems. The only additional component is a reflecting unit underneath the disc that is needed for writing. Micro gratings are written holographically with a highly focused laser beam that is reflected back to create a reflection grating. Holographic recording makes it possible to store several gratings in the same
position by multiplexing. High densities and data rates can be achieved by combining wavelength multiplexing and multiple layer storage while maintaining the optoelectronic system simple and relatively cheap. Volume holographic storage and two-photon or fluorescent storage hold promises for high capacity, high-speed systems. In addition, micro holographic disc or fluorescent multiplayer discs that store the data bit wise as 'fluorescent pits', can also satisfy the requirements for downward compatibility and low cost media. A crucial aspect for the reliability of all these systems is the storage material itself. Many types of materials have been investigated in recent years as optical storage media including inorganic photorefractive crystals, organic photopolymers, and biological systems such as protein bacteriorhodopism or DNA polymer.

Progress in the last few years has been very impressive, particularly in the field of photopolymers that offer a wide variety of possible recording mechanisms including both write-once and rewritable media. In particular new photopolymer materials have been introduced for holographic storage. Optimization and further development of photopolymer media will be the key to success of this and other advanced optical storage technologies.

1.2. Photosensitive materials

These are materials that absorb light of specific wavelength and serve as an activator, also materials that react to light changing their own molecular structure and causing polymerization or cross-linking. Photosensitive materials permanently change their refractive index upon exposure to intense light, enabling a wide range of optical device structure to be rapidly patterned via a single photo-processing step. These materials offer rapid and cost efficient
manufacturing of photonic devices that possess unique optical and physical property with direct impact on micro system for nuclear safety and security. The enhanced versatility afforded by the photosensitive materials \cite{27-34} also plays a key role in the development of new hologram recording materials. There is a need for new photosensitive materials that are as efficient and highly non-linear as conventional photorefractive materials, but more versatile and cheaper.

1.3. Requirement of a photosensitive material

Finding the optimal parameters for the application of holography to data storage is a challenge under taken and the quantitative testing and comparison of a variety of different materials continues to make up significant part of the effort in optical data storage research. There are a number of properties a good holographic storage material should have and is listed below:

- Excellent optical quality
- Phase material
- Thick (>500 microns)
- High recording fidelity
- Large refractive index change
- High sensitivity
- Self-processing
- Non-volatile storage
- Fixable
- Long shelf life, inert
- Cheap
A hologram may be recorded on a medium as a variation of absorption or phase or both. The recording materials must respond to incident light pattern causing a change in its optical properties. In the absorption or amplitude modulating materials, the absorption constantly changes as a result of exposure, while the thickness or refractive index change due to the exposure in phase modulating materials. In the phase modulating materials there is no absorption of light and all the incident light is available for image information, while the incident light is significantly absorbed in an amplitude-modulating medium.

High optical quality and low scatter are required to ensure that the signal bearing wave fronts is not adversely distorted and that the noise level from scattered light is manageable. The resolution capacity of the recording material depends on its modulation transfer function. The non-linear effects of the recording material are minimized for obtaining high quality holographic images.

A thick material is required to use the Bragg effect to its fullest. A large refractive index modulation ensures that there is sufficient dynamic range to multiplex the many holograms and the high recording sensitivity allows high speed at reasonable laser power. The larger the number of holograms that are recorded on a common volume of the material, the weaker each hologram becomes, the signal strength scales as the inverse square of the number of holograms. The greater is the material’s ability to respond, the more holograms can be recorded and ultimately greater data density can be achieved.

The self-processing and fixable requirements go hand in hand. If the application calls for only a read only material, then the off-line recording of the hologram permits the use of additional process steps- even wet processing. This, in turn, assures that the holograms are fixed and will not be destroyed.
upon subsequent reading. The preference, however, is for a read-write material where in data can be recorded, retrieved and erased as required- similar in performance to magnetic or magneto-optic recording. The requirements, therefore, would be for a material that not only self develops upon illumination but one that also can be fixed to render it insensitive to subsequent illumination during the recording of additional holograms or the retrieval of data. The fixing process should also be reversible, so that the information can be erased and a new hologram recorded. Between these two extremes is a recording process where the information can be recorded but not erased; referred to as WORM (write-once-read-many), this process has wide spread applicability in areas such as medical imagery, satellite telemetry, banking and various legal documents. To meet these requirements the recording materials must have a fixing process that is irreversible- the distinguishing feature between WORM and erasable materials.

The materials must faithfully record the data beam amplitude so that high quality image can be reconstructed when the data is read out. Moreover the material should retain the stored hologram for a time consistent with data storage applications, and should do so in the presence of light beam used to read the data. For WORM storage, an irreversible material (such as a photopolymer) can be used, which provides stable recording once exposed. If a reversible material is chosen in order to implement erasable/rewritable data storage, the requirement for non-volatility is in conflict with that of high sensitivity unless a non-linear writing scheme, such as two colour grated recording is used. Long shelf life and inertness imply that the material will remain sensitive over an extended period of time and the hologram, once formed will not degrade. Finally the material must be relatively cheap
If holographic storage has had an archilles heels over years, it has been the recording material. Certainly, many successful materials have been developed, but these requirements, particularly for self-processing and thickness, greatly reduces the number of choices. A material is yet to be discovered which will have high sensitivity of silver halides, high diffraction efficiency and index modulation capability of dichromated gelatin holograms and photopolymers, recyclability of photorefractive crystals and useful at all laser wave lengths.

The ideal material needs to be highly sensitive to light but it should be able to hold a pattern of changes for many years without degrading, despite variations in temperature, humidity or pressure.

Research in both reversible and write once storage materials continue to be an important and active area for optical storage.

The different materials that are studied for recording purpose and their characteristics are shown in tables 2 and 3. The major advantages and drawbacks of these materials are tabulated in table 4. One of the attractive materials that have several advantages and different applications are photopolymers.
Table 2. Characteristics of photosensitive materials used in optical storage

<table>
<thead>
<tr>
<th>Materials</th>
<th>Spectral Range (nm)</th>
<th>Recording process</th>
<th>Spatial Freq (cy/mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Photographic materials</td>
<td>400-700</td>
<td>Reduction of Ag metal</td>
<td>&gt;7000</td>
</tr>
<tr>
<td>Dichromated gelatin (DCG)</td>
<td>250-520 and 633</td>
<td>Photo crosslinkng</td>
<td>&gt;3000</td>
</tr>
<tr>
<td>Photoresists</td>
<td>UV-500</td>
<td>Photo crosslinking or photo polymerisation</td>
<td>&lt;3000</td>
</tr>
<tr>
<td>Photo thermoplastics</td>
<td>Nearly Panchromatic</td>
<td>Formation of electrostatic latent image with electric field produced deformation of heated plastic</td>
<td>400-1000 band pass</td>
</tr>
<tr>
<td>Photochromics</td>
<td>300-450</td>
<td>Generally photo induced new absorption bands</td>
<td>&gt;2000</td>
</tr>
<tr>
<td>Ferro electric crystals</td>
<td>488</td>
<td>Electrooptic effect</td>
<td>&gt;1000</td>
</tr>
<tr>
<td>Photopolymer</td>
<td>UV-700</td>
<td>Photopolymerisation/absorption change</td>
<td>200-1500</td>
</tr>
<tr>
<td>Materials</td>
<td>Types of grating</td>
<td>Processing</td>
<td>Read out</td>
</tr>
<tr>
<td>---------------------------</td>
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<td>----------------------------</td>
<td>----------------------------</td>
</tr>
<tr>
<td>Photographic materials</td>
<td>Plane/Volume amplitude</td>
<td>Wet chemical</td>
<td>Density change</td>
</tr>
<tr>
<td>DCG</td>
<td>Plane, phase, volume phase</td>
<td>Heat</td>
<td>Refractive index change</td>
</tr>
<tr>
<td>Photo resists</td>
<td>Surface relief</td>
<td>Wet chemical</td>
<td>Surface relief</td>
</tr>
<tr>
<td>Photo thermoplastics</td>
<td>Plane phase</td>
<td>Corona charge and heat</td>
<td>Surface relief</td>
</tr>
<tr>
<td>Photochromics</td>
<td>Volume absorption</td>
<td>None</td>
<td>Density change</td>
</tr>
<tr>
<td>Ferro electric crystals</td>
<td>Volume phase</td>
<td>none</td>
<td>Volume phase</td>
</tr>
<tr>
<td>Photopolymer</td>
<td>Volume phase</td>
<td>none</td>
<td>Ref. index change/surface relief</td>
</tr>
</tbody>
</table>
Table 4. Advantages and disadvantages of photosensitive materials

<table>
<thead>
<tr>
<th>Materials</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Photographic materials</td>
<td>1. They are sensitive to light at various degree</td>
<td>1. It is absorptive</td>
</tr>
<tr>
<td></td>
<td>2. It can be coated on both film and glass.</td>
<td>2. It has inherent noise</td>
</tr>
<tr>
<td></td>
<td>3. Can cover very large format.</td>
<td>3. Limited linear response</td>
</tr>
<tr>
<td></td>
<td>4. High resolving power</td>
<td>4. It is irreversible</td>
</tr>
<tr>
<td></td>
<td>5. Easily available</td>
<td>5. It needs wet processing</td>
</tr>
<tr>
<td></td>
<td>6. It has resolution of about 3000 lines/mm</td>
<td>6. It creates print out problems on phase holograms</td>
</tr>
<tr>
<td></td>
<td>7. They have excellent shelf life</td>
<td>7. The silver crystals on the developed film cause scattering.</td>
</tr>
<tr>
<td>Dichromated gelatin (DCG)</td>
<td>1. It has resolution capacity extending beyond 5000 lines/mm</td>
<td>1. ((\text{Cr}_2\text{O}_7)^{-2}) has low sensitivity to light</td>
</tr>
<tr>
<td></td>
<td>2. Response is uniform over a broad range of spatial frequency from 100 to 5000 lines/mm</td>
<td>2. It requires long exposure</td>
</tr>
<tr>
<td></td>
<td>3. The refractive index modulation capacity is high</td>
<td>3. After processing the emulsion must be isolated from moisture. Scaling in glass is used. This makes DCG holograms thick</td>
</tr>
<tr>
<td>Photo resists</td>
<td>4. It has absorption over a wide range of wavelength.</td>
<td>4. It has poor shelf life.</td>
</tr>
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<td>---------------------------------------</td>
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</tr>
<tr>
<td></td>
<td>5. It can give reconstruction without development.</td>
<td>5. It cannot be commercialized.</td>
</tr>
<tr>
<td></td>
<td>6. The thickness of DCG can be increased or decreased by controlling the exposure and processing conditions.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>7. It has less scattering</td>
<td></td>
</tr>
<tr>
<td></td>
<td>8. It has high SNR.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>9. It is transparent.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>10. It has high diffraction efficiency</td>
<td></td>
</tr>
<tr>
<td>Photo thermoplastics</td>
<td>1. Can produce thin relief phase holograms</td>
<td>1. Sensitivity at 488 nm is poor</td>
</tr>
<tr>
<td></td>
<td>2. Adequate sensitivity at 458 nm of He-Cd laser</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1. No chemical treatments are needed for development</td>
<td>1. The maximum resolution attainable with this material is not greater than 1000 cycles/mm.</td>
<td></td>
</tr>
<tr>
<td>2. It is highly photosensitive to all visible light</td>
<td>2. The equipment required for charging and heating the layer is expensive.</td>
<td></td>
</tr>
<tr>
<td>3. Has high diffraction efficiency.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4. Stable at room temperature.</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>5.</strong> It can be reused a number of times</td>
<td><strong>3.</strong> The format of the thermoplastic film or plate is small.</td>
<td></td>
</tr>
<tr>
<td><strong>6.</strong> The recorded holograms behave nearly ideally as a plane phase hologram.</td>
<td><strong>4.</strong> The thermal development of the exposed film is critical</td>
<td></td>
</tr>
<tr>
<td><strong>7.</strong> The material is optically inert when not charged, so there is no degradation from exposure to heat and light.</td>
<td><strong>5.</strong> This film can record only those interference fringes whose spatial frequencies lie within a limited spatial frequency bandwidth.</td>
<td></td>
</tr>
</tbody>
</table>

| **8.** This material is ideal for holographic non destructive testing |  |

<p>| <strong>PHOTOCHROMICS</strong> |  |
| <strong>1.</strong> They are real time recyclable materials | <strong>1.</strong> Photosensitivity of these material is at least three order of magnitude less than that of silver halide photographic emulsion. |
| <strong>2.</strong> The hologram can be read out during or immediately after the recording | <strong>2.</strong> Low sensitivity |
| <strong>3.</strong> They require no processing or development and can be erased and reused. | <strong>3.</strong> Low efficiency |
| <strong>4.</strong> There is no inherent resolution limit since they are grain free and operate in atomic and molecular scale. | <strong>4.</strong> Low storage time. |
| <strong>5.</strong> Their storage capacity is | <strong>5.</strong> The reconstruction beam usually degrades the stored information. |
|  | <strong>6.</strong> Fatigues limit its reusability |</p>
<table>
<thead>
<tr>
<th>Photorefractive crystals</th>
<th>high.</th>
<th>7. The photosensitivity decreases with increasing number of record–erase cycle until finally they become insensitive to light.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1. High resolution</td>
<td>1. Specific problems are there relating the multiple storage of holograms</td>
</tr>
<tr>
<td></td>
<td>2. High efficiency</td>
<td>2. Low holographic sensitivity</td>
</tr>
<tr>
<td></td>
<td>3. High sensitivity</td>
<td>3. Sensitivity is less at longer wavelengths.</td>
</tr>
<tr>
<td></td>
<td>4. Reversibility</td>
<td></td>
</tr>
<tr>
<td></td>
<td>5. No fatigue observed after many recording–erasure cycles.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>6. High storage capacity.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>7. It is possible to record as hologram with 100% diffraction efficiency in a 1 cm thick crystal.</td>
<td></td>
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<tr>
<td></td>
<td>8. It is also possible to record 1000 holograms with usable levels of diffraction efficiency in the reconstructed image</td>
<td></td>
</tr>
</tbody>
</table>
1.4. Photopolymers

Polymers are finding their way into a whole host of components for optical communication, either of their own or in combination with conventional substrates\cite{35-41}.

Polymers are flexible materials. Not only do they exhibit mechanical flexibility, they also enable flexible production process and their physical properties can be manipulated on a molecular level. These properties make polymers ideal for integration into optical components for various applications. Polymers in general show material properties and optical effects – refractive index, dispersion value, optical loss, thermal and mechanical stability, stress-optic coefficient – that can be tailored and optimized by molecular engineering depending on demand. It is this ability to tailor polymers at a molecular level that allows highly compact components to be made. Moreover with polymers, simple blending and copolymerization of suitably synthesized monomers offer a superior index range that offers optical designers greater freedom in building up polymer photonic structures. The advantages of using polymers over other conventional materials are

- Short cycle
- Low cost
- Minimum number of fabrication steps
- High yield
- Higher performance
- Low scattering loss
- Dynamic provisioning
- Multiple functions
- More compact
So perhaps it is time for the optics industry to accept that polymers have advantages over conventional materials, whether used on their own or in combination with other materials. Thus polymers will be an important material used in the next generation data storage. Their use will be driven in general, by customer's desire for components with increased functionality, smaller size and reduced cost.

In recent years, a new class of photosensitive polymers has been introduced to satisfy the demand on adequate materials for holographic storage [41-56]. The recording mechanism is based on laser-induced polymerization. Diffusion of monomers supports differentiation of the bright and dark regions. A light induced grating like modulation of the refractive index occurs during exposure by polymerizing monomers and can be fixed after UV cure. In addition, holographic gratings recorded in photopolymers can be thermally processed to obtain higher diffraction efficiency.

Several photopolymer materials have been characterized for holographic data storage including classical photopolymer systems (DuPont holographic recording films), novel materials designed for storage applications (Aprilis CROP photopolymers), azo benzene side chain liquid crystalline polymers, photorefractive polymers, poly (vinyl alcohol) derivatives etc. Photopolymers such as DuPont or Aprilis are suitable for WORM (write once read only applications. In contrast, a circularly polarized laser beam can erase gratings recorded on azo benzene polymers so that rewritable storage becomes possible.

Several photoresists for excimer laser lithography, based on norbornene polymer, poly (vinyl pyrrolidone), cyclized PVA derivatives, has been synthesized and evaluated. Photoresists for printed circuit boards are designed to be cured by both radical and ionic polymerization. Radical polymerization
mechanism used for high sensitivity and ionic polymerization mechanism used for photosensitive polymers is as follows:

- It must be able to produce patterns at the desired resolution consistently.
- It must provide an edge profile consistent with the processing requirements.
- It must survive and protect the underlying film during the etching process.
- It must be readily removable after the etching process.

Thus photopolymers have been extensively investigated as holographic recording media for several decades\(^{[57-59]}\) for applications including holographic scanners\(^{[60-61]}\), LCD displays\(^{[62-63]}\), helmet-mounted displays\(^{[64]}\), optical interconnects\(^{[65-67]}\), wave guide couplers\(^{[68]}\), holographic diffusers\(^{[69-71]}\), laser eye protection devices\(^{[72]}\), automotive lightening\(^{[73]}\) and security holograms\(^{[74-75]}\).

Holograms (data) are stored in photopolymer materials as spatial modulation of refractive index created in response to an interference pattern generated by the incident laser beam. Because of photoreaction, the refractive index of the irradiated area of a material differ from that of the dark area. The larger the refractive index difference between these two regions, the greater the data storage capacity of the material. The storage capacity of the material is enhanced if the medium is thick (1.5mm), as this enables recording of many holograms in a given volume of the material and results in improved diffraction efficiency of the phase gratings\(^{[76-77]}\). To achieve the desired storage capacity, that would make holographic data storage commercially viable (~100 bits/\(\mu m^2\)) require developing a large index contrast in thick photopolymer material.
Most of the current research is concentrated in establishing a three-dimensional volume memory. However, high-density 2D memory is also of great interest for archival purposes. Although ideal materials seem to be lacking, functionalized polymers appear to be prosperous candidates. Such materials are easy to process, have high diffraction efficiency, high resolution, fast recording and fast erasure.

The important photophysical process occurring in the prominent members of the polymer family like poly (methy methacrylate), poly (vinyl alcohol), poly (vinyl carbazol), acrylamide, poly (acrylic acid) etc, used as hologram recording medium is considered. The choice of the photopolymer strongly affects the utility of the final recording. For display holograms properties like brightness, contrast, colour range and colour saturation might dominate. For holographic optical elements, the extended range of properties that may require manipulation and the choice of material to obtain each property in the required quantity makes a working knowledge of what can be done extremely useful.

1.4.1. Poly (vinyl alcohol)(PVA)

Poly (vinyl alcohol)(PVA) came into use as hologram recording material from late 70's onwards. PVA has been dichromated and was used as a real time material. The images were fixed by heating the film. PVA is easily available, mix and coat. A variety of dyes have been used as sensitizer in PVA for various applications which include methyl orange, thionine, dichromate, fluorescien, ferric chloride, Erythrosin B, Eosin Y, Rose Bengal, methylene blue, Xanthene, chrysodine, mordant, yellow3R, hydrohalic acid of some metals etc\textsuperscript{[78-100]}. 
Light sensitivity and photoimaging characteristics of PVA (PVA)-H\textsubscript{2}PtCl\textsubscript{6} and H\textsubscript{2}PtCl\textsubscript{6} system were investigated and compared with those of silver halide gelatin system \cite{78}. Real time volume hologram recording and reading of transmission holograms were performed on dichromated poly (vinyl alcohol) (DCPVA) and thionine dye-PVA matrix \cite{79,80}. The film obtained in the former case was not erasable where in the latter case a grating reinforcement was observed during the reading process. DCPVA films with and without electron donors and dyes were employed for real time holographic recording and for the fabrication of holographic optical elements. PVA can also serve as a binder for a monomer and act more like other photopolymers. In its dicromated form it is a photo crosslinker and as such has no migration but the latent images in PVA is many times better than the latent images in dichromated gelatin. The integrity of the recording is very high with very little damage done by over writing multiple times. As a crosslinker it is not a saturable media and can be over exposed, however it requires about 100 mJ/cm\textsuperscript{2} to form a strong recording.

Fluorescien dye/PVA, eosin dye/PVA, Cr(VI)/PVA and Fe (111)/PVA systems as promising recording media in the application of holography and non-linear optics has been investigated \cite{81,82}. Detailed study on FeCl\textsubscript{3} doped PVA containing tert-Bu-hydroperoxide is done by taking various parameters like angular selectivity, frequency response of the media, refractive index change etc \cite{83}. The photochemical reactions of methylene blue in gelatin and PVA matrices due to He-Ne laser exposure were reported\cite{84}. Laser irradiation results in the formation of new absorption peak, which matches, with that of thionine. Retention of this optical absorption change due to irradiation for several months was observed. This study also confirms that on irradiation some irreversible changes are also occurring in methylene blue in addition to...
the lueco form. Possibility of permanent recording is also suggested. Studies on photo bleaching of three xanthene dyes like ErythrosinB, EosinY, and Rose Bengal was reported by Manivannan [85]. Evaluated quantum yield suggests that ErythrosinB undergo faster bleaching than the other two in the presence of electron donors. The volume holograms recorded on DCPVA sensitized by Rose Bengal was found to be unfit for hologram imaging of three dimensional objects [85,86].

Methyl orange doped PVA posses all the good characteristics of a known polarization sensitive material [87]. Methylene blue and xanthene dye (XD) sensitised PVA with dark reversibility has been employed for application of correlation peak detection. The effect of various amines on the bleaching efficiency was also studied [88]. A systematic ESR spectroscopic investigation was also performed on this system [89]. Measurement of the spatial resolution for different samples of XD/DCPVA was determined and the results were compared [90]. Dark self-enhancement studies done on DC/PVA films showed enhancement gain of 6 in 3 days. The dark reaction was considered earlier to be only a disadvantage. Now it is shown that the dark reaction after the recording does not distort the diffraction efficiency of the grating but increases it. This effect offers the possibility of using DCPVA in real time measurements for longer periods. The use of self enhancement is of great interest in hologram recording by facilitating shorter exposures than general with these materials and thus vibration free exposures [91-95].

Azo dyes like chrysodine and mordant yellow 3R on PVA were found to be erasable with diffraction efficiency (D.E) of about 27% [96]. Another dry polymeric mixture consisting of a mixture of acrylamide, TEA and methylene blue in PVA can record hologram and is found to have high photosensitivity but low storage stability [97,98]. A study of the influence of the beam ratio and
intensity on the optical quality of the transmission hologram images of diffuse object stored in PVA photopolymer are reported. The hologram film based on a fine grain silver bromide emulsion suspended on a PVA matrix crosslinked with Cr (111) has been investigated. The introduction of functional groups into PVA matrix transforms it into a pH responsive polymer with swelling property. A trypsin substrate was also introduced into this hologram to create a designed hologram.

One disadvantage is that it does not adhere well to glass, which makes it a perfect candidate for transfer hologram. It is soluble in water and unstable at high humidity but it may be possible to stabilize chemically by converting at least some of its molecules back to poly (vinyl acetate) or by adding cross-linking agents. Borax is used to crosslink PVA. Hologram causes it to return to its original latent image state and stabilizes it somewhat against moisture.

1.4.2. Poly (vinyl carbazol) (PVK)

Poly (vinyl carbazol) (PVK) is not soluble in water but dissolves in chloroform and can be sensitized by a variety of sensitizers like 2,4,5,7-tetranitrofluorenone, 2,4,6-trinitrofluorenone, triphenylmethanedye, 9-(3,4,4-tricyano-1,3-butadiene1yl) carbazol containing trinitrofluorenone, azo dyes, spiropyran, ketocowmarin, disperse red I etc. PVK can also be sensitized by halogen to become a photocrosslinker. It should be used where maximum resistance to water is needed.

Best results were obtained for polymers doped with 2,5 dimethyl4-para(nitrophenylazoanisole), which showed maximum diffraction efficiency of 34% and 105mm thick samples. Spiropyran doped PVK films have been
used as erasable reversible holograms. Photoinduced colour change between thermally stable and metastable state of spiropyran molecules can modulate the absorption and refractive index of the doped film $^{108}$.

A new non-silver halide photographic system based on PVK was developed and reported by Yang$^{102}$. Some of the holographic characteristics like $T_o/H$ curve, resolution, diffraction efficiency, sensitivity, etc were investigated on this material. Another PVK matrix suitable for holographic recording was explained by Ikegami, Yoshizumi$^{103}$ which include illumination of photosensitive solution with a radical sensitizer, a sensitizer dye, which produce free radicals thus improving the sensitivity of the material.

The disadvantage of this matrix is that it has short life and is hard to process uniformly. It is sensitive to blue green light and requires an exposure of only a few mJ/cm$^2$. It requires the use of noxions chemicals, some of which are known carcinogens. PVK is also a commonly used photoconductor, which could be used to form relief holograms in thermoplastics and for light intensifiers. If used in holography it has to be sensitized by carbon tetra iodide.

1.4.3. Poly (methyl methacrylate) (PMMA)

The properties of PMMA that makes it unique for its use as a recording material are

- Transparent, hard, rigid.
- Absorb very little visible light but there is 4% reflection at each polymer-air -interface for normal incident light.
- It is a polar material and has a rather high dielectric constant and power factor
• Good water resistance
• Better resistance to hydrolysis.
• Outstanding weather resistance
• Good electrical insulator at low frequencies
• High optical quality
• Good mechanical properties

Preparation of large transparent, gelatin coated PMMA sensitized with nitrocellulose, which can record and display hologram has been described in detail\cite{109}. PMMA doped with certain chemicals like p-benzoquinone \cite{28,110}, photoinitiators like benzil methyl ketal and titanium biscyclopentadienyl dichloride \cite{111}, which under optical irradiation induce scission or crosslinking of the polymer chain. This results in small refractive index change of the material. Holographic characterization like thickness, effects of aging, effect of concentration of the dye \cite{112} are done on azo dye doped PMMA films. These films under actinic light (\(\lambda\)-488nm) showed a local change in refractive index with high diffraction efficiency. The real time kinetics of photoreversibility of azo dye in PMMA matrix is also reported \cite{113,114}. The limiting factor of diffraction efficiency in azo dye doped films were investigated by Blanche \cite{115}. Holographic and spectroscopic characterizations were done on spiropyran doped PMMA films \cite{116}.

Erasable holograms can be recorded on either stable or metastable state of the doped film. Different compositions containing PMMA and its copolymers were found suitable as hologram recording materials \cite{117-120}. Thick dye doped PMMA films have been extensively used for real time holography. The characteristics of thick PMMA films as volume type hologram material were investigated theoretically and experimentally \cite{121}. The multiple storage capacity of a
polymer system containing PMMA with 8-12% weight of residual monomer and titanocene chloride has been experimentally investigated \[122\]. Kinetics of photopolymerisation of PMMA with visible light as sensitizer and polymerization initiator was investigated \[123\]. This material can record stable hologram with high sensitivity and resolution. The relation between photographic properties and kinetics involved was theoretically analyzed using PMMA matrix and anthracene as sensitizer \[124\].

Photochromism and its application in holography are explained using spiro­pyran doped PMMA \[125\] and zinc tetrabenzopropyrene doped MMA \[127\]. Optical storage properties of the unoriented liquid crystal and amorphous side chain azo benzene PMMA films are examined by polarization holographic measurements. The copolymer with 50-75% dye content exhibited largest surface relief. The stored information was stable up to 70°C except in the case of low dye content \[126\]. Complex computer generated holograms are now fabricated in PMMA by partial exposure and subsequent partial developments \[128\]. High optical quality, thick (5-mm) samples without shrinkage were made with phenanthrequinone- doped PMMA. Optically induced birefringence is observed in this material.

### 1.4.4. Acrylamide based polymers

Acrylamide–based poly(vinyl alcohol) films constitute a low cost organic material, and a great deal of attention has been given to the composition of an acrylamide based photopolymeric system initiated by TEA and methylene blue in recent years \[129-132\].

The limitations of the hologram sensitivity of a photopolymer mostly results from an imbalance between photocrosslinking, copolymerisation and mass
transfer process. The developments of new blends containing acrylate and vinyl ether monomer which undergo hybrid-cure polymerization make it possible to evade some of the typical short comings of multiacrylate formulations. Self-processing materials exhibiting hologram sensitivity up to 200 cm²/J and an energetic sensitivity below 20 mJ/cm² are reported [133]. The improvement of reciprocity between exposure and hologram intensity opens up attractive prospects for the above materials for applications requiring holographic exposure for a time less than 5 sec.

A composition containing a mixture of acrylamide-5.2, methylene blue-0.02, acetylacetone-0.1, N,N'-methylenebis acrylamide-0.6, hydroquinone-0.0004 and 0.1N sodium hydroxide-3 parts, placed on a glass cell having 50 spacers responded to He-Ne laser (632.8 nm) at 5000 mJ/cm² [134]. Optimization of an acrylamide photopolymer for use in real time holography is reported in [135]. The optimum sensitivity is obtained by decreasing inhibition time, which is achieved by using another sensitizing system. A sensitivity of 3 mJ/cm² at 633 nm was observed. The effect of intensities, thickness, variations in concentration of each component, optimum sensitivity etc were studied in detail by Braya Salvador [136]. Schilling and Colvin incorporated several high index organic monomers into high optical quality acrylate oligomer based formulations. Using reactivity ratio, reaction kinetics and component refractive index as guidelines, and a six-fold increase in refractive index has been achieved. Samples prepared from different acrylate formulation have been used to multiplex this number of holograms. Using these resins a protocol for the evaluation of photopolymers, as hologram media has been developed [137].

A new aqueous photopolymer containing the monomers methylene-bis acrylamide and zinc acrylate with initiators like 4,5-diiodo succinyl fluorosclien (2ISF), methylene blue and co initiator sodium p-toluene sulphonate was
found to exhibit high energetic sensitivity upon He-Ne laser irradiation. The same mixture with only one dye showed a maximum diffraction efficiency of 15-20\% due to the formation of a photogenerated initiator by the ground state formation of an ion pair complex between methylene blue and 2ISF chromopores\textsuperscript{[138]}.

The outstanding property of poly (acrylamide) polymer is that it is water soluble to infinite molecular weight. Moreover it is hard, brittle and slightly soluble in organic compounds because of its polarity.

\textbf{1.4.5. Poly (acrylic acid) (PAA)}

Photosensitive materials comprising of acrylic acid and catalyst are used to record holograms in the presence of laser beam\textsuperscript{[139]}. Organic sulfinic compounds are best examples for this. The hologram characterization and quality reconstruction on dichromated poly (acrylic acid)) (DCPAA) have been studied by varying the parameters like concentration of dichromate, electron donor and molecular weight of the polymer matrix. Hologram can be effectively recorded without any post processing of the photomaterial because the complex pattern is fixed during recording by photocrosslinking \textsuperscript{[141]}. A photoredox process (Cr\textsuperscript{VI}-Cr\textsuperscript{III}) was observed when DCPAA films were irradiated for hologram recording under UV-VIS spectroscopy. The photoreaction is assumed to go through an acid-base reaction between dichromate ion in excited state and PAA. The resulting unstable chromium polyacrylate undergo redox process to give Cr (V) and a monoradical RCOO\textsuperscript{−}, which decomposes giving carbon dioxide. The presence of DMF makes the overall reaction faster. The direct involvement of Cr(V) in the quality of the resulting hologram is explained\textsuperscript{[144]}.
DCPAA \cite{145} can be used as real time medium for transmission holograms. In this study a simple computer generated hologram grating with a sinusoidal amplitude profile is copied on this recording material by contact copying technique. The theoretical and experimental diffraction efficiency for computer generated hologram copy is evaluated and is reported in \cite{140}.

DCPAA films with dimethyl formamide (DMF) can be used to photofabricate surface relief grating \cite{142}. The modulation depth of these gratings and the spatial frequency response to the DCPAA-DMF films were chosen to characterize the self-developing of these photopolymer system. Laser structuralization of gelatin with acrylic acid compounds for producing high-resolution sensitive media for holographic optics are also discussed by Volkov in \cite{143}.

1.4.6. Dupont’s photopolymers

The characteristics of a holographic photopolymer made by E. Du Pont de Nemours and Company have been described in \cite{146-152}. These are all real time recording materials with the migration of monomer. They work as is or may be enhanced with post exposure baking with the addition of a monomer to swell them to a thicker state. Swelling shifts play back colour and angle in reflection holograms. The sensitivity of some films is down to a few mJ/cm$^2$ but as with DMP-128 they cannot be over exposed. Some films are panchromatic and good full colour holograms can be made with them. The films are over 8 microns. They play back with smaller bandwidths but look clear in about any light. The normal backing is mylar and is birefringent causing some problem with production and making it difficult to make holographic optical elements (HOE’s) with high integrity. The liquid film has been made available so that it
can go in glass and then good quality HOE's are possible. Large number of display holograms have been produced in this material, which is sold in sheets and rolls with machines to expose and process it.

The limited modulation prevents this material from being used in some tasks, but it is a big plus for others. When high angular selectivity or a narrow notch filter is needed it is the material of choice, especially if it is possible to get coatings of 50 microns or more. Optical memories have been made with it. The dye never bleaches all the way out of some of their films so it is useless at short wavelengths, as in DCG and PVK.

One of Dupont's materials forms an excellent embossed surface upon exposure and is great for copying binary or possible shaded masks. The shading may copy with poor linearity depending on light intensities, spatial frequencies and migration rates and distance. This is a very widely used material.

1.4.7. Polaroid Photopolymers

The commonly used Polaroid photopolymer in transmission display holograms is DMP-128. It is a flexible film and is useful for making high-density reflectors. Because of the unique open structure it can be filled with liquid crystals to make disappearing holographic optical elements and DFB laser and narrow band filters. It is easier to stabilize than dicromated gelatin and has about the same high modulation in films of 7 to 15 microns. This material is used mostly with red light but can be made panchromatic more easily than DCG and is much more sensitive, requiring only about 25 mJ/cm² to expose fully.

This material is saturable, once the polymerization material is used up the effects of exposure are nil. This is a great advantage in production because over exposure has almost no effect, except it may compress the contrast range
a little. This is true of all migratory photopolymer systems, including all of Dupont’s photopolymer products.

One disadvantage of this material is that it is coated on a substrate that has a higher index than the unexposed film so that all recordings have a mirror in them and the film is not generally available in liquid form. Environmental controls are important at the exposure station, because the film has to be activated by a fairly precise percentage of water or it will produce noisy holograms. The display holograms are the best and brightest among the mass produced products and last a very long time.

Polaroid has announced the introduction of another photopolymer that needs no wet processing and therefore is much more suitable for precision holographic optical elements making.

1.5. Doping

A variety of organic-polymeric based materials have been investigated for optical recording, including dyes (pigments), dye polymer solution and polymer metal layered or particulate structures. In all instances, the light absorption function is provided by the dye or metal and the polymer serves the role of binder and film former. Dye polymer solid solutions / films appear to offer the most attractive approach for producing high sensitivity. To form a true molecular dispersion, the dye and the polymer must be soluble (compatible) at the appropriate loading. For the film thickness and uniformity required for optical recording, spin-coating methods could be used. The coating and drying dynamics that control the film thickness and morphology have been experimentally \(^{153}\) and theoretically \(^{154}\) determined. Dye concentration will
depend on the absorption and extinction coefficients at the recording wavelength, and for typical dyes, loadings of 10-50-wt% are necessary. Optimising film thickness and recording structures to achieve an optical interference condition aid in maximizing absorption in the film at reduced dye levels.

Dye polymer solutions have been studied in a number of laboratories and detailed recording sensitivity analyses have been published. On the basis of published information, a set of design criteria for dye and polymer materials can be defined for optical recording. The primary function of dye molecule is to absorb the incident laser energy. Several groups have shown that the sensitivity of the dye polymer media is largely determined by the optical efficiency of the thin film. Optical efficiency is a measure of the optical energy coupled into the film and is a function of the dye concentration, dye absorption coefficient and the layer thickness.

Dyes should have absorption coefficient as high as possible at the writing wavelength, because this characteristic will maximize the optical density at minimum dye loadings. Maximizing optical density is an advantage because dye polymer solubility control can be a difficult problem. There is also a limit to increase recording film thickness to increase absorptivity. Dye concentration in the polymer is determined by the chemical structure and solubility characteristics of the dye and the binder polymer molecules. For most dye polymer combinations, dye loadings beyond 40 to 50 wt% results in heterogeneous films with undesirable micro crystals. The electronically excited dye molecules can undergo a number of decay process including radiative deactivation by fluorescence or phosphorescence and nonradiative deactivation by internal conversion and intersystem crossing.
One of the major difficulties encountered in dye films is the propensity of the amorphous material to undergo crystallization with subsequent deterioration of recording performance.

An ideal material for optical recording especially holography needs to be highly sensitive to light but it must also be able to hold a pattern change for many years without degrading, despite variations in temperature, humidity or pressure.

This thesis reports the attempts made to develop and characterize polymer materials doped with dyes, which satisfy the conditions needed for an ideal material for holographic recording that is easy to use and is self-developing. This allows holograms to be recorded in a one step process.

1.6. The specific objectives of the work can be summarized as follows

1. To develop and characterize different dye doped polymer systems having sensitivity in different optical regions.
2. To develop new polymer matrix for methylene blue, which can be used as a permanent recording material.
3. To prepare and characterize a new polymer blend of PVA/PAA system for methylene blue for its use as an optical recording material.
4. To compare the effect of methylene blue in different polymer matrices.
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