STUDIES ON METHYLENE BLUE SENSITIZED POLY (VINYL ALCOHOL): EFFECT OF MOLECULAR WEIGHT OF THE POLYMER AND CROSSLINKING AGENTS ON ITS HOLOGRAPHIC PROPERTIES

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Declaration

I hereby declare that the thesis entitled **"Studies on methylene blue sensitized poly (vinyl alcohol) : Effect of molecular weight of the polymer and crosslinking agents on its holographic properties"** is the original work carried out by me under the supervision of **Prof. Rani Joseph (**Department of Polymer Science and Rubber Technology) and under the co-guidance of and **Prof. K Sreekumar** (Department of Applied Chemistry) and **Prof. C Sudha Kartha** (Department of Physics), Cochin University of Science and Technology, Cochin-22 and has never been included in any other thesis submitted previously for the award of any degree.

Cochin - 22 **Nimmi K P**

Certificate

This is to certify that this thesis entitled “**Studies on methylene blue sensitized poly (vinyl alcohol): Effect of molecular weight of the polymer and crosslinking agents on its holographic properties”** is a report of the original work carried out by **Smt. Nimmi. K P** under our supervision and guidance in the Department of Polymer Science and Rubber Technology, Department of Physics and Department of Applied Chemistry, Cochin University of Science and Technology, Cochin-22. No part of the work reported in this thesis has been presented for any other degree from any other institution.

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To

My loving family.......

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PREFACE

The photopolymer technology has wide diverse applications in the field of electronic materials, printing materials, optical and electro-optical materials, the fabrication of devices and polymeric materials, adhesives and coating materials. These have been exploited in a variety of applications requiring versatile holographic storage media, such as heads-up displays, data storage, holographic optical elements and waveguides. Although other holographic storage materials, particularly inorganic photorefractive crystals, have been used to develop these technologies, it is widely believed that the high sensitivity, low cost, and versatility of photopolymeric media would enable more widespread commercial applications of holography. Combining high storage density and fast transfer rates with durable, reliable, low cost media, holography is poised to become the next generation solution for data storage and archiving. Photopolymer materials are attractive candidates for write-once- read-many times (WORM) data storage applications because they can be designed to have large modulations in their refractive index and high photosensitivity. In recent years, extensive interest has been devoted to the investigation and improvements of media for optical storage. There are different types of photopolymers that may be differentiated by the type of binder, since this component determines to a great extent the choice of monomer, dye and initiator used in the photopolymer. Photopolymers with poly (vinyl alcohol) is hydrophilic and less toxic. In hydrophobic photopolymers, organic solvents were used and they are not environment friendly.

The present study was undertaken to make development of water soluble PVA based photopolymer systems and their characterizations.

The first chapter gives an introduction to the available hologram recording materials, applications of photopolymer technology and a brief review on photopolymer recording systems. Scope and objectives of the present work are also discussed.

Second chapter deals with the materials used in the present study and the experimental techniques adopted for the fabrication and characterization of the photopolymer films. Gravity settling method was used to fabricate the films.

Chapter 3 describes the attempts made to improve the storage life of the methylene blue sensitized PVA/AAm photopolymer film developed in our laboratory by reducing the concentration of the dye. The concentration of each component was optimized by recording gratings using He-Ne laser and by measuring diffraction efficiency (DE) of the recorded gratings. The sensitivity of the film was optimized by recording gratings at different exposure energies and spatial frequency response of the optimized film was studied by changing the angle of recording. Shelf life of the optimized film was monitored by recording gratings at different time intervals. The storage life of the material was determined by measuring diffraction efficiency of the recorded gratings at different time intervals. The glass transition temperature of the optimized film was measured using Differential Scanning Calorimetry and mechanical properties were studied using Universal Testing Machine. By reducing the concentration of dye, storage life and sensitivity of the MBPVA/AAm previously developed in our lab, could be improved. Maximum DE of 75% was obtained at an exposure energy of 80 mJ/cm^2 and even after one year of recording, DE of 43% could be obtained (in the previous studies, DE was 70% at 120 mJ/cm^2 and was reduced to 10% after 6 days of recording). The shelf life of the material also studied and after 3 months of preparation, gratings could be recorded on the samples with a DE of 1% only. For getting a better storage life, the recorded gratings were exposed to UV light using Dymax UV flood lamp (400 W EC power supply). Optimization of UV exposure time was done by exposing the films for different times. The film exposed for 180 seconds has given good results in the material’s storage (63% after one year of recording). For protecting the film from external contaminants, three sealants were tried and their effect on the storage life and shelf life of the material was studied in which 1% PMMA coated film showed better results.

Chapter 4 deals with the effect of two organic crosslinkers, glutaraldehyde (GA) and N, N' -methylene-bis-acrylamide (BMA) on the holographic properties, mainly on the storage life of the optimized MBPVA/AAm films. Glutaraldehyde incorporated films were prepared by gravity settling method and the concentration of glutaraldehyde was optimized by recording gratings. For the optimum concentration of glutaraldehyde, the photopolymer film had diffraction efficiency less than 60%. Regarding the storage life of the material, a decrease in diffraction efficiency on storage was observed. As the expected storage life was very low, glutaraldehyde was replaced by BMA. BMA incorporated films were also prepared by gravity settling method and the concentration of BMA was optimized by recording gratings. For the optimized concentration, DE obtained was 72% and remained as 70% upto one year of recording. The shelf life of the material also could be improved.

The effect of molecular weight of Poly (vinyl alcohol) on the diffraction efficiency, was included in **chapter 5.** Poly (vinyl alcohol) with molecular weight –13,700, 54,500 and 1, 25,000 having the same hydrolysis degree of 86-89% was selected for the study. In this case also films were prepared by gravity settling method. Concentration of PVA was optimized by varying the weight percentage of PVA and by recording gratings. For the photopolymer film with molecular weight of PVA 54,500, and weight percentage of 10, a maximum diffraction efficiency of 83 % was obtained at 20 mJ/cm^2. But on storage, the DE was found to decrease. This case also UV exposure and incorporation of N, N'-methylene-bis-acrylamide were employed to improve the storage life. The UV exposure time was optimized and a maximum DE was obtained for the gratings exposed to UV for 60 seconds. Storage life study on the sample was done and a constant DE could be maintained for 4 months of recording gratings. BMA incorporated samples were prepared by keeping the concentration of BMA as the same used in the previous studies. Gratings were recorded on the samples and a DE of 82% was obtained at 20 mJ/cm^2. But a decrease in DE was observed on storage. Shelf life studies on the samples were also done on these films. From the studies it was clear that, by reducing the molecular weight of the polymer binder, diffraction efficiency and sensitivity could be improved.

Chapter 6 gives the summary and conclusions derived from the work. The scope for the future work is also explained.

List of abbreviations used and list of conferences and publications are also given at the end.

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Chapter 1

INTRODUCTION

1.1 Photopolymers

Photopolymers are imaging compositions based on polymers/ oligomers/ monomers which can be selectively polymerized and/or crosslinked upon image wise exposure by electromagnetic radiation such as ultra-violet, visible or infrared. Typical photopolymer formulations contain a photoinitiator system, monomers and oligomers, a polymer or polymers to provide specific physical and/or processing properties and a variety of additives to modify the physical properties of the light sensitive composition or the final properties of the cured photopolymer [1]. Most of these systems were originally sensitive to UV light but now, a large number of various systems allow to extend the spectral sensitivity to visible lights [2]. Since direct formation of reactive species on the monomer by light absorption is not an efficient route, the initiation step of the polymerization reaction requires the presence of a PI which, under light excitation, is capable of generating these reactive species. Among various factors which affect the efficiency of the polymerization reaction, the photoinitiator (PI) has been recognized as a key factor. Radical, cationic and anionic polymerizations can be initiated by the excitation of suitable photoinitiating systems (PISs) under light.

1.2 Basic Mechanism of Photopolymer Reactions

The basic light initiated reactions used in the diverse applications of photopolymer technology can be grouped into 5 categories based on the chemical and physical processes utilized [1].

1.2.1 Photopolymerization

The photoinitiated polymerization of monomers and oligomers to form crosslinked high molecular weight material is the basis for most of the commercial applications of photopolymer technology [1]. Photopolymerization processes present several important advantages compare to the corresponding thermal reactions. These advantages include low energy requirement, spatial and on and off control and fulfilment of green chemistry because, polymerization processes may operate without solvent.

Photopolymerization is usually applied to all chain processes, namely free radical, cationic and anionic polymerizations, and also step-growth polycondensation [3–5]. However, most of the applications are based on the free radical mode due to the less purity demand, applicability to a wide range of formulations based on (meth) acrylates, unsaturated polyesters, and acrylated polyurethanes and the availability of photoinitiators having spectral sensitivity in a broad wavelength range [6-8]. Cation initiated crosslinking of monomeric materials with epoxy and/or vinyl ether functionality has increased practical use with the development of new high efficiency photoinitiators that generate cationic species (e.g. strong acids) upon exposure [9].

1.2.2 Photocrosslinking

The second class of photopolymer chemistry that is used in some commercial products is based on the reaction of unsaturated moieties attached to an organic polymer. This photopolymer process includes the cycloaddition of the ethylenic groups in poly (vinyl cinnamate), (PVCi) polymers and in the styryl pyridinium [10] and thiazolium [11] derivatives of poly (vinyl alcohol). The main advantage of this chemistry is that, unlike free-radical photopolymerization, they are insensitive to the presence of oxygen. This photopolymer mechanism is principally used in applications employing a washout development process (e.g. resists).

1.2.3 Photomolecular Reactions

The third basic mechanism of photopolymer chemistry relies on the light initiated reaction of small organic molecules to modify the polymer based matrix into which they are incorporated. This class of photopolymer reaction is illustrated by the rearrangement of o- quinonediazide derivatives [12] in microresist materials and by the isomerization of azobenzene derivatives in optical storage devices [13]. Other small organic materials have been used to modify the plasticization of a polymer medium to modulate tack [14] and/or adhesion and to initiate colour changes following exposure to light [15].

1.2.4 Photodegradation

The next general class of photopolymer reactions that can be used in a variety of applications is based on the light induced degradation of polymeric materials. A small number of polymers have been prepared which contain light sensitive linkages within the polymer chain. Upon exposure, these light sensitive linkages fragment leading to the degradation of the polymer into smaller polymeric units. The degradation of high molecular weight polymers to low molecular weight materials can be detected as a change in solubility [1].

1.2.5 Photo/Thermal Reactions

The fifth basic class of photopolymer chemistry that can be used in commercial applications is based more on physical changes in a polymer based matrix than on chemical reactions. A recent application of this technology is the laser ablation [16] of an organic coating on a flat support to directly produce a printing plate. The availability of new high energy lasers will allow more applications to be based on the photo/thermal mechanism.

1.3 Applications of Photopolymer Technology

During the past three decades there has been a rapid increase in the number of commercial applications of photopolymer technology. The practical applications of this technology have been classified into 6 general categories:

- Electronic Materials
- Printing Materials
- Optical and Electro-Optical Materials
- Fabrication of Devices and Materials
- Adhesives and Sealants
- Coatings and Surface Modifications

1.3.1 Electronic Materials

Application of photopolymer technology to electronic products is probably one of the largest imaging categories in terms of sales and total number of patents and publications. A wide variety of products have been developed for the production of printed wiring boards (PWB) and the manufacture of integrated circuits (IC).

1.3.1.1 Manufacture of Printed Wiring Boards

Printed wiring boards, or printed circuit boards, are usually thin flat panels that contain one or multiple layers of thin copper patterns that interconnect the various electronic components (e.g. integrated circuit chips, connectors, resistors etc.) that are attached to the boards. These panels are present in almost every consumer electronic product and automobile sold today. The various photopolymer products used to manufacture the printed wiring boards include film resists, liquid resists, electrodeposited resists [17], laser exposed photoresists [18] and polyimide interlayer insulator films [19].

1.3.1.2 Manufacture of Integrated Circuits

An increasingly important application of photopolymer technology is the use of these materials for the formation of integrated circuits (i.e. chips). Integrated circuits are multilayer microscale electronic components (e.g. transistors) that are prepared on high purity silicone wafers. As more and more transistors are incorporated into the small chips for higher performance, the resolution capability of photopolymer materials is continually being improved through the development of novel photopolymer chemistry and manufacturing processes [20]. Some of the photopolymer products used to manufacture integrated circuits include Deep-UV [21-22] and electron-beam resists [23], direct laser imaging materials plus insulating [24-25] that are used to make conductive and resistive patterns on a scale between the extremes of printed wiring boards and integrated circuits.

1.3.2 Printing Materials

The application of photopolymer technology to a wide variety of imaging applications in the printing industry is quite important. Most printing plates and pre-press proofing products used today are based on, some element of photopolymer chemistry.

1.3.2.1 Printing Plates

Of the many technologies used to manufacture printing plates, photopolymer chemistry is used almost exclusively for the plates that print medium to high quality images. The most common photopolymer printing applications include lithographic printing plates, flexographic plates [26] and new digital laser imageable plates [27].

1.3.3 Optical and Electro-Optical Materials

Many of the newest high "value-in-use" applications of photopolymer technology are in the general area of optical and electro-optical materials. Because of the excellent spatial imaging characteristics of photopolymer materials and their ability to rigidify materials to provide aligned molecular structures, photopolymer materials are uniquely positioned to participate in these emerging "high tech" applications.

1.3.3.1 Liquid Crystal Displays (LCD)

Liquid crystal displays, once limited to small devices such as calculators, are now displacing colour cathode ray tube (CRT) displays in commercial quantities. The ability to fabricate these display devices at high quality and at low cost is partially due to the wide spread use of photopolymer-based materials. Photopolymer technology is being used for the alignment of liquid crystal (LC) elements [28], the orientation of ferroelectric materials [29] and the synthesis of LC polymers [30].

1.3.3.2 Nonlinear Optical Materials

Nonlinear optical materials (NLO) rely on the ability of light to interact with specially designed inorganic and organic compounds to provide uniquely modulated light output. Photopolymer materials are being fabricated into various NLO materials and devices that are being used in applications such as optical waveguides [31], polarizing optical elements [32] and electro-optical switching devices [33].

1.3.3.3 Holographic Materials

One optical application of photopolymer technology that has been receiving a large amount of attention is the area of holographic materials and devices [1]. Polymeric materials are becoming more important for application in information processing [34-35], and one of the most challenging areas for the polymeric materials is holographic recording. Photopolymer properties, such as high diffraction efficiencies, low noise, self-developing, easy preparation, high thickness, low cost etc., make them a suitable media for holography [36].They do not require lengthy controlled processing techniques and can be processed in situ.

1.4 Holography

Holography is a technique that makes it possible to store and reproduce three-dimensional images. It was invented by Dennis Gabor in 1947 and after the invention of laser in 1962; Leith and Upatnieks demonstrated a new approach to holography [37]. The hologram is a record of the interference pattern created when two beams of laser light interfere on the holographic surface. When a hologram is illuminated with a coherent light wave identical to the reference wave, this wave is fixed on the hologram and acts as a sort of a diffraction grating and this diffraction reconstructs the object's image recorded on the hologram. It has many applications in all branches of science, engineering, technology, bio-engineering, bio-medicine, art and advertising, high resolution imaging, information storage and security coding, holographic optical elements and holographic interferometry.

1.5 Types of Holograms

There are many types of holograms, like reflection hologram, transmission hologram, embossed hologram and integral hologram [38].

1.6 Hologram recording materials other than Photopolymers

When examining the suitability of a recording material, various factors to be considered [39];

- Excellent optical quality: This will lead to bright images.
- High Efficiency: The material should have maximum diffraction efficiency and minimum transmission efficiency.
- High sensitivity: The material should be sensitive to react at low exposure energies.
- High Resolution: The full characteristics of the recorded pattern should be there.

- Self-processing: Without any post exposure treatment, the recorded hologram should be readable.
- Long term stability of the recorded image: The recorded hologram should be stable for a long period of time.
- Economic: It should be cheap and easily available.
- Easiness of fabrication: The preparation method should not be complex**.**

In addition to photopolymers, some other materials are also used for recording hologram. They include; silver halide emulsion, dichromated gelatin material, silver halide sensitized gelatin, photoresisits, photorefractive material, photochromic materials, photothermoplastics and additional materials includes chalcogenated glasses etc.

1.6.1 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 its 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. 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 [40]. 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 and 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 and post processing. This has enabled the user to make choice from wider varieties. Most of the work has been on improving the diffraction efficiency (DE) and signal to noise ratio (SNR), particularly for reflection holograms.

1.6.2 Dichromated Gelatin (DCG) Material

Dichromated gelatin finds use in holography due to its excellent holographic properties, including low scattering and high index modulation [41]. The drawbacks of dichromated gelatin include the raw material's variability, complex wet processing, poor shelf-life, and environmental instability requiring hermetic sealing. The efficiency of dichromated gelatin system is based on the difference in swelling between exposed and unexposed gelatin. The recording sensitivity of DCG has been extended to red wavelength making it possible to record multicolour reflection holograms.

1.6.3 Silver Halide sensitized gelatin

Recent development of ultra-fine grain silver halide emulsion has increased an interest in the silver halide sensitized 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 organic solvent. The dried SHSG hologram includes only gelatin and micro voids of air [42]. 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 [43].

1.6.4 Photoresists

Photoresists are suitable for producing surface relief holograms for making masters needed for replication by embossing techniques. This material is most sensitive to ultraviolet light only. Efforts have recently been made to make photoresists sensitive at red wavelength. A typical photoresists (Shipley AZ -1350) for holography has sensitivity of about 10 mJ/cm^2. It is sensitive to UV and visible upto 500 nm. The Waycoat HPR series represents another photoresists for optical imaging. Towne laboratories, Inc. manufactures coated photoresists for holography [44].

1.6.5 Photorefractive Material

The photorefractive (PR) 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 of light, interference between the beams results in a pattern of dark and light fringes throughout the matrix. Photorefractive crystals and photorefractive polymers include in this category. In photorefractive crystal, the refractive index (RI) of crystal changes in the regions where the field is strongest. This causes a spatially varying refractive index grating throughout the crystal and are very promising materials for real-time holography. $LiNbO_3$, $LiTaO_3$, $BaTiO_3$, $KNbO_3$, $Bi_{12}TiO_{20}$ are widely employed in holographic data storage. However, the difficult crystal growth and sample preparation required for inorganic photorefractive (PR) crystals has limited the widespread use of these applications [45]. Holograms recorded in this medium are erased on read out, making crystals like $LiNbO_3$ unsuitable for archival storage applications [46-47].

Rapid advances in the field of PR polymers and composites have lead to the development of high performance materials with RI modulations approaching 0.01 and diffraction efficiencies (DEs) close to 100%. The PR effect refers to spatial modulation of the index of refraction under non-uniform illumination via space-charge field formation and electro-optic nonlinearity. The hologram recorded in this material can be erased by uniform optical illumination. The spectral sensitivity of PR polymers can be changed by using different dopant sensitizers. PR polymers need long fabrication steps, required high bias voltage and their response time is also low.

1.6.6 Photochromic materials

Reversible colour change in a material after exposure to light is called photochromism. Photochromic materials darken after exposure to ultraviolet or blue light and either darkening or bleaching of photochromic material can be the mode of hologram recording. Since photochromism involves photochemical reactions at the molecular level, the material is grainless; hence its resolution is more than sufficient for holography and no development is required to form the hologram. The hologram recorded in this material can be erased either thermally or optically and the material is reusable. The photosensitivity of this material is at least three orders of magnitude less than that of silver halide photographic emulsion. The photosensitivity of this material decreases with increasing number of record-erase cycles and finally they become totally insensitive to light; that is the reusability of this material is limited [39].

1.6.7 Photo thermoplastics

Holograms can be recorded in a thermoplastic film by causing its structure to deform in accordance with the light intensity variations of holographic interference patterns. Thermoplastics are usually not photosensitive and must be combined with a photoconductor in a film structure which respond to light. It is highly photosensitive to all visible light and requires no lengthy wet development. Hologram recorded in this material has moderately high diffraction efficiency and is stable at room temperature until intentionally erased. The material can be reused a number of times. But the maximum resolution obtainable with this material is not much greater than 1000 cycles/mm. In addition, high quality film is difficult to prepare and the thermal development of the film is critical [48].

1.6.8 Additional Materials

Chalcogenide glasses, ferroelectric photoconductors, liquid crystals, magneto-optic films, metal and organic dye-ablative films, transparent electrographic films and light harvesting protein (bacteriorhodopsin) [44] are other materials used for recording hologram.

1.7 Photopolymers in holography

According to holographic point of view, photopolymers can classified into two large groups; one which able to produce high diffraction efficiency or generates phase holograms (formation of grating by modulation in refractive index) such as acrylamides, acrylates, methyl methacrylates or those which are photocrosslinkable systems like poly (vinyl carbazole) (PVK), dichromated poly (vinyl alcohol) (DCPVA), poly (acrylic acid) (PAA) and other with low diffraction efficiency or generate amplitude holograms (grating formation as a result of modulation in absorption) such as doped polymers (photochromic compounds, bacteriorhodopsin). Photopolymerizable systems include within the first group. The photopolymerizable system can be further divided into two large categories; liquid compositions and dry films. The latter can be sub divided into acrylates, methylmethacrylates, acrylamides etc depending on the type of monomer used [39].

1.8 Photopolymers as hologram recording media- A brief review

Since about 1970, a number of photopolymer based refractive index imaging systems have been discussed [48]. Their versatility, ease of use and self processing ability give them many advantages over more traditional materials such as silver halide and DCG. [49-50]. Photopolymers have been considered for use as holographic recording media for several decades [51]. The ability to change sample shape, and the inherent tunability of the physical properties for most polymer systems by changing component content and ratios are additional advantages [46].

Photopolymers were first used as a holographic recording material by *Close et al.* in 1969. They mentioned the use of a polymeric solution formed with acrylates and methylene blue (MB). For this, the exposure needed was 1- 30 mJ/cm^2 for a working wavelength of 694 nm with diffraction efficiency of 45 %. This material had a short shelf life. Fixing process was also done using UV irradiation [52].

Jenney was the first to report the use of an acrylamide (AAm) system as a holographic recording material in 1970 and the system was a solution of acrylamide initiated by methylene blue and p-toluenesulfinic acid. This photopolymerizable solution was sandwiched between two glasses and producing an energy sensitivity around 0.6 mJ/cm^2 and diffraction efficiencies of nearly 20% was obtained when irradiated at 633 nm. Here also fixing process was used [53].

The property of this mixture was improved by *Van Renesse* in 1972 by adding N, N'- methylene-bis-acrylamide (BMA) to speed up polymerization reaction to this system. Sensitivity of the material was 5 mJ/cm^2 but the recorded hologram could be stored only for one week [54]. *Sugawara* et al. reported the use of acrylmide and methelene-bis-acrylamide with acetyl acetone or triethanolamine (TEA) as photo reductant and they got a diffraction efficiency of ~ 65% for exposure of 50 mJ/cm^2 [55]. *Sutherland et al.* demonstrated by using liquid crystals in an acrylate system and DE reaches 100% for holograms registered at 488 and 514 nm [56].

Fimia et al. continued the work of Sugawara et al and used two aqueous solutions, one containing polymerizable system with acrylamide, zinc acrylate and N,N'-methylene- bis- acrylamide and photo initiator system with MB and rose bengal (RB). Here pre-exposure was given and a DE of 50% was obtained with energetic sensitivity lower than 10mJ/cm^2 [57].

D J Lognot et al. reported a self processing formulation based on β-hydroxy ethyloxazolidone acrylate and hologram recorded using Ar^+ and reconstructed using He-Ne laser. They developed a formulation named as PHG-530N having a maximum DE of 80% with exposure energy less than 150mJ/cm^2 [58].

Bartkiewicz and Miniewicz developed methylene blue sensitized poly (methyl methacrylate). Phase and/or amplitude holograms could be written in the methylene blue sensitized films of poly (methyl methacrylate) (PMMA) with He-Ne laser operating at 632.8 nm. Diffraction efficiencies of 60% were found for thick holograms [59].

Zhao used gelatin as binder along with acrylamide and acrylic monomers, methylene blue, p-toluenesulphonic acid and triethanolamine as initiators and a maximum DE above 80 % was obtained with exposure energy of 2 mJ/cm^2 [60].

Fimia et al. reported a new aqueous photopolymer containing the monomer acrylamide, BMA and zinc acrylate. The initiators used were 4,5,di iodo succinylfluorescein (2ISF) and MB and co-initiator sodium p-toluenesulphinate and DE of 15-20% obtained with 15-60 mJ/cm^2 [61]. *Diamond et al.* used Epotek-21 resin as a polymer binder, dipentaerythriol pentacrylate (monomer) and a DE of 3.5% was obtained [62].

Pavel Cheben introduced a modified silica glass containing titanocene photoinitiator and ethyleneglycol phenyl ether acrylate.

Hologram was recorded using Ar^+ laser and He-Ne laser was used as read-out laser. A DE of 98% obtained with exposure of 0.23 J/cm^2 [63].

Using 2-hydroxyethyl methacrylate in PMMA containing dye 1,3,5,7,8 pentamethyl-2,6-diethylpyrromethane difluoroborate as a photo initiator, *Blaya et* al. got a DE of 60% in 500μm film with exposure energy of 1J/cm^2 [64]. *Ushamani et al.* used complexed methylene blue sensitized poly (vinyl chloride) (PVC) for holography and a DE of 4.46% obtained for 193 lines/mm [65].

Carretero reported acrylamide, BMA, triethanolamine and yellowish eosin in silica glass and a DE higher than 80% obtained with 10mJ/cm^2 having the film thickness of 113μm [66]. *Park and Kim* prepared sol gel-organic-inorganic composites with thickness greater than 200μm on the basis of aromatic methacrylates and DE>95% was obtained with 532 nm laser light [67].

Shelkovnikov et al. introduced a hybrid organic-inorganic matrix prepared by the synthesis of N-vinylpyrrolidone and triethoxyvinylsilane copolymer followed by hydrolytic condensation of the copolymer with a tetraethoxy silane presol. Here acrylamide and acrylomorpholine (monomers), bis-acryloyl piperazine (crosslinking monomer), triethanolamine and mercaptomethyltriazole (initiators), MB (photo sensitizer) were used. For a thickness of 0.46 mm, holograms with DE of 80% were recorded at exposure of 300 mJ/cm^2 [68].

Kim proposed a new phase stable acrylamide based photopolymer with PMMA as binder, TEA as co-initiator and MB as photosensitizer.

Here methacrylic acid was introduced into the system for phase stability and DE higher than 90% was obtained using He-Ne laser [69].

B.M John et al. developed a new reusable photopolymer medium containing MB as sensitizer, PVA as binder and vinyl acetate (VAc) as monomer. For optimized ratio of PVA-VAc, a DE of 6.3% was obtained with 750 mJ/cm^2 at a dye concentration of 9.3 x 10^{-4} M [70].

Dae –Won Chung et al. could record gratings with DE of 48-50% in poly dimethyl siloxanes having four epoxide functionalities [71]. *B.M. John et al.* reported MBPVC film with enhanced DE and storage life by the incorporation of pyridine as electron donor. Without electron donor, the DE was 0.2% with exposure energy 2000mJ/cm^2 and storage life was just 24 hrs. For a particular concentration of pyridine, DE improved to 0.46% and could be stored for 2-3 days [72].

Jeong et al. used photopolymer system based on epoxy resin. Here yellowish eosin was used as the sensitizer, acrylamide as monomer and TEA as co-initiator. DE of 9% obtained with exposure 11.7 x10^{-3} J/cm^2 [73].

Ortuno et al. reported riboflavin sensitized PVA/sodium acrylate, TEA and (DHEBA) and they got a DE of 77% in this system [74].

Yasushi Takamastu et al. developed a holographic photopolymer based on SU-8 epoxy resin as the binder. Here trimethylolpropane ethoxylate triacrylate (TET) (monomer) with an iodonium salt (photoinitiator) were used. A diffraction efficiency of 93% was obtained from a 16μm thick sample with write beam intensities of 50mW/cm^2 at a wavelength of 514.5 nm, at an exposure time of 60 s, and a post baking at 65°C for 1 h [75].

In addition to the above photopolymer system, PVA/acrylamide systems are widely used as hologram recording material.

1.8.1 PVA/acrylamide photopolymer

In 1975, *Jeudy and Robillard* were the first to use acrylamide in a poly (vinyl alcohol) film, and a diffraction efficiency of ~ 80% obtained for energy density of 100 mJ/cm^2 but it should be used within 4-5 days after preparation [76].

Calixto in 1987 reported a DE of 10 % with energetic sensitivity of 94 mJ/cm^2 using acrylamide as monomer, methylene blue as sensitizer, tri ethanol amine as electron donor and poly (vinyl alcohol) as binder [77]. A method was used by *Fimia et al.* to raise the sensitivity of acrylamide photopolymers by dropping the inhibition time caused by oxygen. The system comprised of two photosensitizers, MB (sensitive at 633 nm) and RB (sensitive at 546 nm) and a DE of 40 % with exposure energy of 3 mJ/cm^2 was obtained [78,79].

Calixto's photopolymer was optimised for recording in the 514 nm region by the addition of xanthenes dye and a DE greater than 80% was obtained with exposure energy of 80 mJ/cm^2 having spatial frequency 2750 lines/mm [80].

Wiess et al. improved the sensitivity of Close material at 514 nm by adding diphenyl iodonium chloride (DPI) as sensitizer and triethanolamine as electron donor. Here glutaraldehyde was used as the second crosslinker and DE of higher than 90 % was achievable with exposure of 12 mJ/cm^2 [81].

When bisacrylamide was added to PVA/acrylamide system with erythrosine B (ErB) as sensitizer, *Martin et al.* got a DE of 40% at exposure energy of 300mJ/cm^2 [82].

Blaya et al. in 1998 reported poly (vinyl alcohol)/ acrylamide photopolymer film with 80 % DE with energetic exposure of 40 mJ/cm^2 . The thickness of the film was 35 μm and a spatial frequency of 1000 lines/mm was obtained [83]. In another approach, *Blaya et al.* prepared acrylamide and BMA in PVA system with a DE of 80% with an exposure of 12 mJ/cm^2 having a spatial frequency of 1000 lines/mm. Here the molecular weight of PVA used was 25,000 and the thickness was 75μm [84]. *Blaya et al.* [85] reported acrylamide photopolymer by adding N, N-dihydroethylenebisacrylamide (DHEBA) as crosslinker and a DE of 70 % obtained with 5 mJ/cm^2.

Lawrence et al. prepared PVA/acrylamide photopolymer containing BMA as crosslinker and ErB as sensitizer and holograms were recorded using Ar$^+$ laser and reconstructed by He-Ne laser. A DE of 80% obatained with 1000 lines/mm and 30% DE at 2750 lines/mm [50].

Mallavia et al. used an ion pair (RB and MB) in PVA/ acrylamide system. Irradiation using He-Ne and Ar$^+$ laser, DE of 60%

and 38% was obtained with sensitivity of 30 and 125 mJ/cm^2 with spatial frequency of 1000 lines/mm [86].

Pascual et al. reported PVA/acrylamide photopolymer with yellowish eosin as sensitizer and TEA as photoinitiator. When gratings were recorded on the film with thickness 70± 5μm using Ar$^+$ laser and reconstructed with He-Ne laser, a DE of 75% was obtained [39]. *Pascual et al.* could improve the DE of the above system to 80% by increasing the film thickness to 110± 5μm with energetic sensitivity of 200mJ/cm^2 [39].

Yao et al. developed PVA/acrylamide photopolymer system with BMA with a DE of 55% for an exposure of 60 mJ/cm^2 with thickness 150μm and a spatial frequency of 2750 lines/mm using Ar$^+$ laser [87].

Garcia et al. prepared PVA/acrylamide photopolymer films with yellow eosin as sensitizer and triethanolamine as initiator. They used frequency doubled Nd:YAG (532 nm) Q-switched laser for recording and a DE of 62 % was obtained [88].

Blaya et al. developed PVA based photopolymers (PPMs) by the co-polymerization of acrylamide with 2-hydroxyethyl methacrylate (HEMA) and a DE of 70% was obtained with exposure energy of 65 mJ/cm^2 when recorded using He-Ne laser and reconstructed with He-Cd laser [89].

Huang et al. prepared 150 μm layers containing PVA, ErB, TEA, AAm and BMA. At optimum concentration, hologram with

DE ~55% was recorded at an exposure energy of 60 mJ/cm^2 with 2750 lines/mm [90].

Neipp et al. prepared photopolymer film using acrylamide and BMA as monomers, TEA as initiator, yellowish eosin as sensitizer and poly (vinyl alcohol) as binder. A DE of 80% obtained with spatial frequency of 545 lines/mm and 60% DE obtained with 1125 lines/mm [91].

Gallego et al. used dimethylacrylamide (DMAA) in PVA/ acrylamide system containing yellowish eosin as sensitizer and triethanolamine as initiator. A DE of 98% was obtained for a film thickness of 75±2 μm using Ar^+laser and He-Ne laser for recording and reconstruction [92].

Blaya et al. have developed PVA/acrylamide system with methylene blue as sensitizer and triethanolamine as co-initiator and hologram was recorded using He-Ne laser. A DE of 80% was obtained at exposure energy of 35 mJ/cm^2 with spatial frequency of 1000 lines/mm. Here BK 7 glass plates were used and films were prepared using thin layer coater (TLC) coater and a thickness of 65μm was obtained [93].

Gallego et al. reported PVA/acrylamide system containing N,N'-methylene-bis-acrylamide having a DE higher than 90% when heated to 80^oC. Here yellowish eosin was used as the sensitizer. Ar^+ laser was used for recording and He-Ne laser was used for reconstruction [94].

Kim et al. reported photopolymer system with acrylamide and N,N'-methylene- bis- acrylamide as monomers, triethanolamine as initiator, methylene blue as sensitizer and poly (vinyl alcohol) replaced by poly (methyl methacrylate) as binder. Here a methacrylic acid unit was inserted to enhance the phase stability and a DE close to 90 % was obtained [95].

Gong et al. used N-Phenyl glycine (NPG) as co-initiator in PVA/acrylamide system containing BMA and ErB. In a 150μm film, DE of 50% obtained with 60mJ/cm^2. When Diphenyl iodonium salt was introduced into the mixture, sensitivity increased to 24mJ/cm^2 with DE of 40% with spatial frequency 2751 lines/mm [96].

Ortuno et al. reported a DE of 70% in PVA/acrylamide system with yellowish eosin as sensitizer and BMA as crosslinker with exposure energy of 35mJ/cm^2 having the film thickness of 110μm [97].

Gong Qiao-Xia et al. developed a new photopolymerizable holographic recording material based on acrylamide and N-hydroxy methyl acrylamide (HMA). Here ErB was used as photosensitizer and TEA as co-initiator. Ar$^+$ laser was used to record hologram and He-Ne laser used to readout the diffraction pattern. A DE of 50% obtained with exposure energy of 80 mJ/cm^2 having a spatial frequency of 2275 lines/mm [98].

Jallapuram et al. could record transmission gratings with DE of 50% with spatial frequency of 3000 lines/mm in PVA/acrylamide photopolymer system [99].

B.M. John et al. developed copper doped PVA/AAm system containing methylene blue as photo sensitizer and triethanolamine as co-initiator. For optimized film, a DE of 24% was obtained and remained as such for more than three months [100]. *Okhawa and Sekine* reported PVA/acrylamide –triethanol system with methyl violet as sensitizer with a DE of 40% obtained [101].

Katherine Pacheco et al. have reported acridine orange sensitized acrylamide. In which, N,N'-dimethylacrylamide (DMAA) and N,N'-methylene- bis- acrylamide (BMA) were used as the crosslinking agents. With DMAA, DE of ~ 10% was obtained at spatial frequency 1000 lines/mm and with DMAA combined with BMA, a DE of 40% was obtained with a spatial frequency of 2000 lines/mm [102].

Katherine B Pacheco used PVA/acrylamide system containing BMA as crosslinker and a DE of 40% was obtained with a spatial frequency of 1767 lines/mm using He-Ne laser [80].

Lu Hai et al. used different photo-initiators in PVA/acrylamide system containing MB as sensitizer and BMA as crosslinking agent. Maximum DE of 59% was obtained for TEA with sensitivity of 1.72×10^{-3} mJ/cm^2. Here film had a thickness of 270-300 μm [103].

1.8.2 Commercially available photopolymers

E.I. Dupont de Nemours made a dry form of the photosensitive system, which consists of liquid acrylic monomer, cellulosic binder and photoinitiating system, and a plasticizer [77,104-109]. Diffraction efficiencies of up to 90% could be obtained with an optimum exposure of 30 mJ/cm^2 and the material has a resolution of 3000 lines/mm. But it has very poor spatial frequency response. Because of the limited resolution this material could not be used for reflection holograms. To rectify this, DuPont developed the Omnidex photopolymer system [110-113]. This material has a resolution of about 6000 lines/mm with efficiency of 99%. These results could be achieved with exposure energies of 50–100 mJ/cm^2. The material is a dry layer consisting of an acrylic monomer, a photosensitising dye, an initiator, a chain transfer agent, a plasticizer and a polymer binder coated on to polyethyleneterephtalate film substrate.

In another case, poly (methyl methacrylate) was used [77,114-117] with p-benzoquinone as sensitizer. Diffraction efficiency of ~70% could be obtained with exposure 1-8 J/cm^2, but problems with irreproducibility of results have been found. Mixtures of photopolymer containing PMMA were studied [118-120] and a refractive index of ~ 10^{-2} was obtained.

Another approach in the fabrication of photopolymers was done at RCA laboratories [121-122]. They used alfa diketones and matrices used were acrylics, poly (esters) and epoxies. In this case, a DE of ~ 70% was obtained with high exposure of ~ 240 J/cm^2.

The recording media of the HRF series (HRF-150,HRF-800) designed by Dupont containing aromatic or aliphatic acrylate monomers in cellulose acetate butyrate with DE -100% was obtained at exposure of 3 mJ/cm^2 in 100μm thick layer [123].

A commercial material, DMP-128, was developed by Ingwall et al. of the Polaroid Corporation. It consists of a mixture of methylenebisacrylamide and lithium acrylate as the monomer and a poly (N-vinylpyrrolidone) as binder. The dry material must be incubated in a 50% humidity environment before use. Post recording treatment was needed to increase the efficiency from 0.1% to 80%. The material can be used to record transmission and reflection holograms with exposure energies between 5 and 30 mJ/cm^2. Although it is more sensitive than the Du- Pont material the need for wet chemical processing is a significant disadvantage [124].

1.8.3 Nano Photopolymers

During polymerization in photopolymer system, there occurs considerable volume shrinkage due to loss of covalent bond and formation of Vander Waals attraction and this leads to reduction in effective thickness and this will affect the stored grating period.

Inorganic materials possess a wide variety of refractive indices (RIs) that give us the opportunity of obtaining much higher index modulation as compared with conventional photopolymers. The inclusion of nanoparticles also contributes to rapid build up of fixed holograms and noticeable suppression of polymerization shrinkage, thus giving high recording sensitivity and dimensional stability. In pure polymer system, it is difficult to achieve large RI modulation, therefore; *Bunning et al.* pioneered the idea to use inorganic nanoparticles (NP), having substantially higher or lower RI, in holographic mixtures as a movable non-reactive component [125].

Later this idea has been further developed by three different groups; particularly successful was the application of TiO_2 nanoparticles. The values of RI modulation ranging from 0.005 to 0.015 have been achieved [126-130]. SiO_2 dispersed in methacrylate photopolymer got a DE close to 100 % in 90 μm thickness film [133].

Suzuki and Tomita reported ZrO_2 nanoparticles in acrylate photopolymer system and RI modulation of 5.3×10^{-3} obtained [132].

Sakhno et al. in 2007 developed surface modified ZrO_2 and TiO_2 nanoparticles in acrylate polymer system with high RI modulation and the ZrO_2 incorporated polymer composite showed much photo stability than TiO_2 incorporated polymer matrix [133].

Leite et al. reported aluminophosphate nano crystals incorporated PVA/acrylamide system and a DE of 70 % obtained and can be applied in optical sensors [134].

1.9 Mechanism of Hologram Formation in PVA/ acrylamide photopolymer system

The hologram formation in the photopolymer film has been discussed by several researchers [135-136]. Lawrence et al. [49] has studied the mechanism in acrylamide photopolymer, in which gratings were recorded by photopolymerization of acrylamide.

It consists of photo-physical and photo-chemical processes.

Photo-physical process

When the dye molecule D, is exposed to laser, it absorbs a photon and is promoted into a singlet excited state $^1D^*$

$$D + h\upsilon \longrightarrow {}^{1}D^{*} \text{ .... } (1.1)$$

The singlet excited state dye can return to the ground state by fluorescence

$${}^{1}D^{*} \longrightarrow D + h\upsilon \text{ .... } (1.2)$$

or by radiation less transfer to another molecule and here it is the electron donor (ED).

$${}^{1}D^{*} + ED \longrightarrow D + ED^{*} \text{ .... } (1.3)$$

The singlet state can also undergo inter-system crossing into more stable and longer lived triplet state

$${}^{1}D^{*} \longrightarrow {}^{3}D^{*} \text{ .... } (1.4)$$

Here the excited dye molecule can undergo a reaction with the electron donor by abstracting two hydrogens to form leuco form of the dye. Here the electron donor is triethanolamine and it donates an electron to the excited triplet state of the dye, leaving the dye with one unpaired electron and an overall negative charge

$${}^{3}D^{*} + (OHCH_2CH_2)_3N\colon \longrightarrow D^{\bullet -} + (OHCH2CH2)_3N^{\bullet +} \text{ ..... } (1.5)$$

The radical cation of the electron donor loses a proton and becomes a free radical.

$$(OHCH2CH2)_3N^{\bullet +} \longrightarrow (OHCH_2CH_2)_2NC^{\bullet}HCH_2OH + H^{+} \cdots (1.6)$$

The radical anion of the dye molecule abstracts hydrogen from the free radical of the electron donor.

$(OHCH_2CH_2)_2NC^{\cdot}HCH_2OH + H^+ + D^{\cdot-} \longrightarrow (OHCH_2CH_2)_2NCH{=}CHOH + H_2D$ …(1.7)

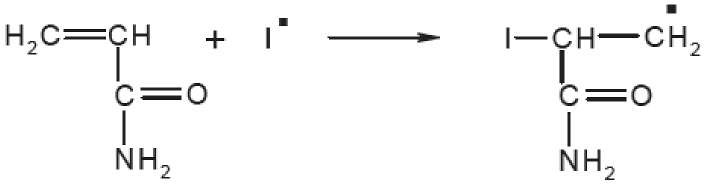
Photo-chemical process

The photo-chemical process involves free radical polymerization [49]. It consists of three steps, initiation, propagation and termination.

Initiation

Initiation takes place when the free radical initiator attaches to the monomer by addition across the C-C double bond.

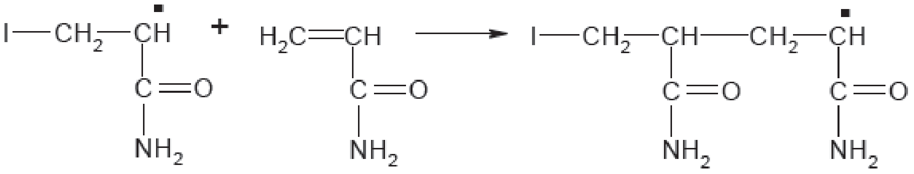
While bond formation, in order to attach itself to the monomer, the free radical uses its own unpaired electron and a π electron from C-C bond. This leaves one of the carbons with an unpaired electron therefore the monomer becomes free radical (scheme.1.1).



Scheme 1.1. Initiation

Propagation

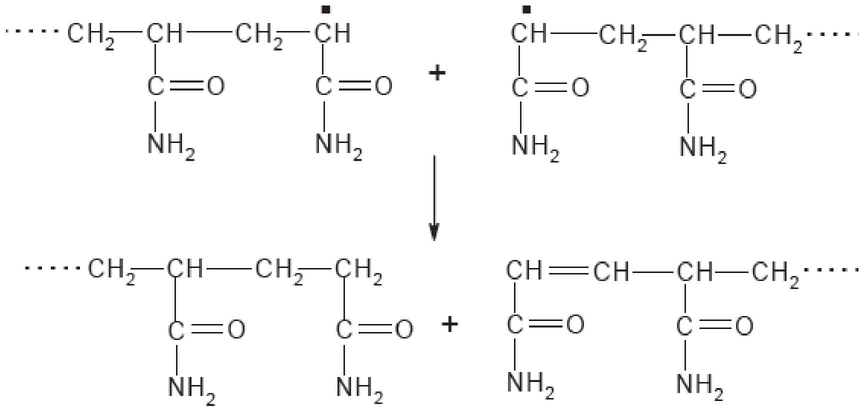
Propagation occurs when the new radical attaches itself to another monomer by addition across the double bond by the same method as above. The second monomer now becomes a radical and in this way a polymer grows (scheme.1.2).



Scheme 1.2. Propagation

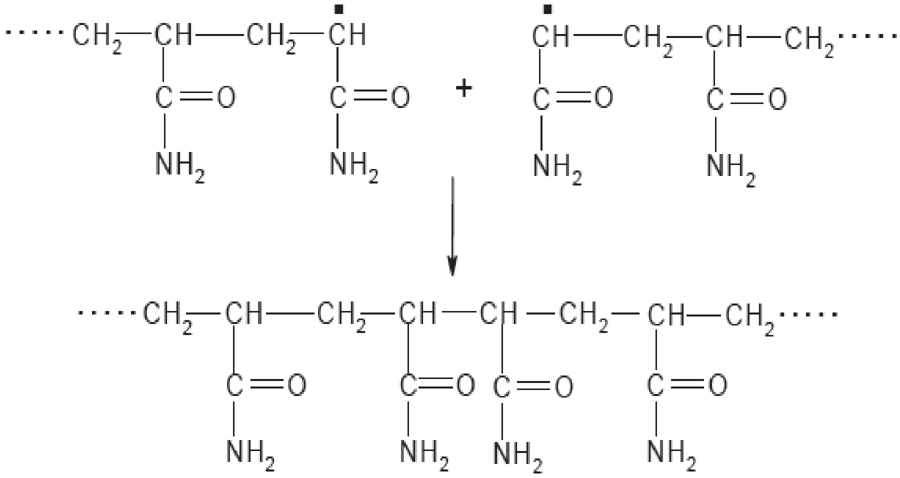
Termination

After initiation and propagation, the newly formed chain will continue to grow until it is stopped by a termination reaction. This process can arise by two reactions known as disproponation or combination [49]. Disproponation takes place when hydrogen is abstracted from one propagating chain by another. The hydrogen reacts with the free radical and the original double bond is reformed. This process results in two separate chains (scheme.1.3).



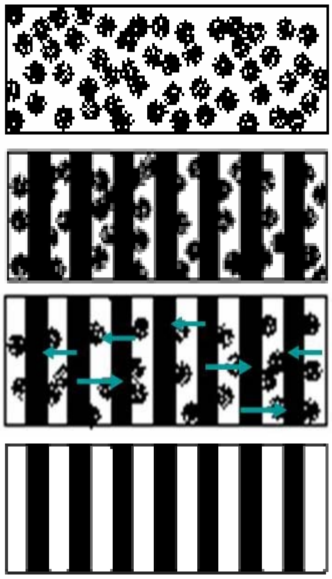
Scheme 1.3. Termination by disproponation

The second method of termina`1tion is combination, this consist when the radicals at the ends of two propagating react forming one long chain (scheme.1.4)



Scheme 1.4. Termination by Combination

On polymerization, each carbon double bond is converted into a carbon single bond, lowering the molar refractivity. This lowers the refractive index of the material and this is usually accompanied by an increase in density which leads to an increase in refractive index. The combination of these two processes results in a higher refractive index in polymerised regions compared to unpolymerized regions so that a refractive index modulation exists between exposed and unexposed areas. It is also thought that during exposure, monomer diffuses into bright region as a result of the concentration gradient induced by the depletion of these components. This causes a further difference in density (and so refractive index) between bright and dark regions. As a result of modulation in refractive index, phase hologram is recorded [49].



Monomer, dye and co-initiator are uniformly distributed in the polymer matrix

On laser exposure, dye get excited and polymerization starts

Monomer diffusion from dark region to bright region

Formation of grating as a result of modulation in refractive index

Fig. 1.1. Mechanism of grating formation

1.10 Objectives of the work

Photopolymers are write-once, read-many times (WORM) materials and therefore, storage life has great importance [94]. Methylene blue sensitized poly (vinyl alcohol)/ acrylamide films were developed in our lab with 70% diffraction efficiency at 120 mJ/cm^2. But a decrease in DE was observed on storage (decreased to 10% within 6 days after recording). The reason for decrease in DE is due to the diffusion of monomers from destructive interference region to constructive interference region and instability of the leuco state of the dye [137]. So for stabilizing the gratings, the concentration of the dye was reduced. For stabilizing grating, incorporation of crosslinkers are reported [102] as one of the method and therefore, crosslinkers were tried. In another approach to stabilize the grating, UV exposure was employed. When the photopolymer film was used for application, it must be protected from external contaminants and therefore, sealants must be used and the sealants used will not affect the properties of the film. Experiments were done for optimizing the sealant used. The molecular weight of the polymer binder has influence on the diffraction efficiency [138] of the photopolymer film and therefore, the effect of molecular weight of poly (vinyl alcohol) on the diffraction efficiency was also studied.

1.11 Conclusions

An introduction to photopolymers and different mechanisms used in the applications are discussed. The application of the photopolymer technology in various fields especially in the field of holography was presented. A brief description about different types of hologram recording materials was given and a brief review of photopolymers as hologram recording media was also presented.

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Chapter 2

MATERIALS AND METHODS

Contents

This chapter describes the materials used and the experimental techniques adopted in the present study.

2.1 Materials Used

The photopolymer system generally comprise of one or more monomers, initiator and sensitizer. The dry photopolymers consist of an additional polymeric binder. Other components are added to control a variety of properties such as pre-exposure shelf life, and viscosity of the recording medium. Vinyl monomers, such as acrylate and methacrylate are used in most photopolymer systems. Binders are included to modify the viscosity of the formulation, to aid sample preparation, and to enhance holographic exposure [1].

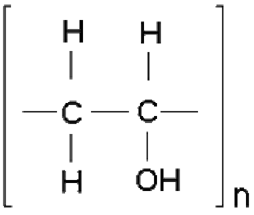
2.1.1 Host matrix

In this work, Poly (vinyl alcohol) (PVA) was selected as the base matrix. It appears as white free flowing granules.

Vinyl alcohol, the true monomer of poly (vinyl alcohol), does not exist in the free state and the polymer is industrially manufactured from vinyl acetate monomer. Partially hydrolysed and fully hydrolysed PVA are commercially available and are soluble in water; this makes them important in the photopolymer film preparation. Solubility of PVA in water depends on its degree of hydrolysis. The presence of large number of hydroxyl groups cause it to have high affinity to water, with strong hydrogen bonding between the intra- and inter-molecular hydroxyl groups in fully hydrolysed PVA, greatly reduces its solubility in water.

On the other hand, the residual acetate groups in partially hydrolysed PVA, are essentially hydrophobic, and weaken the intra- and inter-molecular hydrogen bonding of adjoining hydroxyl groups. The presence of an adequate amount of acetate groups increases the water solubility [2]. It is used as a moisture barrier film for food supplement tablets and for foods that contain inclusions or dry food with inclusions that need to be protected from moisture uptake.

Structure of poly (vinyl alcohol)



$$\left[-CH_2-CH(OH)- \right]_n$$

In the study, poly (vinyl alcohol) with molecular weights 13,700, 54,500 and 1,25,000 and degree of hydrolysis (86-89%) were used.

2.1.2 Photo-initiator- Dye

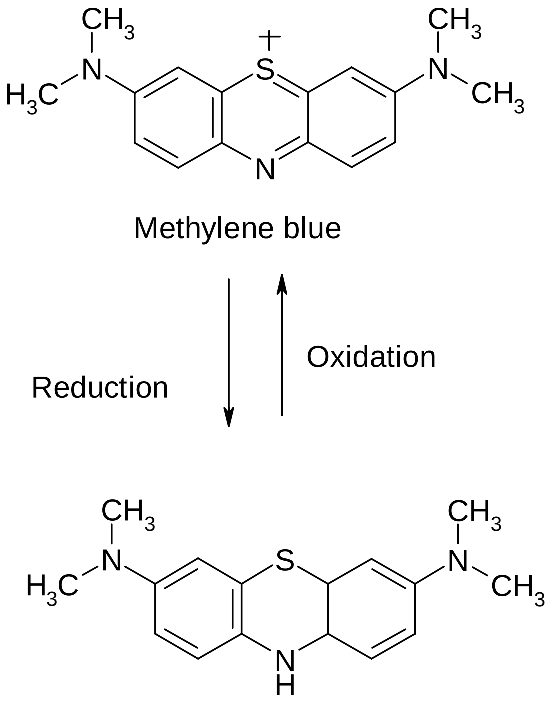
Holographic photopolymer systems typically use molecules which are sensitive to the visible region. A photosensitizer molecule absorbs the imaging light, and in its excited state, interacts with a radical generator molecule, either through energy transfer or through a redox reaction, to produce the initiating species. There are two types of photo initiators; type I photoinitiators are unimolecular photoinitiators and type II photoinitiators are bimolecular photoinitiators. Unimolecular photoinitiators undergo homolytic bond cleavage upon absorption of light. Here radical generation follows first order kinetics. In the case of type II photoinitiators, the excitation energy is not enough for bond cleavage, but it can react with another constituent of the polymerization mixture- the so called co-initiator (COI) to produce initiating radicals. Here radical generation follows second order kinetics. There are two distinct pathways for radical generation by type II photoinitiator,

1) By hydrogen abstraction from a suitable hydrogen donor
2) Photoinduced electron transfer reactions and subsequent fragmentation [3].

In this study, methylene blue (MB) (Molecular weight- 319.85), a photoreducible thiazene dye was used. It is an odourless, dark green crystalline powder soluble in water. Methylene blue is widely used as a redox indicator in analytical chemistry and in medicine and sulphide analysis. It is a bimolecular photoinitiator and has highest absorption in the red region (663 nm). Here, initiating radicals are generated by photoinduced electron transfer and energy transfer is not thermodynamically favourable in these systems due to low excitation energy of the dyes. Here, electrons get transferred from the co-initiator to the excited dye molecule which yields radical cations of the co-initiator and radical anions of the dye and it get transferred into colourless leuco form. The former can initiate the polymerization and the species derived from dye molecules do not react with monomer molecules. Radical generation follows the equation (2.1) [3].

$$D^{*} + COI: \rightarrow (D....COI)^{*} \rightarrow D^{-\bullet} + COI^{+\bullet} \quad \text{..................} (2.1)$$

The chemical structure of methylene blue and its leuco form is;

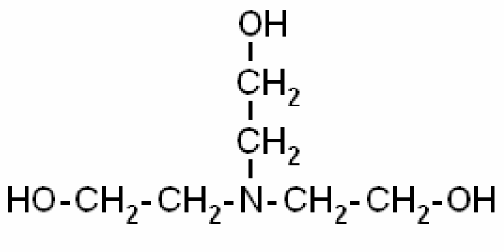


Leuco methylene blue

2.1.3 Co-initiator

The radical cations formed from the co-initiator react with monomer molecules and polymerization starts. Commonly used co-initiators with photoreducible dye are amines, phosphines and arsines, sulfinates, heterocycles, enolates, organotin compounds and borates [3]. In this work, triethanolamine (molecular weight- 149.19) was used. It is a colourless hygroscopic liquid with characteristic odour. Triethanolamine is used primarily as an emulsifier and surfactant. It also serves as a pH regulator in many different cosmetic products - ranging from cleansing creams and milks, skin lotions, eye gels, moisturizers, shampoos, shaving foams etc.

The chemical structure of triethanolamine is;



$$HO-CH_2-CH_2-\overset{\begin{array}{c}OH\\|\\CH_2\\|\\CH_2\\|\end{array}}{N}-CH_2-CH_2-OH$$

triethanolamine (TEA)

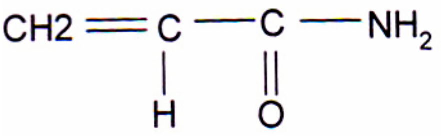
2.1.4 Monomer

Recording of grating happens in photopolymer system by the polymerization and then diffusion of monomer within the film. Vinyl monomers are used in free radical polymerization and here acrylamide (molecular weight- 71.03) was used. It is a white crystalline solid and easily soluble in water. Acrylamide is used for the production of high molecular weight polyacrylamide which is modified to produce different physical and chemical properties suited to a wide variety of industrial applications. Large quantities of polyacrylamide gel are produced on site for use as a grouting agent, particularly for the sealing of mineshafts in the mining industry. Polyacrylamides are used in large quantities as flocculators (substances that aid the separation of suspended solids from aqueous systems) in the following industries:

Water treatment, pulp and paper processing, crude oil production processes, mineral ore processing, concrete processing, soil and sand treatment. Smaller quantities of polyacrylamides are used in the following applications:

Cosmetic additives, permanent press fabrics, electrophoresis, molecular biology applications, photographic emulsions, adhesive manufacture and food processing.

The chemical structure of acrylamide is



$$\mathrm{CH2} = \underset{\displaystyle \mathrm{H}}{\underset{|}{\mathrm{C}}} - \underset{\displaystyle \mathrm{O}}{\underset{\|}{\mathrm{C}}} - \mathrm{NH_2}$$

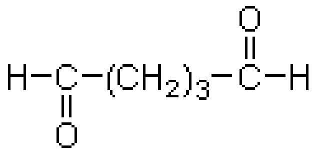
2.1.5 Crosslinker

Crosslinkers were used in the study for better storage life of the recorded grating. Glutaraldehyde, and N-N’-methylene- bis-acrylamide were used as crosslinkers.

Glutaraldehyde

Pentanedial or glutaraldehyde is a common crosslinker used in PVA and its molecular weight is 100.12. It is a colourless oily liquid, soluble in water. It is a chemical, frequently used as a disinfectant and sterilizing agent against bacteria and viruses (2% solution), an embalming fluid and tissue fixative, a component of leather tanning solutions, and an intermediate in the production of certain sealants, resins, dyes, and electrical products.

Structure of Glutaraldehyde

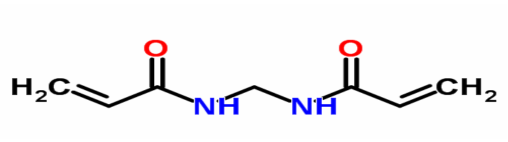


$$H-\underset{\underset{O}{\|}}{C}-(CH_2)_3-\overset{\overset{O}{\|}}{C}-H$$

N-N’-methylene- bis-acrylamide (BMA)

BMA is commonly used with acrylamide photopolymer system. Molecular weight of BMA is 154.20 and it is an odourless white crystalline powder, soluble in water.

Structure of BMA



2.2 Film fabrication

For the fabrication of photopolymer film, different methods are available like, dip coating, spin coating, doctor blading, gel casting, gravity settling, spraying etc. [4]. Here gravity settling method was used. This is a very simple method of layer coating and it can produce the thickest layers. In this method, a known volume of the photosensitive mixture was placed on a levelled glass substrate (dimension of glass plate: 7.6 cm x 2.6 cm x 0.1 cm) and allowed to dry by evaporation. These films were covered to avoid dust particles and 48 hrs of drying was required and these dried films were used for the study.

The sample preparation was done at 30 ± 2^{o}C and Relative Humidity (RH) was 55-65 %.

2.3 Characterization

2.3.1 Tensile studies

Tensile properties of the samples were measured using UTM Shimadzu Autograph AG-1 Series as per ASTM D882-02. Here the samples were casted into sheets of rectangular samples of dimension 10cm x 1cm and three to four pieces of each set of samples was used for the study and mean value was taken. The thickness of the test pieces were measured using thickness gauge. Studies were done using the machine gauge length of 40 mm at a speed of 50 mm / minute.

$$\text{Tensile Strength} = \text{Force}/\text{Cross sectional area } (\text{N/mm}^2) \quad \text{.......(2.2)}$$

$$\text{Elongation at break} = L_1 - L_0 / L_0 \quad \text{........(2.3)}$$

Where L_0 – Initial length and L_1- Final length

2.3.2 Differential scanning Calorimetry (DSC)

The glass transition temperature (T_g) of the polymer was measured using DSC Q-100- TA instruments at a heating rate of 2^oC / minute. A sample of 0.5 mg -0.6 mg was taken in a pan and covered with a lid and cubed. This was put in the sample chamber and heated from 30^oC to 150^oC. The glass transition temperature of the samples was obtained from the DSC curve.

2.3.3 Laser exposure

The holographic characterization of polymer films was done by exposing the films to continuous wave He-Ne laser (632.8 nm, 15 mW, Melles Griot) because the dye used MB has its absorption maxima in the red region of the spectrum. The laser beam was expanded using spatial filter arrangement. The power density was measured using power meter (Ophir model PD-200) and exposure energy (mJ/cm^2) was calculated by multiplying power density and time in seconds and the exposure time was controlled by an electronic shutter. All these experiments were performed on an indigenously fabricated vibration free table [4].

2.3.4 Optical absorption studies

On exposure to He-Ne laser, the dye absorbed light, got excited and became colourless and this is clear from the absorption spectra of the sample. The absorption spectra of the dye doped film were recorded by JASCO V- 570 spectrophotometer using undoped polymer sample as the reference.

2.3.5 Thickness Measurement

Dektak 6m Stylus Profiler was used to measure the thickness of the fabricated photopolymer films. The stylus profiler is an advanced thin and thick film step height measurement tool capable of measuring step even below $100A^0$.The instrument contains the mechanical and optical components for sample placement, sample viewing and scanning/ measurement. A diamond tipped stylus permits accurate measurement in a wide range of applications and the surface profile was obtained as hills and valleys. As the stage moves the sample, the stylus rides over the sample surface and the sample thickness can be readily obtained from the monitor [5].

2.3.6 Recording of grating

In order to optimize the concentration of components and to optimize the exposure energy, plane wave gratings were recorded on the dried films using double beam interferometry. The experimental setup is shown (fig. 2.1). The laser beam was split into two using a beam splitter (B) with R/T ratio 50/50 and these beams were directed to the film using front silvered mirrors (C). These beams were expanded using spatial frequency filter (D) and collimated (E- collimating lens). The collimated laser beams were allowed to interfere inside the film (F). The exposure time was controlled by an electronic shutter (A) placed in front of the laser. Gratings were recorded by varying the inter beam angles so as to record gratings with different spatial frequencies. The spatial frequency (number of lines recorded on the material) was determined using Bragg's equation.

$2d\sin\theta = n\lambda$ .... (2.4)

Number of lines, $N = 1/d$ .... (2.5)

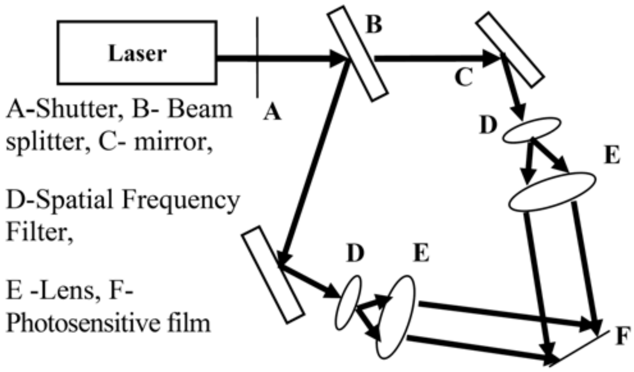


Fig. 2.1. Experimental setup for recording grating- double beam interferometry

2.3.7 Diffraction efficiency measurement

The experimental setup to measure the diffraction efficiency (DE) is shown (fig.2.2). Unexpanded laser beam was allowed to fall on the grating recoded film placed at Bragg's angle. The diffracted beam was observed on the screen at Bragg's angle and its intensity was measured using Ophir 200 power meter. The intensity of the laser beam was reduced to 1μW using neutral density filters (ND filter). The intensity of incident beam (I_i) and diffracted beam (I_d) was measured. The percentage diffraction efficiency (η) of the recorded grating was measured as the ratio of intensity of the diffracted beam to intensity of the incident beam.

$\eta = (I_i / I_d) \times 100$ .... (2.6)

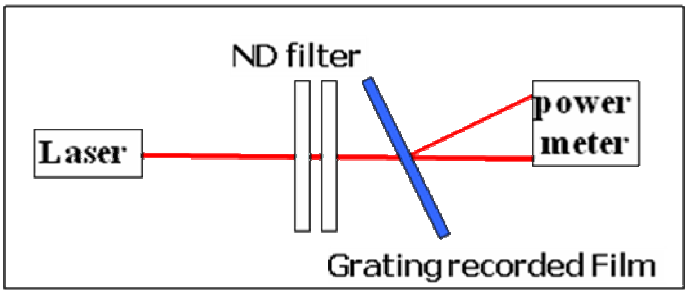


Fig. 2.2. Experimental setup for diffraction efficiency measurement.

2.3.8 Calculation of Refractive Index Modulation

On laser exposure, monomers in the exposed region get polymerized and monomer from the unexposed region diffuses to the exposed regions. This induces a change in refractive index (RI) between the exposed and unexposed regions. The modulation in the RI was calculated using Kogelink's coupled wave theory. This theory treats the relationship between diffraction efficiency, grating thickness, wavelength of incident radiation, and the angle of incident radiation.

$$\Delta n \;=\; \mathrm{Sin}^{-1}(\eta^{1/2}) \times \lambda \cos\theta / \pi \times d \ldots\ldots\ldots\ldots \quad (2.7),$$

where, Δn – RI modulation, η - DE, λ - wavelength of reading beam, θ - angle inside the material measured from the normal to the surface and d –thickness of the film.

2.3.9 Storage life and Shelf life

In the case of dye doped polymer films, the diffraction efficiency can be reduced or remained unaltered on storage. Storage life of the recorded grating gives an idea about how long a period; the recorded data could be stored by the material. Storage life of the recorded grating was monitored by measuring the diffraction efficiency each day after recording.

Shelf life of the material gives an idea about up to what time, a data could be freshly recorded and this is done by recording grating every day after sample drying.

2.3.10 Effect of different sealants

For protecting the films from direct contact with air and for avoiding sample cracking, the films were sealed with glass plates and also coated with PMMA. When glass plates were used to cover the films, two sealants, an epoxy sealant and cyanoacrylate sealants were used.

Epoxy sealant was prepared by mixing epoxy resin and room temperature amine hardner in a ratio 10:1 and this was then applied to the sides of clean glass plate placed over the film. In the case of cyanoacrylate sealant, it was directly applied as before. Different concentrations of PMMA solution was prepared by dissolving different weights of PMMA granules in chloroform and the film was then dipped into it for different times.

2.3.11 Effect of UV exposure

Inorder to study the effect of UV exposure on the storage life of the material, the recorded gratings were exposed to UV irradiation for different times. For this, 400 W Dymax UV flood lamp model EC 5000 was used (fig.2.3).

Fig.2.3. UV Flood Lamp

2.3.12 Recording of Hologram

Transmission holograms were recorded on the polymer film using single beam technique as shown in fig.2.4. Laser beam (S) was expanded using a spatial frequency filter arrangement (E). Object (O) was placed in the path of the expanded laser beam and polymer film (F) was placed near the object at an angle. The laser beams scattered by the object act as the object wave and directly transmitted beam act as the reference wave. The position of the film was adjusted to collect maximum object wave. The reference wave and object wave interfere at the film and thus the hologram was created. The hologram was reconstructed by illuminating with an expanded laser beam.

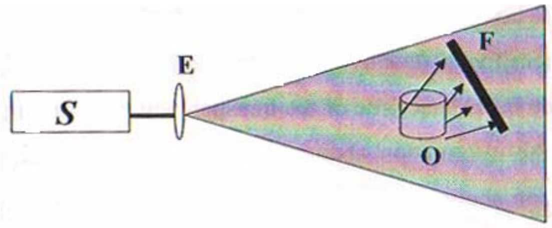


Fig. 2.4. The experimental technique to record transmission hologram

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* * *

CORRECTIONS

The properties of the polymer films are dependent on the concentration of the ingredients. However, the concentration of ingredients corresponding to some of the samples is not clearly indicated in the thesis .Eg.: The concentration of acrylamide corresponding to aa1, aa2…. Aa7 is not given, except a general statement that “Concentration was varied from 0.25 M to 0.5 M and the films was named as aa1, aa2 ….. aa7”. Similarly, the amount of TEA used for preparing the samples corresponding to Fig. 3.1 to 3.3 is not mentioned In the case of tensile studies (2.3.1), it is stated that 3 to 4 pieces of samples were used for the evaluation. However, in the subsequent chapters only the mean value is shown in the graph depicting the results. A plot with scatter band would have given a better idea about the trend in the measured properties. It is not mentioned whether the remaining characterizations were carried out as a single measurement or in multiplicates.	The concentration of acrylamide was varied from 0.25 M to 0.5M. aa1-0.25 M, aa2-0.3M, aa3-0.32M, aa4-0.35M, aa5-0.38M, aa6-0.45M, aa7-0.5M. Methylene blue concentration is C 20- 2.09x10^{-4} M, C14-1.4x10^{-4} M, C11- 1.1x10^{-4}M, C 0.14-1.4x10^{-5}M, C 0.07-0.7x10^{-5} M Glutaraldehyde concentration is GA1-0.005M, GA1-0.01M, GA3-0.05M. GA4-0.1M, GA5-0.15M, GA6-0.2M. BMA concentration is BMA1-0.001M, BMA2-0.002M, BMA3-0.005M, BMA4-0.01M, BMA5-0.02M,BMA6-0.03M, BMA7-0.05M The concentration of TEA used to prepare the samples corresponding to fig.3.1 -3.3 is 0.05 M. All the experiments were repeated a number of times (at least 10 experiments were done and average value is reported)

Chapter 3

STUDIES ON METHYLENE BLUE SENSITIZED POLY (VINYL ALCOHOL)

Contents

3.1 Introduction

Photopolymers were first introduced as holographic recording material by Close et al. in 1969 [1]. Vinyl monomers, such as acrylate and methacrylate are used in most photopolymer systems.

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 this photopolymeric system initiated by triethanolamine and methylene blue in recent years [2-8]. Blaya et al. reported a DE of nearly 80 % in PVA/acrylamide system initiated with methylene blue and triethanolamine with 40 mJ/cm^2. But they prepared films using scientific thin layer chromatographic plate coater and also concentration of each component kept different [9]. In the present work, methylene blue sensitized acrylamide photopolymer system was used. Here films were prepared by gravity settling method. Optimization of each component is found to contribute to the holographic performance of the film [10].

Previously our research group has successfully recorded holographic gratings in acrylamide incorporated poly (vinyl alcohol) film, prepared by gravity settling method, with diffraction efficiency more than 70% with exposure energy of 120 mJ/cm^2, having a dye concentration of 2.09x10^{-4}M. But on storage, DE was reduced to 10 % within 6 days after recording [11]. The reason for the decrease may be due to the diffusion of residual dye molecules from destructive region to constructive region and by the instability of leuco form of the dye molecule [8]. Photopolymers are WORM materials and therefore the recorded gratings should be stable in these systems. In this chapter, studies were done to stabilize the recorded gratings by reducing the dye concentration.

3.2 Experimental

Film Preparation

All the materials used in this work were analar grade and were used without further purification. Photopolymer solution was prepared by dissolving 10 g Poly (vinyl alcohol), in 100 ml cold distilled water. (Molecular weight; 1, 25,000 and degree of hydrolysis, 86-90%). To this, acrylamide (AAm), Triethanolamine (TEA) and methylene blue (MB) were added and the solution was stirred well to get a homogeneous solution. The polymer film was prepared by gravity settling method under normal laboratory conditions (Relative Humidity-55-65%, temperature-30±2°C) and 48 hours of drying was required. The concentration of each component is given in Table 3.1.

Table 3.1. Composition of each component

Constituents	Concentration
PVA	10% by weight
Acrylamide	0.25 – 0.5 M
Triethanolamine	0.01 – 0.1 M
Methylene blue	2.09×10^{-4}M - 0.7×10^{-5} M

3.3 Characterization

Tensile properties of the samples were measured using UTM-Shimadzu autograph AG-1 series and T_g was measured using TA DSC-Q- 100 instrument at a heating rate of 2°C/minute from 30°-150°C under nitrogen atmosphere.

The optical characterization was done using Jasco V-570 spectrophotometer and modulation in refractive index was calculated using Kogelnik’s coupled wave theory. Optimization of various components was done by recording plane wave gratings on the film, using He-Ne laser (632.8 nm) by standard double beam method (chapter 2) and the gratings were reconstructed by 1µW He-Ne laser. Variation in spatial frequency, optimization of beam ratio, storage life and shelf life of the material were also measured.

3.4 Tensile Studies

For studying the effect of each component in the tensile properties of PVA, studies were done on pure PVA and PVA containing other additives. For this, samples were prepared and cut into rectangular pieces as explained in chapter 2.

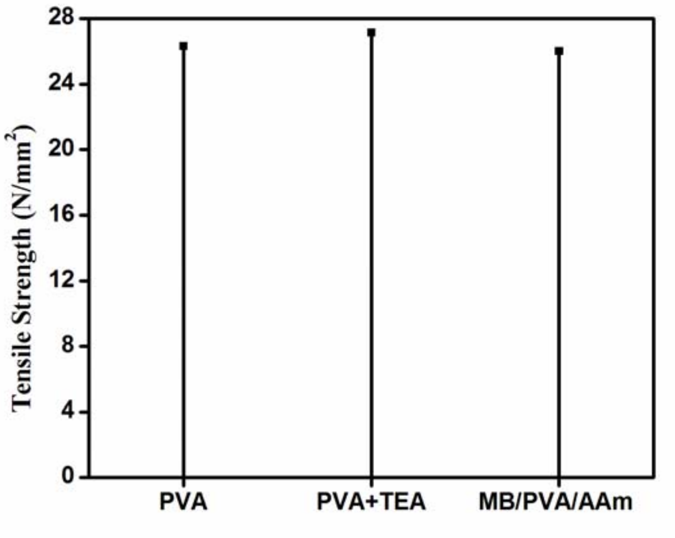

Fig. 3.1. Material Vs Tensile strength

From (fig.3.1), it is clear that no change in tensile strength was observed by the addition of TEA and doping with methylene blue (tensile strength of PVA- 26 N/mm^2, PVA+TEA -27 N/mm^2 and MB/PVA/AAm film-26 N/mm^2).

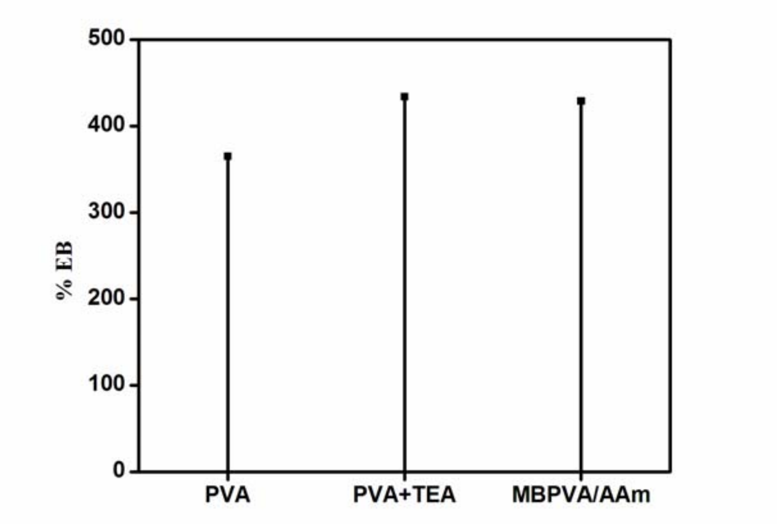

Fig. 3.2. Material Vs % Elongation at break

But a change was observed in the case of elongation at break of the sample. From (fig.3.2), it can be seen that addition of TEA enhanced the % elongation at break of PVA from 365 to 434. Addition of electron donor cause an increase in DE as reported by B.M. John et al. [12] and enhancement in elongation at break of PVA support the above statement. Here TEA acts as a plasticizer and increases the chain flexibility and inturn enhances the elongation at break of PVA. During hologram recording, it appears that polymerization of monomer starts and proceeds rapidly in regions exposed to bright interference fringes. As conversion of monomers to polymer occurs, fresh monomer diffuses in from neighbouring dark regions, thus setting up concentration and density gradients that result in refractive index modulation [8]. If the chain flexibility is increased by the addition of TEA, this increases the diffusion of monomers and refractive index (RI) modulation. As diffraction efficiency (DE) depends on RI modulation, this will also get increased upon the addition of TEA.

3.5 DSC studies

From tensile studies it was clear that only TEA influences the mechanical properties of the polymer binder and therefore DSC studies were carried out with pure PVA and PVA containing the co-initiator TEA. Fig.3.3, gives the DSC thermogram of these two.

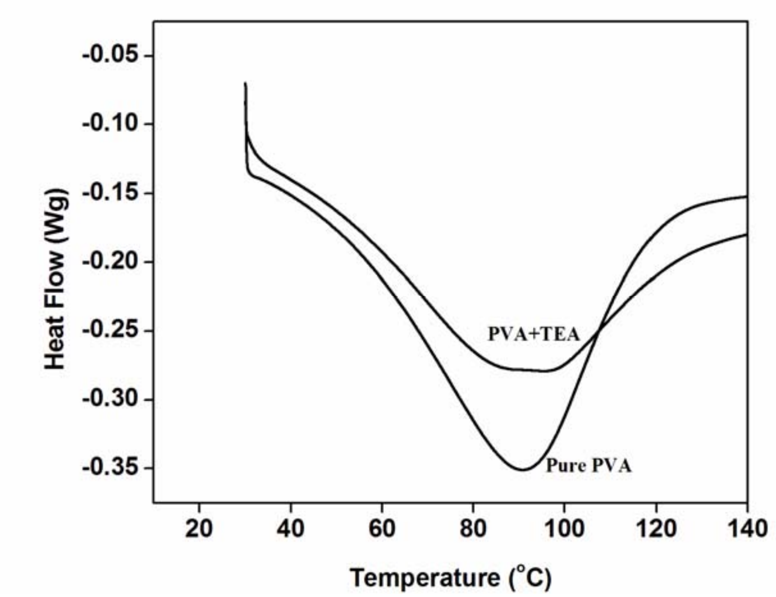

Fig. 3.3. DSC curve of Pure PVA and PVA+TEA

The glass transition temperature (T_g) of PVA is 86^{o}C and addition of TEA has decreased the T_g to 83^{o}C. This is due to the plasticizing action of TEA on PVA matrix. Plasticizers are usually low molecular weight non-volatile substances, which when added to a polymer improves its flexibility, processibility and hence utility. As the lowering of Tg of PVA occurs, the flexibility of polymer chain increases, then diffusion become easier and diffraction efficiency of the recorded grating also increases.

3.6 Optimization of methylene blue concentration

The photoinitiator determines the zone of absorption and therefore the wavelength used to record gratings. MB has absorption maximum in the red region of spectrum. So, for optimizing the concentration of the dye, gratings were recorded using He-Ne laser (emission at 632.8 nm). Methylene blue concentration was varied (keeping the concentration of all other component's constant; weight % of PVA- 10, concentration of acrylamide -0.38 M, concentration of TEA- 0.05M) from 2.09 x 10^{-4} M to 0.7 x10^{-5} M and samples were named as C 20, C14....C 0.07 in (fig.3.4). Gratings were recorded at different exposure energies from 5 mJ/cm^2 to 130 mJ/cm^2 by keeping the recording angle 40^o (our research group previously optimized the recording angle as 40^o and further optimization in this material was done later) and power at the recording position as 4mW. From the figure, it can be seen that, for all the dye concentrations with the increase in exposure energy, RI modulation increases and resulted in increased DE, reaching a maximum and then decreases. At high exposure, decrease in DE might be caused by cross-talk of holograms [13]. For C 20, maximum DE of 70% was obtained at exposure energy 120 mJ/cm^2 and for C14, the optimized exposure energy was 100 mJ/cm^2. For C 11, C 0.14 and C 0.07, the optimized exposure energy was 100 mJ/cm^2, 80 mJ/cm^2 and 50 mJ/cm^2 respectively. It is not possible to reduce or increase the concentration of dye beyond a limit; because if the concentration is very low, photopolymerization will be inefficient and if concentration is very high, the dye near the surface will act as a filter for the dye beneath it. Thus, unless the initiator fades to a non absorbing material during irradiation, only the monomer near the surface will be polymerized [14]. A maximum DE of 75% with exposure energy of 80mJ/cm^2 was obtained for the sample named as C 0.14 (dye concentration: 1.4x10^{-5}M) (fig. 3.4). For this, a DE of 62 % obtained at 5 mJ/cm^2 itself.

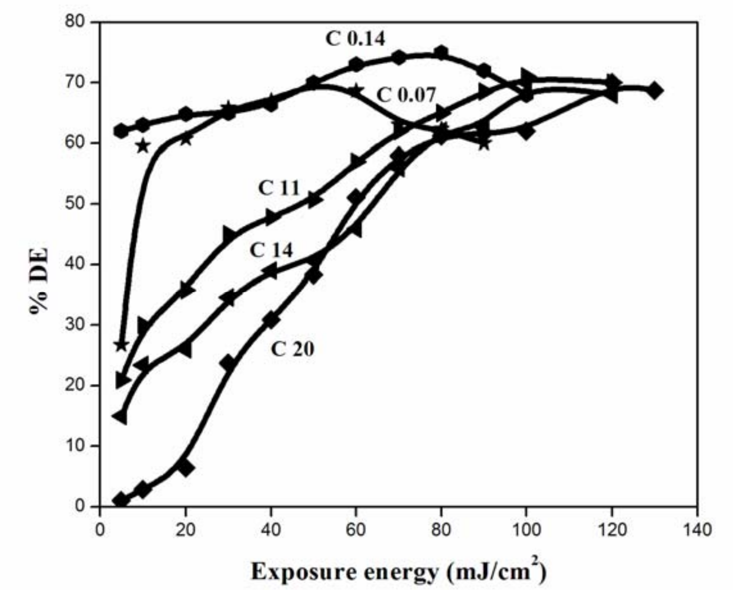

Fig. 3.4. Optimization of concentration of methylene blue

3.7 Optimization of concentration of acrylamide

For optimizing the concentration of acrylamide, MBPVA/AAm films were prepared by keeping the concentrations of methylene blue and triethanolamine constant. Acrylamide concentration was varied from 0.25 M to 0.5 M and the films were named as aa1, aa2... aa7. When the material was illuminated with He-Ne laser at a spatial frequency of 1080 lines/mm, photoreduction reaction occured, yielding radicals that initiate radical polymerization reaction. When the concentration of acrylamide was increased, the energetic exposure necessary to obtain maximum DE was decreased, ie, sensitivity increased. But it is not possible to increase the concentration of acrylamide indefinitely because the compatibility and solubility of this monomer in PVA is limited [9]. The maximum DE achieved remained approximately constant at high concentration of acrylamide, (fig.3.5).

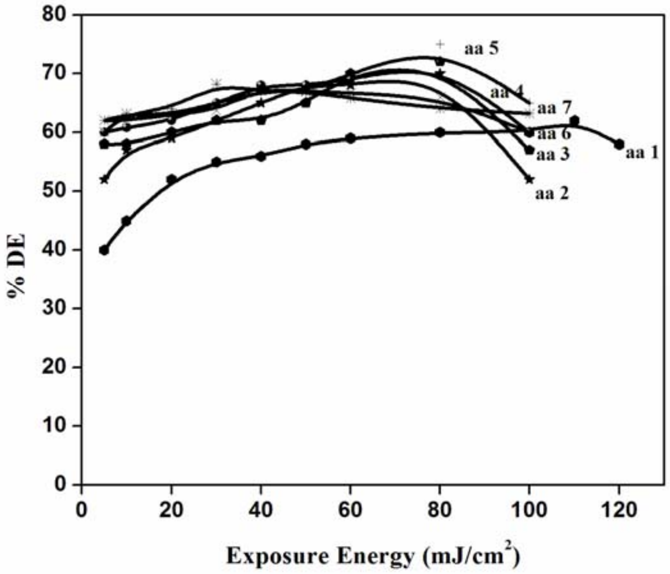

Fig. 3.5. Optimization of acrylamide concentration

Here for film aa7, this is the highest concentration, we have obtained a maximum DE of 68% at 30 mJ/cm^2, but DE obtained for all other samples remained nearly the same and a maximum DE of 75% was obtained for film aa5 (0.38 M) with exposure energy 80 mJ/cm^2. This was selected as the optimum concentration

3.8 Optimization of triethanolamine concentration

Inorder to optimize the concentration of triethanolamine, films were prepared by keeping the concentration of acrylamide and methylene blue constant. Concentration of triethanolamine was varied from 0.01 M to 0.1 M. During exposure, the incident light in a photoreduction reaction progressively converts the dye molecules into leuco methylene blue. As a result of this transformation, radicals capable of initiating photopolymerization reaction are generated [9]. Fig.3.6 shows concentration of TEA Vs % DE at 80 mJ/cm^2 with 1080 lines/mm. As the concentration of TEA increased, DE also increased, reaching a maximum and then decreased. Here maximum DE of 75% was obtained for 0.05 M. Amine acts as plasticizer that smoothens the network, favouring the solution and stability of the other components in the matrix and consequently the performance of the material [15]. After achieving a certain concentration, when the concentration of amine increased further, the primary free radical formation rate increased and the polymerization will also get speeded up. But the excess concentration will lead to cage effect, making the combination of free radicals terminated easily thus causing a reduction in diffraction efficiency [16].

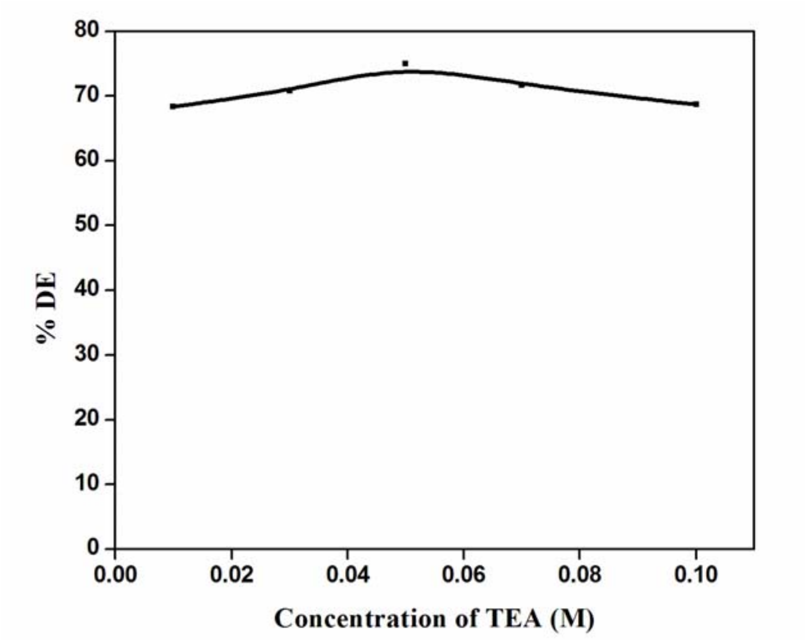

Fig. 3.6. Optimization of TEA concentration

So the optimized film is having concentration of methylene blue: 1.4 x10^{-5} M, acrylamide: 0.38 M, triethanolamine: 0.05 M. Further studies were done on this optimized sample.

3.9 Optical absorption studies

The film was exposed to an energy density of 80 mJ/cm^2 and the absorption spectra of the exposed and unexposed regions were taken. Fig. 3.7 shows a peak around 660 nm which is characteristic of methylene blue. But on exposure, the intensity of the peak decreased showing that bleaching occurred during irradiation.

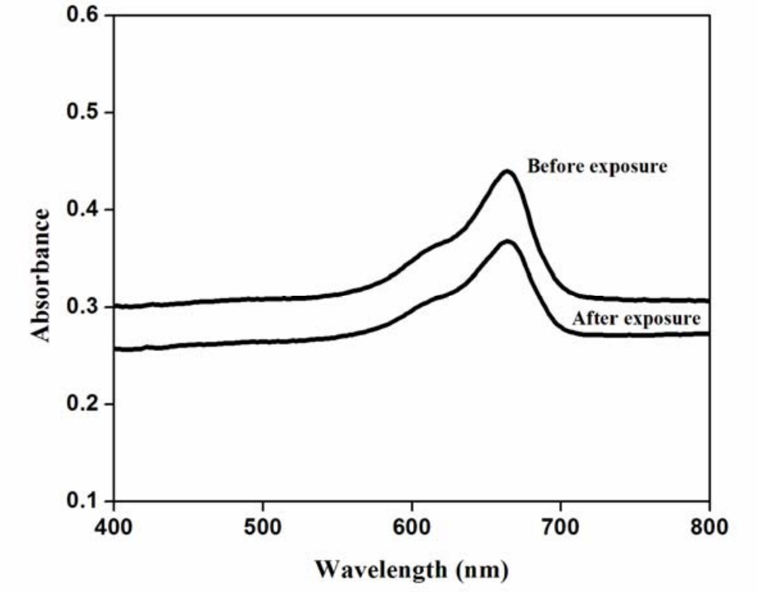

Fig. 3.7. Optical absorption spectra of optimized MBPVA/AAm film

3.10 Thickness measurement and calculation of RI modulation of the optimized film

The thickness of the dried film was measured using Dektak 6m Stylus profiler and a thickness of 130μm was obtained in the central part of the film.

The modulation in refractive index of the optimized sample before and after exposure was calculated using Kogelnik coupled wave theory;

$\Delta n = \mathrm{Sin}^{-1} (\eta^{1/2}) \times \lambda \cos\theta / \pi \times d$, where Δn – RI modulation, η - DE, λ - wavelength of reading beam, θ - angle inside the material measured from the normal to the surface and d –thickness of the film.

Using this equation a RI modulation of 1.52×10^{-3} was obtained.

3.11 Resolution of the optimized film

To find out the resolution of the material, gratings were recorded on the optimized sample at different inter-beam angles by keeping the exposure energy as 80 mJ/cm^2. Spatial frequency of each grating was determined using Bragg's equation. Fig.3.8 is the plot of variation of DE with spatial frequency. Inter-beam angle was varied from 30^{o}-80^{o} and the corresponding spatial frequency was 818-2032 lines/mm. The efficiency was slightly increased with increase in spatial frequency, reaching a maximum of 75 % at 1080 lines/mm and then decreased.

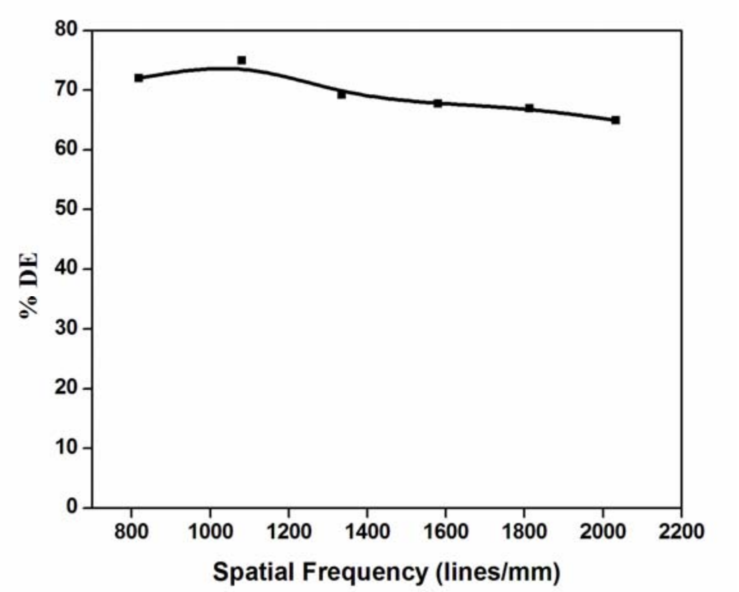

Fig. 3.8. Spatial frequency studies on the optimized film

When the spatial frequency reached to 2032 lines/mm, diffraction efficiency reduced to 65%. The reduction in DE with spatial frequency could be due to migration of polymer chains, which have been initiated inside a bright region but grow into an adjoining dark region. This would lead to averaging of the recorded refractive index profile. Such an effect would produce a weaker refractive index modulation and correspondingly lower DE at higher spatial frequencies [17].

3.12 Optimization of beam ratio

In order to study the effect of beam ratio on the diffraction efficiency of the recorded gratings, the intensity ratios of the two beams were varied by placing spatial frequency filters in the path of one beam. Gratings were recorded on the optimized film at exposure energy of 80 mJ/cm^2 and spatial frequency of 1080 lines/mm. The DE for different beam ratio is plotted (fig.3.9). A maximum diffraction efficiency of 75% could be achieved for beam ratio of 1: 1.

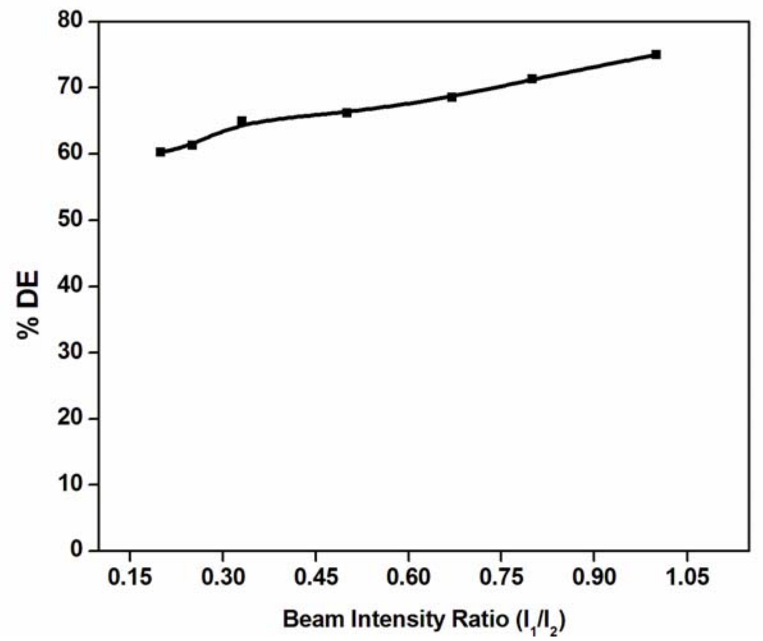

Fig. 3.9. Variation of DE with beam ratio

3.13 Storage life of the grating

Photopolymer films are WORM materials and therefore, storage life has great importance. To study the material storage life, kept at room temperature, gratings were recorded on the optimized sample at exposure energy of 80 mJ/cm^2 with spatial frequency 1080 lines/mm and diffraction efficiency was measured on successive days. The variation in DE with time is plotted (fig.3.10). Initially the material had a diffraction efficiency of 75% and after 2 months, it remained as 73% and after 5 months, the efficiency was 67% and after one year it was 43%. After this also, a decrease could be observed and after 3 years of recording, gratings could be read with low DE of 2 %.

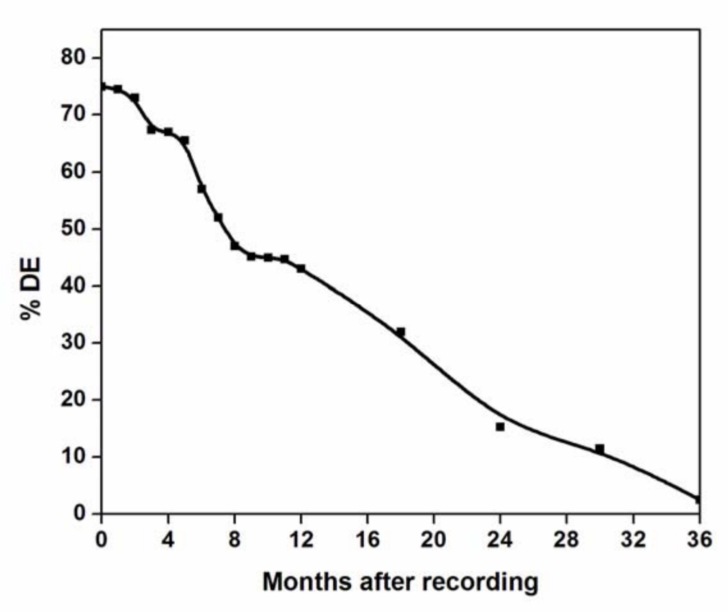

Fig. 3.10. The DE of MBPVA/AAm film on storage

The reason for decrease in the diffraction efficiency may be due to the diffusion of dye molecules from destructive region to constructive region [8]. But in the present case, the concentration of dye molecule was very low and no more dye molecules may remain in the destructive region and storage life of MBPVA/AAm film could be improved by reducing the dye concentration.

3.14 Shelf life of the material

Shelf life of the material was studied by recording gratings on the optimized film at different time intervals after drying the sample. In all cases, gratings were recorded with an energy sensitivity of 80mJ/cm^2 with spatial frequency 1080 lines/mm. Fig.3.11 is the plot of decrease in DE on ageing of the film.

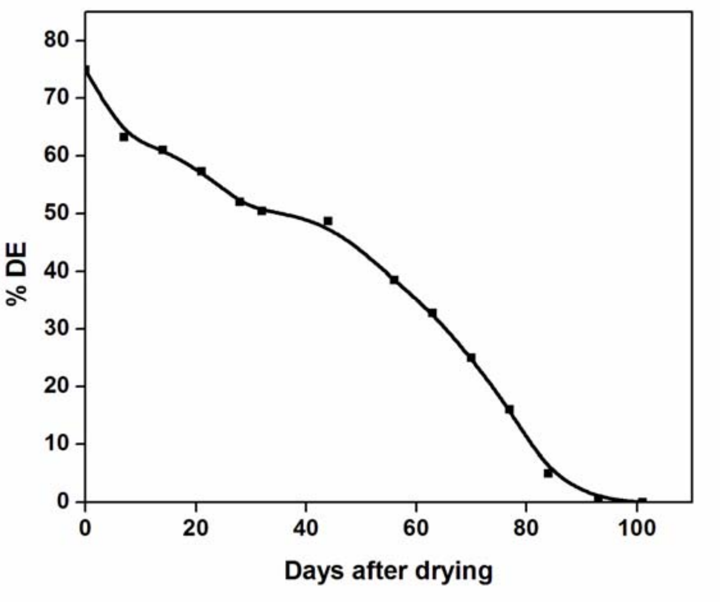

Fig. 3.11. Shelf life of the film

Grating with DE of 60% could be achieved up to two weeks and DE was decreased to 52% after one month. After 2 months, DE further reduced to 30 % and after 3 months, gratings could be recorded on this sample with low diffraction of ~ 1 % DE and after 100 days, no gratings could be recorded.

In the case of commercially available Polygramma, which is in solution form, has a shelf life less than 6 months when the solution was kept below 20°C [18]. So inorder to improve the shelf life, the photopolymer mixture was kept in the solution form and stored at a temperature of 5°C ±3°C and a relative humidity of 30-50%. DE was monitored in each month by preparing the film and gratings were recorded as before. In this case, the same diffraction efficiency of 75% could be achieved after five months of solution preparation (fig.3.12).

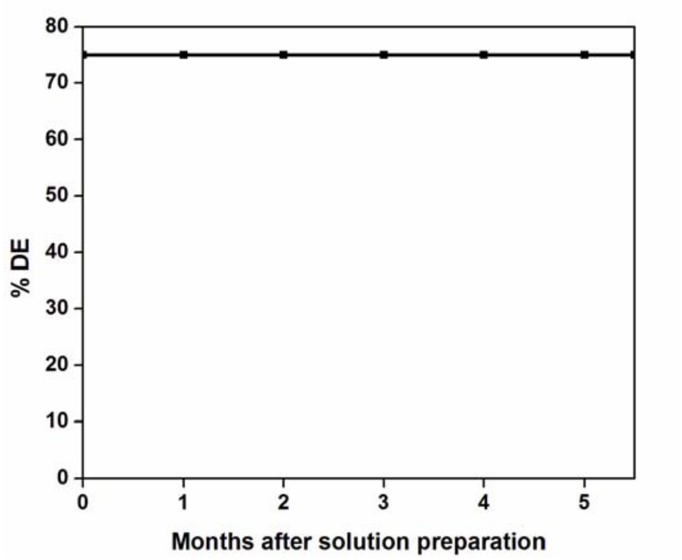

Fig. 3.12. Improved shelf life of the optimized photopolymer solution

From the figure, it is clear that, by keeping the polymer mixture in solution form under controlled conditions, shelf life of the material could be improved.

3.15 Effect of UV Exposure on the storage life

Photopolymers usually subjected to post UV irradiation for stabilizing the gratings and upon UV exposure, the remaining dye molecules get reduced and the acrylamide monomers get polymerized and therefore no more diffusion occurs between the dark and bright regions and will get a stable DE. In order to study the effect of UV exposure on the storage stability of gratings, the recorded gratings were illuminated with a UV lamp for different times. When the films were exposed for more than 300 seconds, DE obtained was very low (therefore the results not included here). At high exposure, the decrease in DE is due to crosslinking of PVA chain [19]. A DE of 75% was obtained without UV exposure and the (fig.3.13) shows the variation in DE with UV exposure.

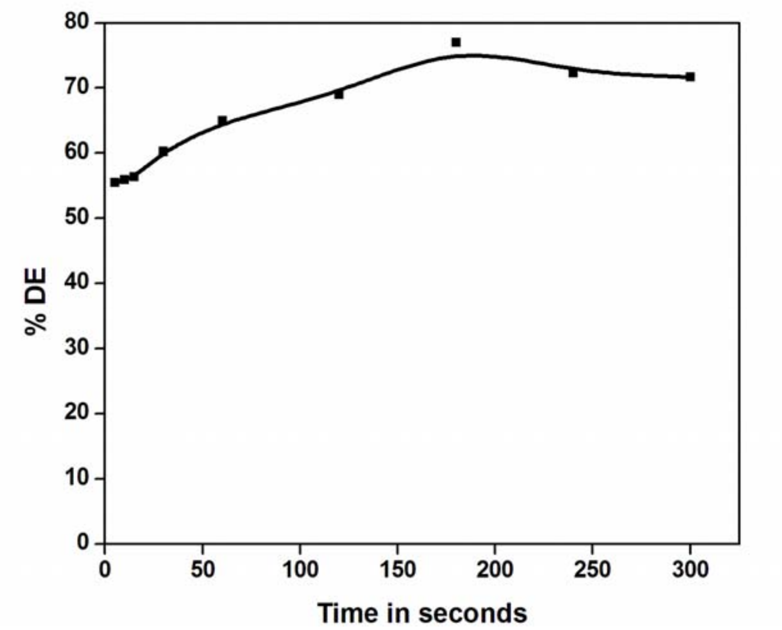

Fig. 3.13. Optimization of UV exposure time

DE of the grating exposed for 5 seconds, 10 seconds and 15 seconds was reduced to 55% and for the grating exposed for 30 seconds; DE was decreased to nearly 60 %. After this, an increase in DE was observed and a maximum DE of 77% was obtained when exposed for 180 seconds and after this, a reduction in DE could be observed. Depending on the PVA chain length, dye concentration and UV exposure, the optical recording efficiency was improved, diminished, or had no change [19].

For studying the storage life of the grating upon UV exposure, DE of the gratings was monitored at different time intervals and the values of DE on storage are plotted (fig.3.14).

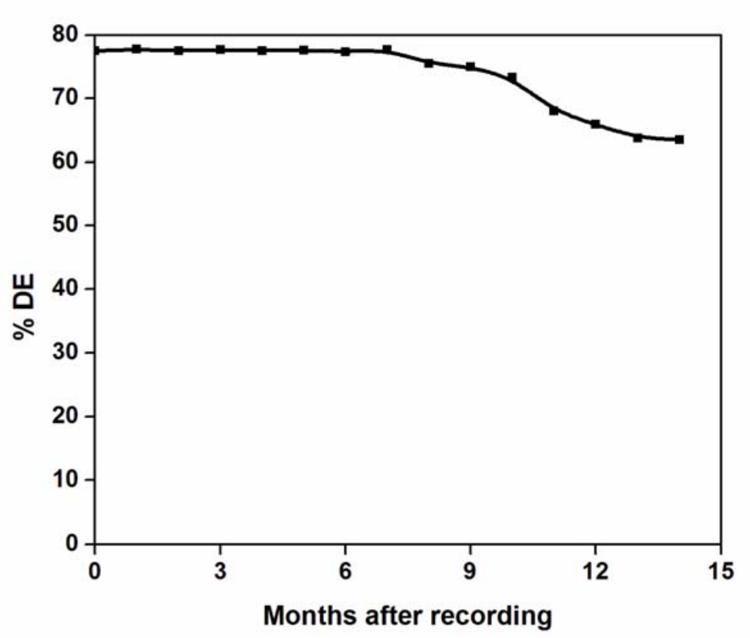

Fig. 3.14. Effect of UV exposure on storage

From the figure, it is clear that upon UV exposure, DE increased from 75% to 77% and it remained as such for months. A reduction in DE was observed only after 7 months and it reduced to 75%; in 10 months, a DE of 73% could be achieved and gratings could be read with a DE of 65% within one year of recording and after one year, DE was reduced to 63%.

Inorder to confirm the absence of crosslinking, the tensile strength of the exposed PVA films were compared with that of unexposed film and shows in (fig.3.15). From this it is clear that there was no crosslinking in PVA as crosslinking is expected to improve tensile strength.

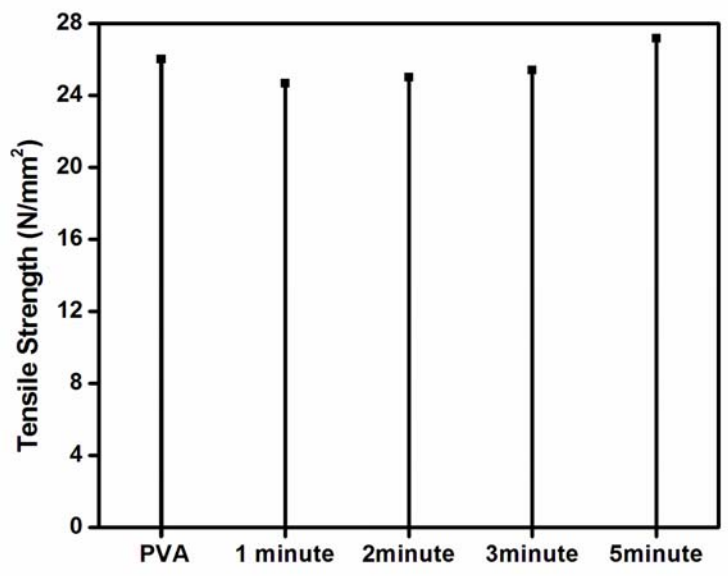

Fig. 3.15. Comparison of tensile strength of UV exposed films with unexposed film

The comparison of the storage life of MBPVA/AAm film with and without UV exposure is given in table 3.2

Table.3.2. Comparison of storage life of grating with and without UV exposure

Material	Storage life (one year)
MBPVA/AAm film without UV exposure	43%
MBPVA/AAm film after UV exposure	63%

From the table, it is clear that UV exposure has improved the storage life of the material.

3.16 Protection of the film

Optical disk media must be protected from physical and environmental damage and from particulate contamination. Favoured protective schemes include encapsulation and air-sandwich structures. Both systems are designed to keep dust particles away from the plane of focus at the recording surface, thereby reducing impact on signal quality. Encapsulation is achieved by solvent coating a polymer film over the recording layer. In the air-sandwich structure, which consists of two disks bonded face to face and separated by a spacer-defined air gap, the substrate becomes the protective layer [20].

The use of sealing techniques to improve the properties of holographic materials are common. Materials such as dichromated gelatin must be sealed from the environment to prevent water absorption destroying the gratings. Silver halide films typically have an inert outer layer at their surface, referred to as an anti-stress layer. In 1997, Ketai et al. reported the use of PMMA as a sealant, the holographic recording material in this case being methylene blue-sensitized dichromated gelatin.

DuPont Omnidex HRF-700X001-20 material is supplied sandwiched between two A5 sized sheets of Mylar and stored in a light-proof wrapping [21].

In the present case, recording layer was sealed using air-sandwiched and encapsulated structures. Epoxy sealant and cyanoacrylate sealant were used as air-sandwiched structures and PMMA sealant was used as encapsulated structure and their effect on storage and shelf life of the recorded gratings were studied.

3.16.1 Effect of epoxy sealant on the storage life and shelf life of gratings

Preparation of epoxy sealant was given in chapter 2 and this was applied on the sides of a clean glass plate placed over the recording layer. The sealant was applied before and after recording the grating and the DE was almost the same in both the cases (DE-67%). The DE on storage was monitored and plotted (fig.3.16). After 3 months of recording, DE was 62%, after 6 months, 58% and one year 47%. In the case of unsealed film, in the initial stages of storage, a higher DE was obtained compared to the sealed films but after one year of recording, the DE was the same as that of sealed films. But after 3 year, gratings could be read with a DE of 12% (unsealed film, it was only 2%). From this it is clear that, the rate of reduction in DE was low in sealed films compared to the unsealed films and by using epoxy sealant, the storage life of the film could be slightly improved.

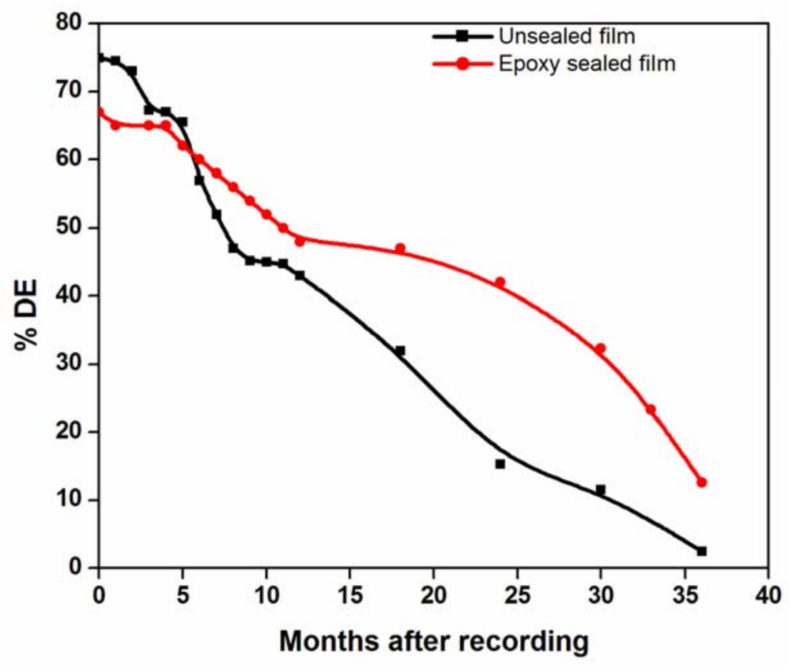

Fig. 3.16. Comparison of DE on storage of MBPVA/AAm film with epoxy sealant

For studying the shelf life of the film, gratings were recorded using the optimized parameters for different times after drying the film and the change in DE with time is plotted (fig.3.17). Upto one month, a DE of 60% could be obtained, within 2 months, DE reduced to 35% and in 3 months, it was nearly 20%. Again a reduction could be observed and gratings could be recorded with low DE in the 4th month after drying the films (in the case of unsealed films, no gratings could be recorded after 3 and half months, section 3.14). So shelf life of the film could be improved by using epoxy sealant.

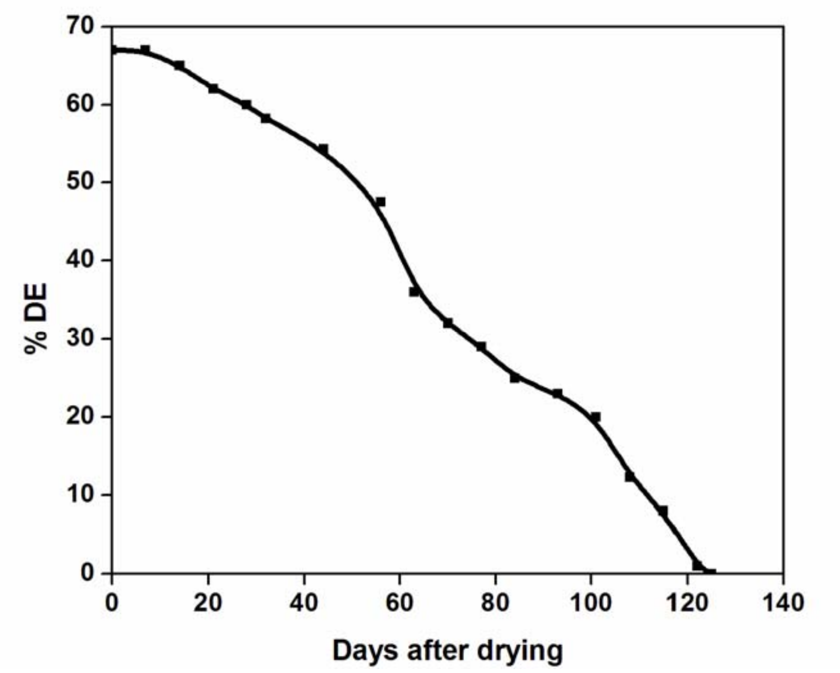

Fig. 3.17. DE on ageing of epoxy sealed MBPVA/AAm film

3.16.2 Studies on the storage life and shelf life of MBPVA/Am films with cyanoacrylate sealant

The acrylate sealant was applied as done in the case of epoxy sealant, before and after recording the gratings and the DE obtained was almost similar in both the cases (nearly 60%) and DE on storage was studied and plotted (fig.3.18). The DE was not stable and reduced to 56% within one month after recording and after two months, DE was reduced to 53% and then to 45% after 3 months.

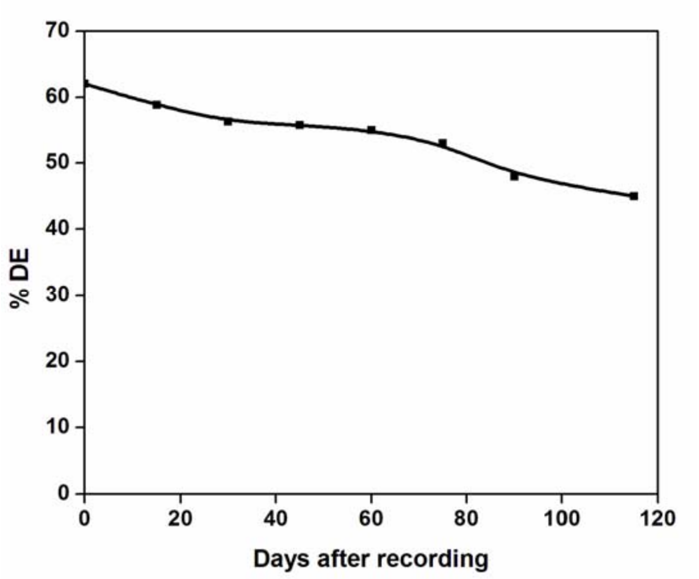

Fig. 3.18. DE on storage of cyanoacrylate sealed MBPVA/AAm films

For studying the shelf life of the sealed film, gratings were recorded and the variation in DE with ageing of the film is plotted (fig.3.19).

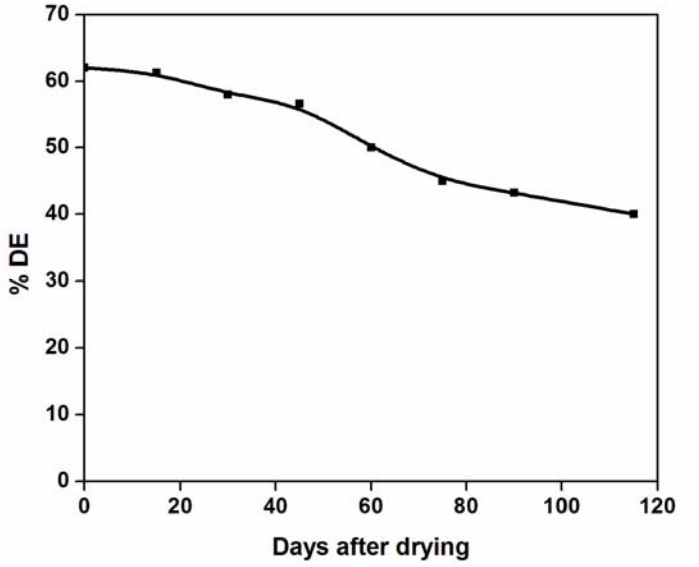

Fig. 3.19. DE on ageing of cyanoacrylate sealed MBPVA/AAm films

It can be seen that DE of 60% was obtained only for a few days after drying and after one month, DE of 56% was obtained and after 2 months, DE of 50% could be obtained. After 3 months of film preparation, gratings could be recorded with 40% DE. It can be seen that, by using cyanoacrylate sealant, the shelf life of the film could be slightly improved compared to epoxy sealed film.

3.16.3 Effect of PMMA sealing on the storage life and shelf life of the MBPVA/AAm films

When epoxy sealant or cyanoacrylate sealant were used, the film could be sandwiched between two glass slides and also there was no significant improvement in material’s properties, PMMA was used as sealant and in this case no sandwiching of the film was needed but the films were dipped in PMMA solution and kept for drying. Here different concentrations of PMMA solutions were prepared (1% -5%). For optimizing PMMA concentration, films were dipped in these solutions before and after recording of grating for one to three times. But only for the film dipped in 1% PMMA solution had better film quality. Therefore studies were done on these films only and better results were obtained when gratings were recorded, after dipping the film in 1% PMMA solution for two times.

Inorder to find the storage life of the sealed film, DE of the recorded gratings were monitored at different time intervals and plotted (fig.3.20). From the figure, it is clear that, there was no reduction in the initial DE compared to sandwiched sealants and a DE of 69% could be achieved after 6 months also, (in the case of epoxy sealed films, a DE of 58% could be obtained after 6 months, section 3.16.1).

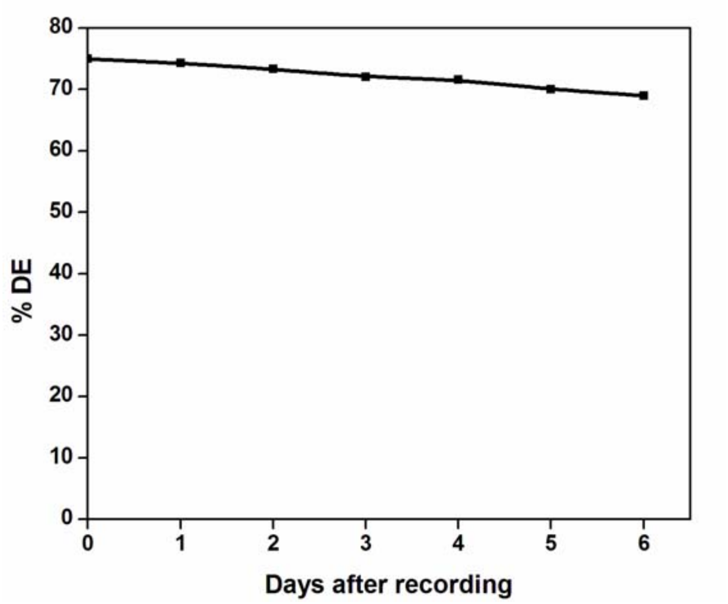

Fig. 3.20. DE on storage of PMMA sealed MBPVA/AAm films

For studying the shelf life of the film, the films were dipped twice in 1% PMMA solution and kept for drying. Gratings were recorded on the films on ageing of the film and DE with ageing is plotted (fig.3.21). From the graph, it is clear that gratings could be recorded with a DE of 70% even after 3 months of preparation (for epoxy and acrylate sealed film, DE of 20% and 40% respectively could be obtained after 3 months, section 3.16.1 and 3.16.2). So the results showed that PMMA sealed films had better DE on storage and ageing compared to epoxy and acrylate sealants.

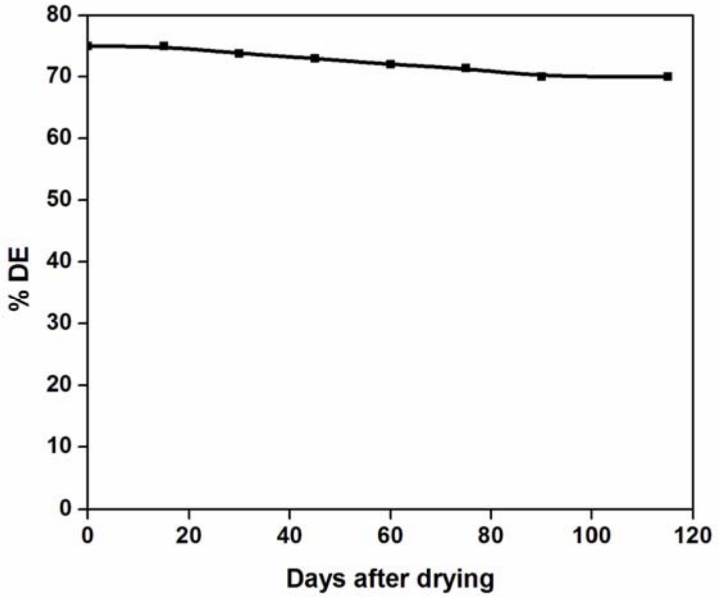

Fig. 3.21. Variation in DE on ageing of PMMA sealed MBPVA /AAm films

Comparison of the results of unsealed and sealed film is given in table 3.3.

Table 3.3. Comparison of storage life and shelf life of the material with and without sealant

Material	Storage life (3months)	Shelf life (3months)
Unsealed MBPVA/AAm film	67%	1%
Epoxy sealed film	62%	20%
cyanoacrylate sealed film	52%	40%
PMMA sealed film	70%	70%

So PMMA sealed films had better storage life and shelf life and it could be used for sealing the films more easily.

3.17 Conclusion

Methylene blue sensitized PVA/AAm films were fabricated; but possessed poor storage life and by reducing the concentration of the dye, storage life of the material could be improved. The shelf life of the material could be improved by keeping the photopolymer mixture in solution form under controlled temperature. Upon exposure to UV light for 180 seconds, the storage life of the material could be further improved. For protecting the films from external dust and contaminants, sealants were used and the storage life and shelf life of the material could be improved by sealing; out of which, PMMA sealed films showed better results.

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CORRECTIONS

Sec.3.4 & 3.5	
It is concluded that TEA acts as a plasticizer and therefore, it increases the elongation at break of PVA from 365% to 434% and decreases the glass transition temperature from 86 to 83^{o}C. However, the tensile strength is not affected by the plasticization. The reason for this unexpected trend may be given.	The addition of TEA has increased the elongation at break (%) of PVA due to the plasticization effect. Triethanolamine may be occupying positions in between the polymer chains. There can be some interaction between triethanolamine and PVA which can lead to a minor increase in tensile strength
The MB/PVA/AAm film has given tensile strength identical to PVA (Fig.3.1) , despite the incorporation of a fairly large quantity of acrylamide in the film (1.8 g to 3.8). This also needs explanation.	MB/PVA/AAm film contains acrylamide as the monomer, methylene blue as the sensitizer, triethanolamine as the initiator and PVA acts as a matrix to the components. Methylene blue has absorption in the red region of the spectrum and after the absorption of light it changes to leuco form and leads to polymerization .Therefore there is a chance for the polymerization of the monomer during drying of the film under sunlight. This may lead to the formation of a semi interpenetration network with the same tensile strength.

Sec.3.5:fig.3.3 The DSC curves of all the 4 samples appear as a broad endothermic peaks starting from room temperature to approx.140^{o}C. What is the phenomenon/transition corresponding to the broad DSC peaks? How was the Tg inferred from the peaks?	DSC studies were done on different samples and the glass transition temperature was determined by taking the tangent.

Chapter 4

EFFECT OF ORGANIC CROSSLINKERS ON THE HOLOGRAPHIC PROPERTIES OF METHYLENE BLUE SENSITIZED POLY (VINYL ALCOHOL)

Contents

4.1 Introduction

Holography breaks through the density limits of conventional storage by going beyond recording only on the surface, to recording through the full depth of the medium [1]. In recent years much has been done on the research of photopolymerizable compositions as holographic recording materials. Compared with other holographic materials, such as dichromated gelatin or holographic emulsions, these materials have the great advantage of recording and reading holograms in real time. Also, it is equally good as the dichromated gelatin plate in diffraction efficiency and resolution and much better than the silver halide light sensitive material [2]. Due to high viscosity and low T_g value of poly (vinyl alcohol), the diffusion coefficient of the components of the material will be very low [3]. As a consequence, the mechanism of grating's formation will mainly involves the non-uniform photopolymerization of acrylamide at the bright zones. The local refractive index is altered wherever polymerization occurs and the hologram is thus recorded [4].

The major drawback of the dye sensitized PVA/acrylamide is the reduction in diffraction efficiency on storage [5-7]. Therefore, only short term storage is possible in this material. The decrease in DE is due to the diffusion of monomer and dye molecules from the region of destructive interference to that of the constructive interference. As a result, the gratings become blurred and DE decreases. Eventhough an enhancement in DE and storage life could be achieved in MBPVA/AAm film by reducing the concentration of dye, UV exposure was needed to get long term stability of the gratings (section 3.15). When a crosslinker is added to the system, it can inhibit further diffusion of molecules and as a result the grating becomes undisturbed and hence constant diffraction efficiency can be obtained [7]. Organic compounds and metal ions can be used as crosslinkers in the PVA/AAm system. When metal ions like Chromium (III) and Copper

(II) were used in MB/PVA/AAm system, eventhough constant DE was obtained, the initial DE was low [8]. The present chapter describes the effect of two organic molecules, glutaraldehyde and N-N'-methylene- bis- acrylamide as crosslinking agents in the storage life of the gratings recorded in the optimized MBPVA/AAm film. After the optimization of the crosslinker, other holographic properties like exposure energy, resolution and shelf life of the material was also studied.

4.2 Experimental

Preparation of the Films

All the materials used in this work were analar grade and were used without further purification. Photopolymer solution was prepared by dissolving 10 g Poly (vinyl alcohol), in 100 ml cold distilled water. (Molecular weight; 1, 25,000 and degree of hydrolysis; 86-90%). To this, acrylamide (AAm), Triethanolamine (TEA) and methylene blue (MB) were added and the solution was stirred well to get a homogeneous solution. The details are given in chapter 2.

The photopolymer solution was divided into two parts: to one portion, glutaraldehyde solution was added in amounts varying from 0.005M - 0.2M. To the other part, N-N'-methylene- bis- acrylamide (BMA) was added in different concentrations from 0.001M - 0.05M. The polymer film was prepared by gravity settling method under normal laboratory conditions (relative humidity-55-65%, temperature-$30^{o}\pm 2^{o}C$) and 48 hours of drying was required. The concentration of each component is given in Table 4.1.

Table 4.1. Concentrations of different constituents

Constituents	Concentration
PVA	10% by weight
Acrylamide	0.38M
Triethanolamine	0.05M
Methylene blue	1.4 $\times 10^{-5}$ M
Glutaraldehyde	0.005- 0.2M
N-N’-methylene- bis- acrylamide	0.001-0.05 M

4.3 Characterization

DSC studies were done on the samples using TA DSC-Q-100 instrument at a heating rate of 2^{o}C/minute from 30^{o}-150^{o}C under nitrogen atmosphere.

The optical characterization was done using Jasco V-570 spectrophotometer and modulation in refractive index was calculated using Kogelnik’s coupled wave theory. Optimization of various components was done by recording plane wave gratings on the film, using He-Ne laser (632.8 nm) by standard double beam method and the gratings were reconstructed by 1μW He-Ne laser. Spatial frequency response, storage life and shelf life of the material were also measured.

4.3.1 Incorporation of glutaraldehyde into optimized MBPVA/ AAm system

Glutaraldehyde is a common crosslinker used with PVA and can form acetal crosslinks with PVA.

4.3.1.1 Optimization of glutaraldehyde concentration

Inorder to study the effect of glutaraldehyde (GA) on the diffraction efficiency of MBPVA/AAm film, films were prepared with glutaraldehyde concentration from 0.005 M - 0.2 M, (named as GA 1, GA2…GA6 respectively) by keeping the concentration of AAm, TEA and MB constant. Plane wave gratings were recorded on these samples at spatial frequency of 1080 lines/mm with an exposure energy of 80 mJ/cm^2 using He-Ne laser. Fig. 4.1 is the plot of variation in DE with exposure energy at different concentrations of glutaraldehyde.

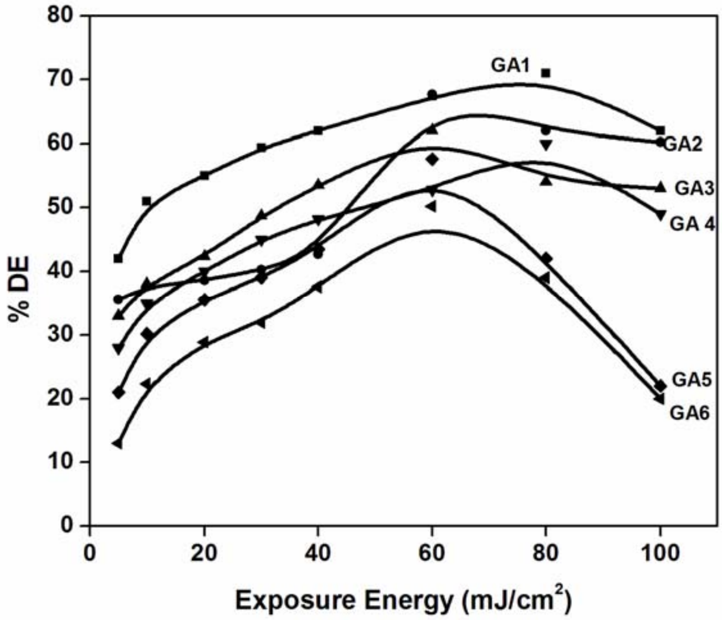

Fig. 4.1. Optimization of concentration of glutaraldehyde in optimized MBPVA/AAm film

It can be seen that DE of MBPVA/AAm film decreased with increase in concentration of GA and maximum DE of 71 % was obtained for the film with GA concentration of 0.005 M (GA1 in figure). With increase in concentration of glutaraldehyde, crosslinking of PVA increases and this results in decrease in diffusion rate and hence a decrease in DE was observed.

4.3.1.2 Diffraction efficiency on storage

The diffraction efficiency of the recorded gratings was monitored on storage and decrease in DE with time is given (fig.4.2). The sample GA1, initially showed a good efficiency of 71 %, but was reduced to 43 % within one week. In the case of all other samples also, a sharp decrease in DE was observed, except for MBPVA/AAm films with higher concentrations of GA (GA 5 and GA6).

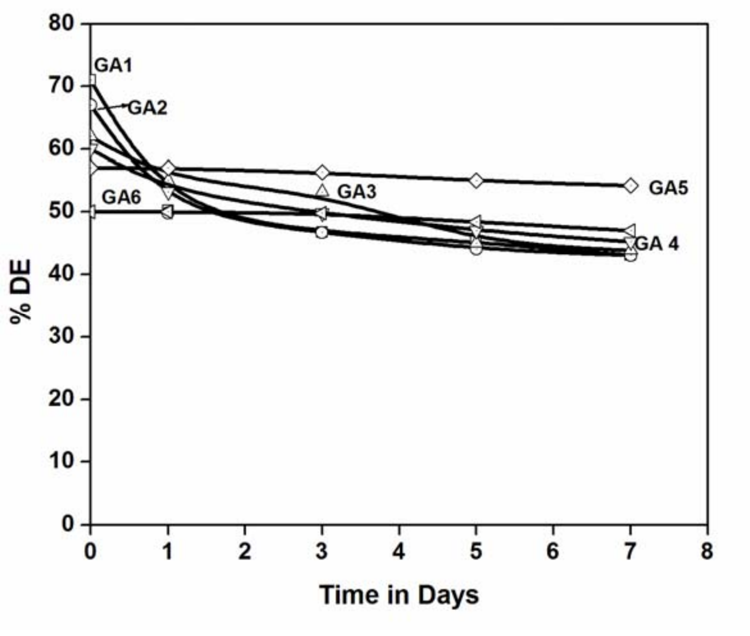

Fig. 4.2. DE on storage of MBPVA/AAm/GA films

For MBPVA/AAm film with GA concentration of 0.15 M and 0.2 M (named as GA 5 and GA6), the reduction in DE was slow. But for GA6, initial DE was low and therefore, a detailed study on storage life was done only for the sample named as GA 5 and the values of DE with time are plotted (fig.4.3). It can be seen from the figure that, a DE higher than 50 % could be obtained for MBPVA/AAm film with GA 5 after one month of recording and again a reduction was observed and after 2 months, DE reduced to 38 %.

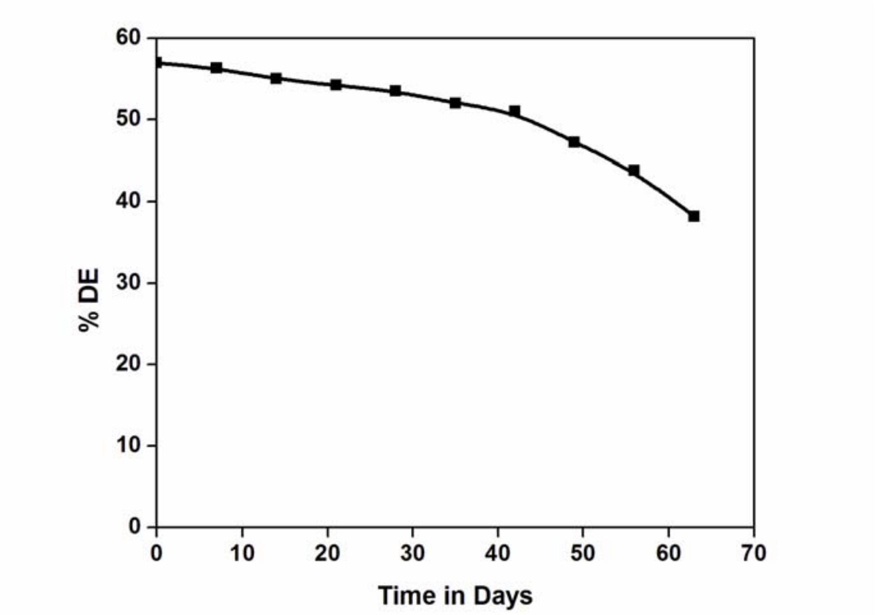

Fig. 4.3. DE on storage of MBPVA/AAm/GA5

4.3.1.3 Diffraction efficiency on ageing of MBPVA/AAm/GA5

To determine the shelf life of the film, gratings were recorded on GA5 film on each day after preparation (drying) of the film. The films were kept in a dark box at room temperature. The films showed the highest efficiency of 57 % only for few days after preparation. The efficiency was found to be decreased on ageing and after two weeks, no gratings could be recorded on it. The decrease in DE on ageing is due to the polymerization of monomer and the decrease in DE on ageing is plotted (fig.4.4). The shelf life of the GA doped film is lower than that of undoped film and the transparency of the film was also lost on ageing. This may be due to the oozing out of glutaraldehyde on to the surface of the film.

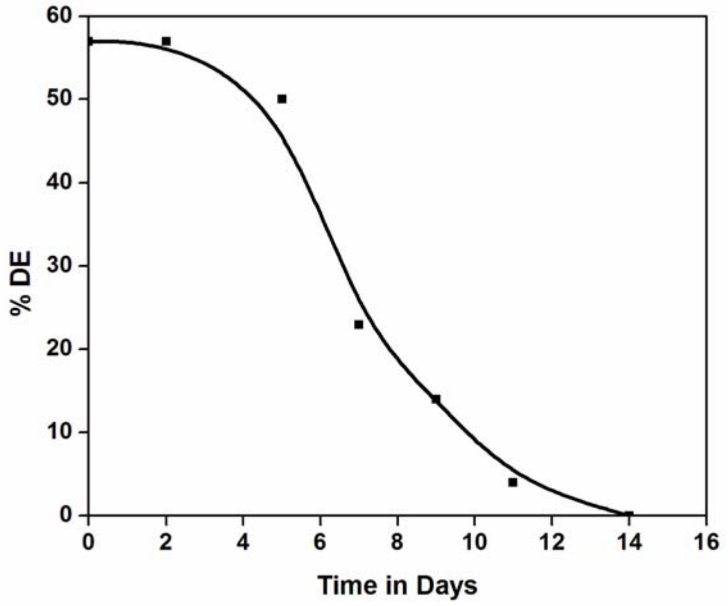

Fig. 4.4. DE on ageing of MBPVA/AAm/GA5

A better storage life was not obtained in the case of GA doped MBPVA/AAm, compared to the uncrosslinked film. Maximum DE and shelf life of the GA crosslinked films also not improved and therefore another organic crosslinker was tried.

4.3.2 Incorporation of N-N’-methylene- bis- acrylamide as crosslinker

N-N’-methylene- bis- acrylamide (BMA) is a commonly used crosslinker in acrylamide based photopolymer systems. In the normal case, when acrylamide based photopolymers are used; the DE of the recorded gratings is found to be decreased on storage. In the case of photopolymer film containing only acrylamide, after photopolymerization, linear polyacrylamide is obtained. When BMA was added to the MBPVA/AAm system, BMA builds crosslinks to form a copolymer which is transparent with higher density and lower mobility [9].

Several works were published in literature regarding PVA /AAm system containing BMA as crosslinker with different sensitizers. Blaya et al. reported a DE of 80 % in MBPVA/AAm system containing TEA as co-initiator and BMA as crosslinker. But they used low molecular weight PVA (25,000) and films were prepared not by gravity settling method [10]. In 2010, Lu Hai et al. reported a DE of 59 % in MBPVA/AAm system with TEA and crosslinked with BMA and here films were prepared by gravity settling method [11].

4.3.2.1 Optimization of concentration of BMA

For optimizing the concentration of BMA in the optimized MBPVA/AAm film, named as C 0.14, concentration of BMA was varied from 0.001M to 0.05M and the concentration was optimized by recording grating with exposure energy 80mJ/cm^2 at a spatial frequency of 1080 lines/mm using 15 mW He-Ne laser. Fig. 4.5 is the plot of variation of DE with BMA concentration. Here for BMA with low concentrations, DE of ~75 % was obtained which was similar to the uncrosslinked sample. When the concentration was increased, DE was reduced to 66 %. The reason for the decrease in DE with BMA concentration is that, when BMA is added, into this system, it binds with polyacrylamide, (PA), chains together, which are formed during the recording process, greatly reducing their mobility [12]. As the concentration of BMA was increased, this resulted in more crosslinked PA with low mobility. As the mobility of PA chain decreases, rate of diffusion decreases which resulted in low DE.

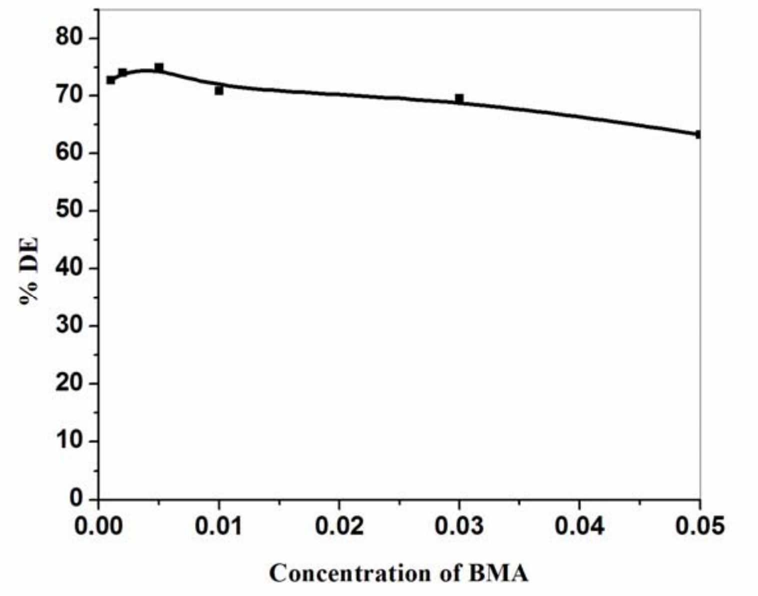

Fig. 4.5. Variation of DE with concentration of BMA

4.3.2.2 Efficiency on Storage

Diffraction efficiencies of all the samples were monitored and plotted (fig.4.6) and samples were named as bma1, bma2 ….bma7, which corresponded to the concentrations 0.001M… 0.05 M respectively. It is clear from the graph that, stable DE was obtained for bma6 and bma7. But for bma7, DE was only 66 % and therefore bma6 was selected as the optimum one. Films with low concentration of BMA have the effect of increasing mobility of the PA chains. Thus spatially periodic concentration distribution in the material, formed by the polymer chains, can disperse more rapidly. The resulting increase in the rate of diffusion of PA chains can be observed holographically as the decrease in diffraction efficiency with time [13].

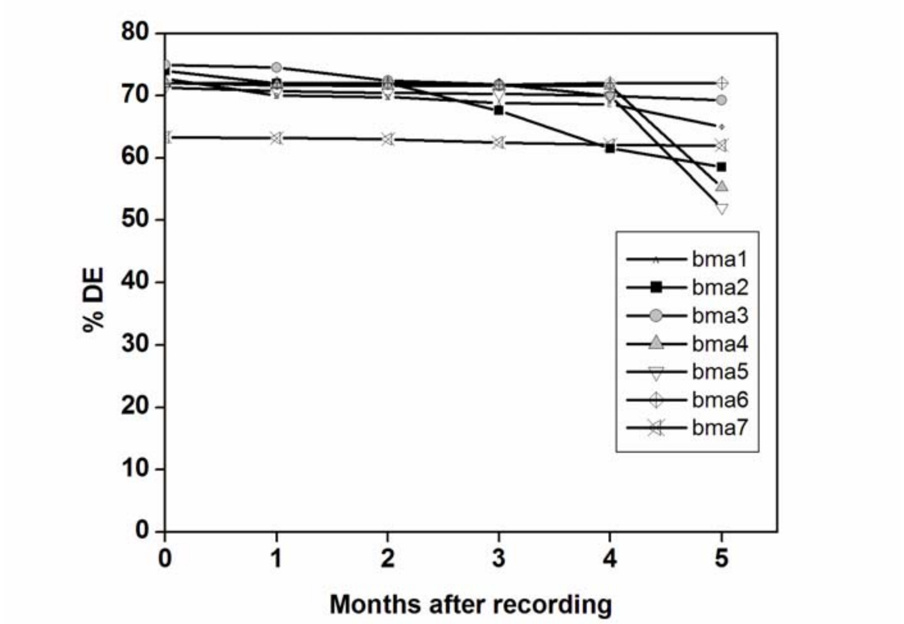

Fig. 4.6. DE on storage of MBPVA/AA film with BMA

4.4 Characterization of the optimized sample

MBPVA/AAm film with BMA concentration 0.03 M (BMA6) (fig.4.6) was selected as the optimized sample and further studies were done on this sample.

4.5 DSC Studies

DSC studies were done on the optimized sample before and after exposing to laser, to study the effect of crosslinking. Fig.4.7 is the DSC curve of exposed and unexposed MBPVA/AAm with the optimized BMA concentration.

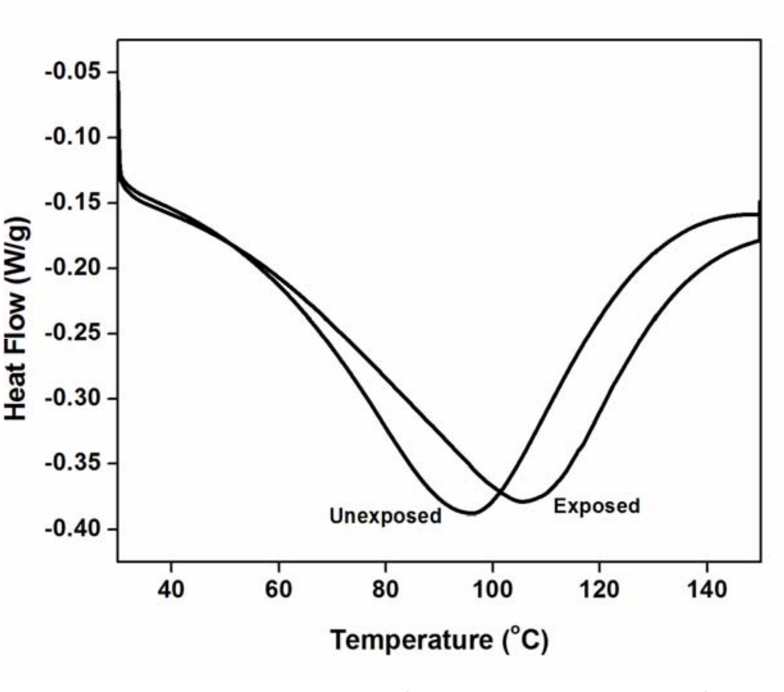

Fig. 4.7. DSC thermograms of MBPVA/AAm/BMA6 films

The T_g depends on the molecular weight, side branches, steric hindrance, covalent and non-covalent bonding within the molecular structure, presence of plasticizer and copolymers. It is clear from the figure that addition of BMA has caused an increase in T_g of the MBPVA/AAm system in the case of unexposed sample (83^oC-90^oC). Increase in T_g indicated that the polymer network became more rigid on the addition of BMA and this may be because of the formation of more thick polymer network on the addition of a large molecule like BMA. The T_g of the exposed sample showed a further increase to 102^oC and this suggests the formation of a copolymer with high density and low mobility. This increase in glass transition temperature has caused a reduction in initial DE to 72% compared to uncrosslinked sample, 75 % (chapter 3).

4.6 Thickness measurement and calculation of RI modulation

Thickness of the optimized MBPVA/AAm/BMA was measured by Dektak 6 m Stylus Profiler and the film had a thickness of 130μm.

The modulation in refractive index of the optimized sample before and after exposure was calculated using Kogelnik coupled wave theory;

$\Delta n = \mathrm{Sin}^{-1}(\eta^{1/2}) \times \lambda \cos\theta / \pi \times d$, where Δn-RI modulation, η-diffraction efficiency, λ-wavelength of reading beam, θ-half angle between the two beams and d-thickness of the film.

Using this equation a RI modulation of 1.47×10^{-3} was obtained.

4.7 Sensitivity of the optimized material

Optical absorption spectrum of the optimized MBPVA/AAm /BMA was taken and plotted (fig.4.8). No change in the characteristic peak of MB was observed and this means that addition of BMA did not affect the material's absorption.

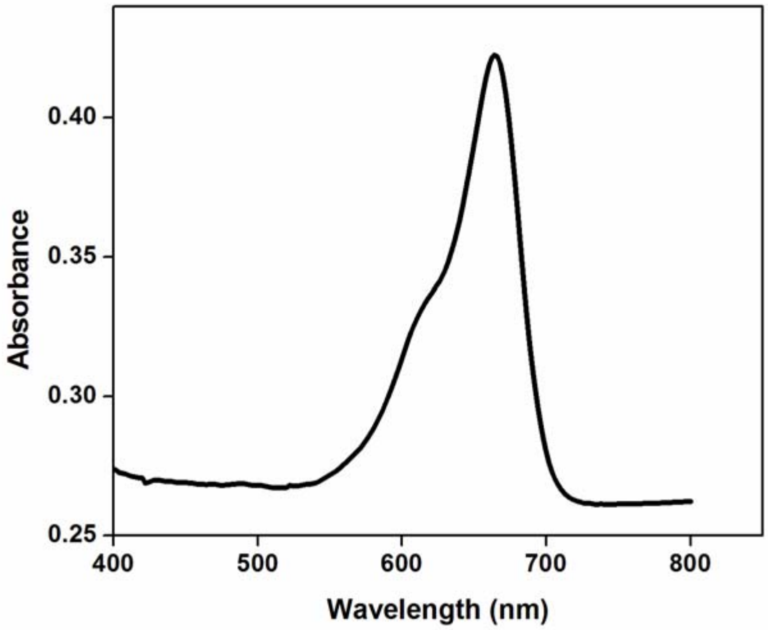

Fig. 4.8. Optical absorption spectrum of MBPVA/AAm/BMA6

Inorder to optimize the exposure energy, plane wave gratings were recorded on the sample using 15 mW He-Ne laser by varying the exposure energy from 5 mJ/cm^2 to120 mJ/cm^2 with 1080 lines/mm and variation of DE with exposure energy is plotted (fig.4.9). It is clear from the study that the sensitivity of the material was not affected by the incorporation of BMA. A maximum DE of 72% was obtained for exposure energy of 80 mJ/cm^2. After reaching a maximum, DE was decreased. A small decrease in DE was observed compared to the uncrosslinked MBPVA/AAm sample which may be due to the crosslinking of acrylamide which would cause a further decrease in diffusion and hence a reduction in DE [14].

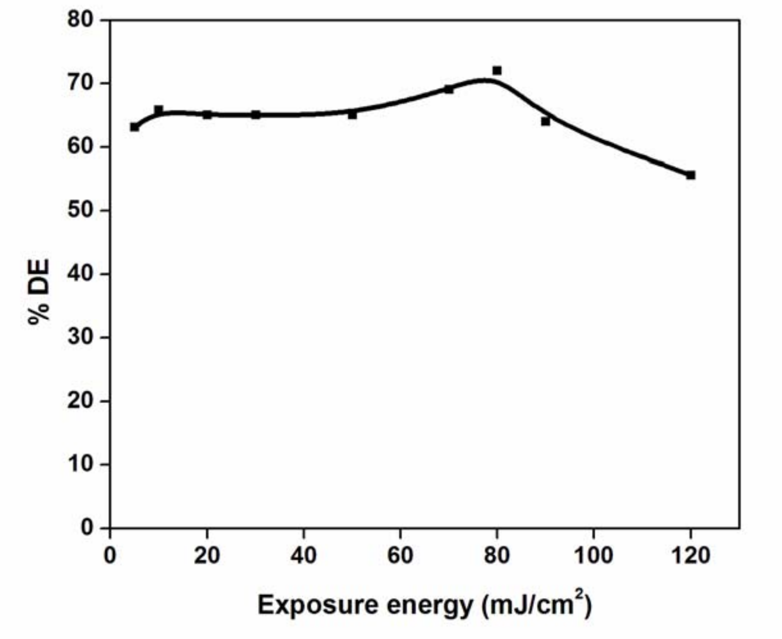

Fig. 4.9. Variation of DE with exposure energy of MBPVA/ AAm/BMA6

4.8 Resolution of the film

For optimizing the resolution of the optimized film, gratings were recorded by changing the inter-beam angle from 30^o-80^o and spatial frequency was calculated using Bragg's equation. Fig.4.10 is the plot of variation in DE with spatial frequency. For 818 lines/mm, a DE of 70 % was obtained, at 1080 lines/mm, DE increased to 72 % and then a slight decrease in DE was observed. When spatial frequency reached 2032 lines/mm, DE of 65 % was obtained. No significant reduction in DE was observed, when spatial frequency was increased from 818 lines/mm to 2032 lines/mm.

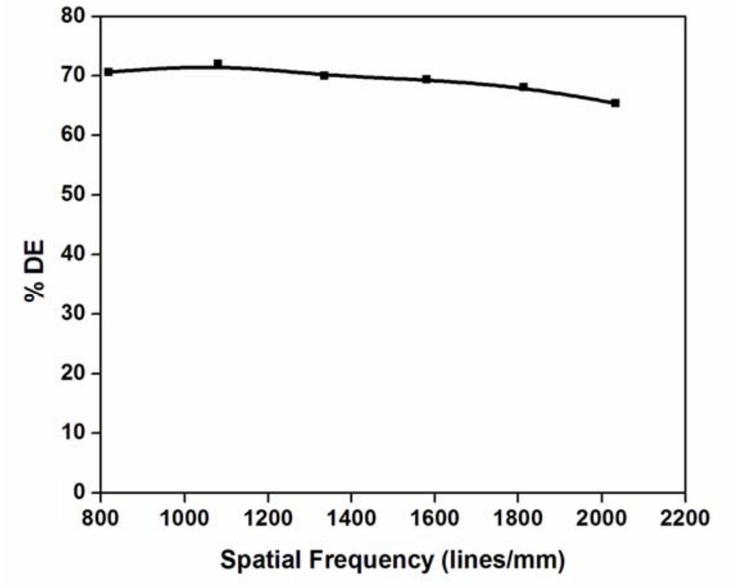

Fig. 4.10. Variation of DE with spatial frequency of MBPVA /AAm/BMA6

4.9 Storage life of grating

Long term stability of the gratings, recorded in the optimized MBPVA/AAm/BMA was monitored by measuring DE in different time interval and plotted (fig.4.11). From the figure, it is clear that within one year of recording, a DE of 70 % was obtained and after this, a small decrease in DE could be observed and in one and half year, it was reduced to 60 %. The stability obtained for grating recorded in this material is due to the crosslinked PA chain within the polymer material. In earlier studies by Van Renesse using BMA in acrylamide photopolymer system, they have reported that eventhough good DE could be achieved, it could be kept in good condition for only one week [15].

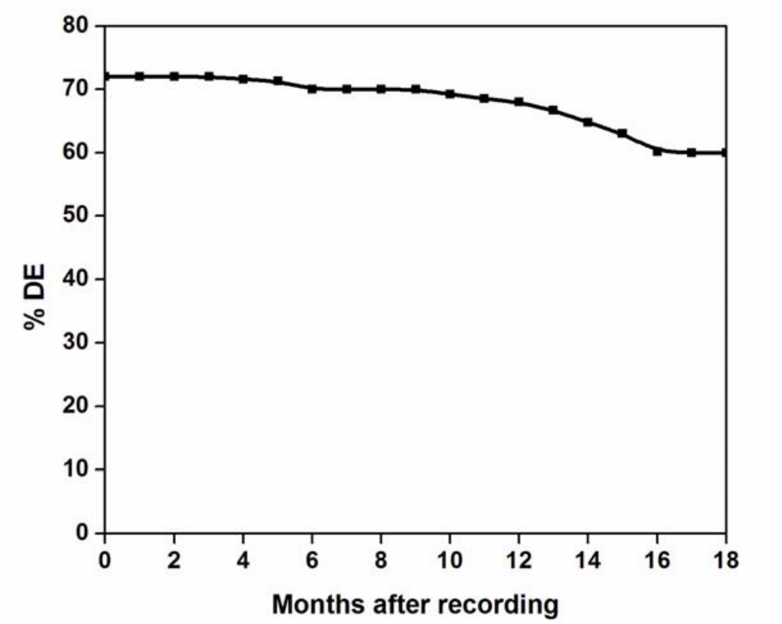

Fig. 4.11. MBPVA/AAm/BMA6 film on storage

4.10 Shelf life of the optimized MBPVA/AAm/BMA film

To determine the shelf life of the film, gratings were recorded on the optimized film in different intervals of time after preparation (drying) of the film. Fig. 4.12 is the plot of variation in DE with ageing of the film. Even after 3 months of preparation, a DE of 70 % could be maintained and after 5 months of preparation, a DE of 52% could be achieved. Then it was reduced to 30 % and to 17% and gratings could not be recorded on the films prepared 8 months before. The shelf life of the MBPVA/AAm film could be improved by the addition of BMA (for MBPVA/AAm system, after 3 months of preparation, gratings with only low DE of ~1% was obtained, section 3.14).

In this case also, shelf life of the material could be improved by keeping in solution form as in the case of MBPVA/AAm system and a DE of 72 % could be achieved after five months of preparation of solution.

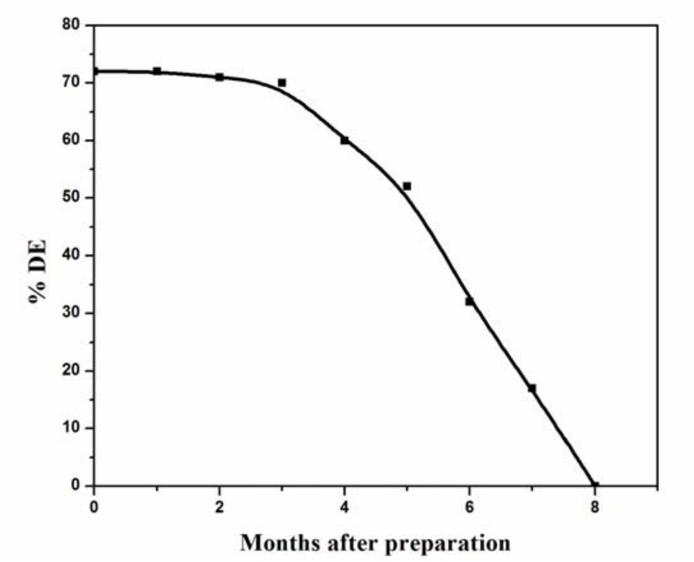

Fig. 4.12. Shelf life of MBPVA/AAm/BMA6 film

4.11 Comparison of uncrosslinked and BMA crosslinked MBPVA/AAm Films

The gratings were stabilized by crosslinking with BMA. Table 4.2 is the comparison of uncrosslinked and BMA (BMA6) crosslinked films.

Table 4.2. Comparison of uncrosslinked and BMA crosslinked films

	Uncrosslinked MB/PVA/AAm	**BMA crosslinked MB/PVA/AAm**
Efficiency	75 %	72 %
Storage life	43 % (one year)	70 % (one year)
Shelf life	~1% (3 months)	70 % (3months)

4.12 Conclusion

Two organic crosslinkers, glutaraldehyde and N-N'-methylene-bis-acrylamide were incorporated into the optimized MBPVA/AAm film. The introduction of glutaraldehyde resulted in a lower diffraction efficiency and a decrease was observed on storage. Incorporation of N-N'-methylene-bis-acrylamide resulted in better stability of the recorded gratings without affecting sensitivity and resolution of MBPVA/AAm film. DE as high as 70% could be maintained for one year of recording for a particular concentration of N-N'-methylene-bis-acrylamide. The shelf life of the material was also improved; even after 3 months of preparation, gratings could be recorded on the samples with a DE of 70%.

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* * *

CORRECTIONS

Section:4.5 and fig. 4.7 The DSC curves of all the 4samples appear as a broad endothermic peaks starting from room temperature to approx.140^{o}C. What is the phenomenon/transition corresponding to the broad DSC peaks? How was the Tg inferred from the peaks?	DSC studies were done on different samples and the glass transition temperature was determined by taking the tangent.

Chapter 5

EFFECT OF MOLECULAR WEIGHT OF POLY (VINYL ALCOHOL) ON THE HOLOGRAPHIC PROPERTIES OF MBPVA/AAm FILMS

Contents

5.1 Introduction

Recent digital revolution makes everything from general documentation to entertainment and photography require huge amount of data to be archived. This raises the requirement for a suitable storage medium to keep huge quantity of such valuable data available for immediate use and storage.

Photopolymer recording materials are attractive media for optical holography, diffractive optical elements, or holographic memories. Photopolymer systems can spontaneously develop their holographic image during recording without requiring post-exposure processing steps. In holography, poly (vinyl alcohol) sensitized with ammonium dichromate is one of the most promising self developing photopolymers that has been reported as a storage medium [1-2]. In recent years, the PVA/acrylamide based photopolymer system has drawn much research interests because of its good properties such as real time dry imaging, adjustable spectral response range, high refractive index modulation, good angular selectivity, easy preparation of large area photosensitive film, and low cost etc [3-7]. Some applications of holographic data storage, holographic interferometry, holographic display etc also have been reported by using PVA/acrylamide based photopolymers [2, 4, 8-12].

In the case of PVA/ acrylamide system, photosensitivity is in the range of 60-150 mJ/cm^2 and spatial frequency in the range of 1000-2000 lines/mm [14]. Cristina Solano et al. studied the dependence of DE on the molecular weight of polymer in PVA/malachite system and maximum DE was obtained for PVA with a medium molecular weight [13]. Jianhua Zhu et al. reported a detailed study on the effect of molecular weight of PVA on DE in MBPVA/AAm system and they got DE upto 90% with photosensitivity of 80 mJ/cm^2 when PVA with molecular weight of 15,000 was used. But they used BMA and acrylic acid as additional monomers to get this high sensitivity and DE, in MBPVA/AAm system [14].

Optimization of MBPVA/AAm system and the effect of two organic crosslinkers on the storage life of the optimized film have been given in the previous chapters. The present chapter deals with the effect of molecular weight of PVA on the holographic properties of the optimized MBPVA/AAm system.

5.2 Experimental

Film Preparation

All the materials used in this work were analar grade and were used without further purification. In this study, PVA of three molecular weights were selected and the solution was prepared by dissolving different weights of PVA of different molecular weights. Films were prepared as described in previous chapters under normal laboratory conditions (Relative Humidity-55-65%, temperature-30±2^{o}C) and 48 hours of drying was given. Table 5.1 gives the details of the materials used in the present work.

Table 5.1. Composition of various components

Constituents	Concentration
PVA	
Mol.wt-13,700	7.5% - 15 % by weight
″ 54,500	7.5% - 15 % by weight
″ 1,25,000	7.5% - 15 % by weight
Acrylamide	0.38 M
Triethanolamine	0.05 M
Methylene blue	1.4 x 10^{-5} M

5.3 Characterization

5.3.1 Studies on PVA with molecular weight 13,700

5.3.1.1 Optimization of concentration of PVA

For optimizing the concentration of PVA, different weight percentage PVA solutions were prepared and using each concentration of PVA, photopolymer films were prepared by gravity settling method. Gratings were recorded on the dry films at spatial frequency of 1080 lines/mm using He-Ne laser and the variation in DE with exposure energy for each PVA samples are plotted (fig.5.1).

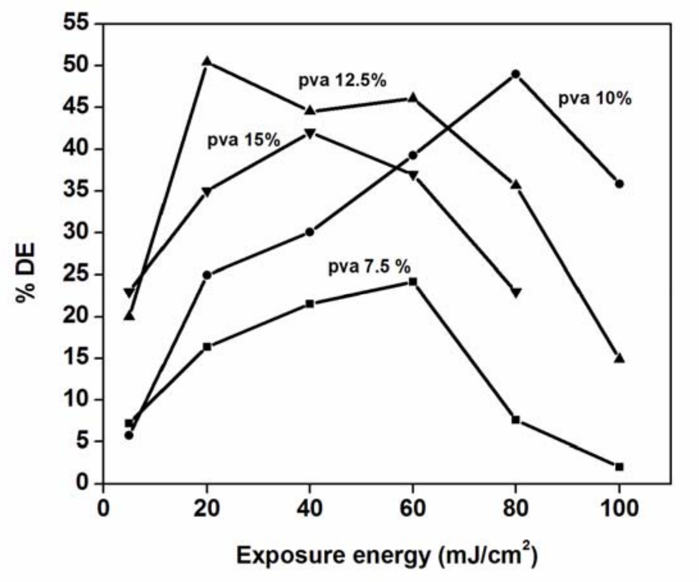

Fig. 5.1. Variation of DE with exposure energy for different concentrations of PVA

For 7.5 % PVA, maximum DE of 20 % was obtained with exposure energy of 60 mJ/cm^2. When the weight percentage of PVA was increased to 10 %, maximum DE around 50 % was obtained at 80 mJ/cm^2 and for 12.5 % PVA also, the maximum DE was around 50 %

at 20 mJ/cm^2. For 15 % PVA, DE was reduced to 40 %; therefore, 12.5 % PVA was selected as the optimum concentration. In all the cases, when exposure energy was increased, DE was also increased and after reaching a maximum, DE decreased; this may be due to the crosstalk of holograms [15].

5.3.1.2 Optimization of angle of recording (MBPVA/AAm film with PVA 12.5 %)

For getting maximum DE, recording angle was varied and spatial frequency was calculated using Bragg equation. Fig.5.2 is the plot of variation of DE with spatial frequency 549-1335 lines/mm (20^o-50^o respectively). A maximum DE of 70 % was obtained at spatial frequency 818 lines/mm for exposure energy of 20 mJ/cm^2. When angle of recording was increased, DE decreased and for 1335 lines/mm, a maximum DE of only 25 % could be obtained.

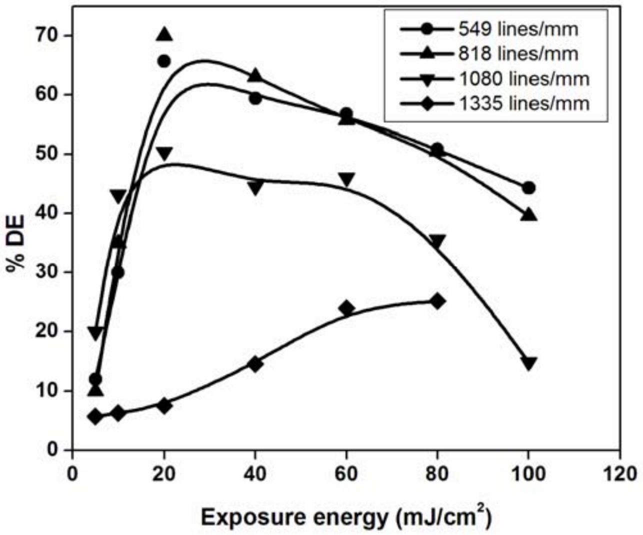

Fig. 5.2. Variation in DE with exposure energy at different spatial frequency

So the optimized parameters for MBPVA/AAm film with 13,700 PVA is;

Concentration of PVA: 12.5 %
Exposure energy: 20 mJ/cm^2
Spatial frequency: 818 lines/mm
Maximum DE: 70 %.

5.3.2 Studies on PVA with molecular weight 54,500.

5.3.2.1 Optimization of concentration of PVA

For optimizing the concentration of PVA, MBPVA/AAm films were prepared with different weight percentage of PVA from 7.5 % - 15 % and gratings were recorded on these dry films using He-Ne laser at 1080 lines/mm. Fig.5.3 is the plot of variation in DE with exposure energy for different concentration of PVA.

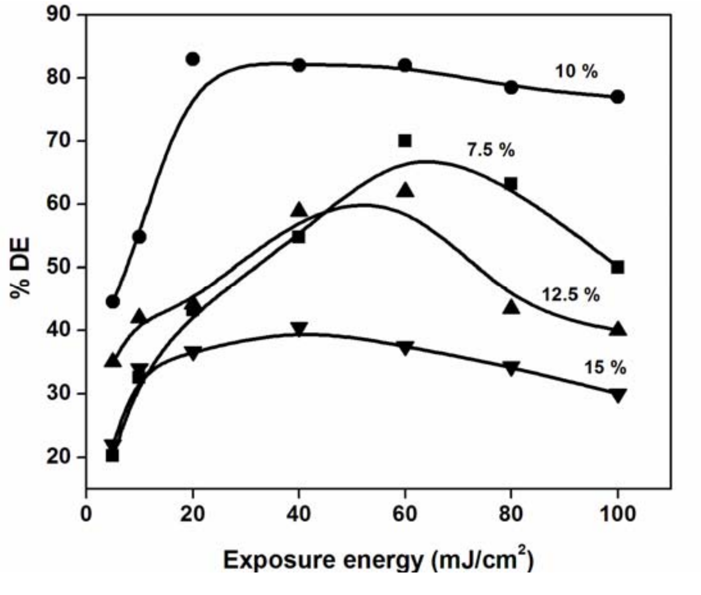

Fig. 5.3. Optimization of PVA concentration

For 7.5 % PVA, a maximum DE around 70 % was obtained at 60 mJ/cm^2, for 12.5 % PVA, DE of nearly 60 % and for 15 %, the maximum DE was reduced and only 40 % could be obtained. In the case of PVA with 10 % film, a maximum DE of 83 % was obtained at 20 mJ/cm^2 and after reaching this maximum DE, it remained nearly the same at higher exposure.

5.3.2.2 Optimization of recording angle

Inorder to optimize the angle of recording in MBPVA/AAm film with PVA of molecular weight 54,500, PVA with 10 % was used and gratings were recorded on this film at different angles from 30^o – 80^o. Spatial frequency was calculated in each case and variation in DE with exposure energy at different spatial frequency is plotted (fig. 5.4). When spatial frequency was 818 lines/mm, maximum DE of 79 % was obtained at 20 mJ/cm^2 and at 100 mJ/cm^2, DE was reduced to 55 %. For 1080 lines/mm, maximum DE of 83 % was obtained at 20 mJ/cm^2 and above this, a small reduction was observed. In the case of DE at other spatial frequencies, the maximum DE obtained was less than 83 % and with increase in exposure energy, a reduction in DE was observed. Here the maximum DE was obtained at 1080 lines/mm with exposure of 20mJ/cm^2. At this exposure, for higher spatial frequency of 2032 lines/mm also, DE of 75% could be obtained (when molecular weight of the photopolymer was 1,25,000, at this spatial frequency DE was 65%. Chapter 3, section 3.11).

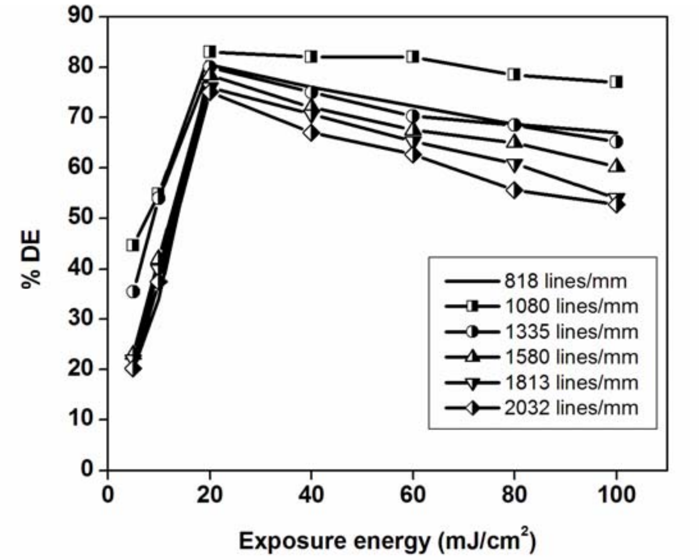

Fig. 5.4 Variation in DE with exposure at different spatial frequency

So the optimized parameters in this case are;

Concentration of PVA: 10%

Exposure energy: 20 mJ/cm^2

Spatial frequency: 1080 lines/mm

Maximum DE: 83 %

5.3.3 Optimization of concentration of PVA with molecular weight 1, 25,000

PVA with this molecular weight was used in the previous studies (chapter 3 and 4) and angle of recording and exposure energy was already optimized and optimization of concentration of PVA was only studied.

For this, concentration of PVA was varied from 7.5% to 15% and gratings were recorded at 1080 lines/mm with 80 mJ/cm^2

exposure energy. The variation of DE with concentration of PVA is plotted (fig.5.5).

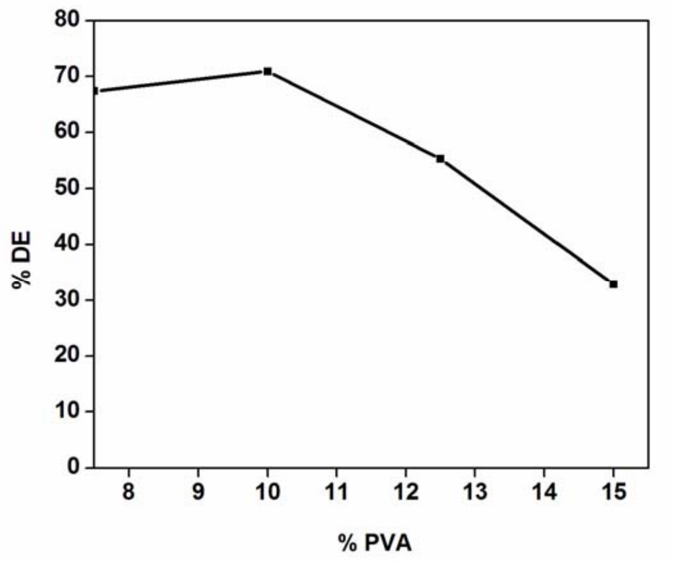

Fig. 5.5. Variation in DE with concentration of PVA

For 7.5% PVA, DE of 67 % could be obtained, for 10 % PVA, DE of 75% and after increase in concentration of PVA, DE was reduced and for 15% PVA, DE of only 30 % was obtained.

The result obtained can be summarized as given in table 5.2.

Table. 5.2. Comparison of the optimized parameters for PVA with different molecular weights

Molecular weight of PVA	Concentration of PVA	Exp.energy	Spatial Frequency	Max. DE
13,700	12.5 %	20 mJ/cm^2	30^o	70 %
54,500	10 %	20 mJ/cm^2	40^o	83%
1,25,000	10%	80 mJ/cm^2	40^o	75%

From the table, it is clear that sensitivity and maximum DE obtained were high for MBPVA/AAm film with molecular weight of PVA 54,500 at 10% by weight concentration. Maximum DE obtained for PVA of higher molecular weight was lower than that for medium molecular weight PVA. Lowering the molecular weight of the polymer binder, the photosensitivity of MBPVA/AAm system could be improved from 80 mJ/cm^2 to 20 mJ/cm^2. This is because, low molecular weight PVA can decrease the viscosity of the photosensitive film; this will make the diffusion of monomers from the dark region to the bright region much easier and faster. The increase in rate of diffusion will improve the photosensitivity. Besides, more monomers are transferred into bright region to take part in the photopolymerization reaction, which will help to increase the refractive index modulation and diffraction efficiency [14].

When the PVA chain length is too high and as it gets crosslinked, there is limited mobility and also high water content in the case of high molecular weight PVA, inter molecular distance is greater and grating formation is not only the function of concentration of dye molecules and monomer but also of distance between PVA chains [13]. As a result, the DE obtained was also low compared to low molecular weight PVA.

For comparing the results, studies like optical absorption and thickness measurement were done in MBPVA/AAm films with different molecular weights.

5.4 Comparison of thickness of the films

Thickness of the MBPVA/AAm films of optimized concentration of components were measured using Dektak 6m Stylus Profiler and given in table 5.3.

Table 5.3. Comparison of the thickness of the optimized MBPVA /AAm films

Molecular weight of the photopolymer	Thickness (μm)
13,700	125
54,500	128
1,25,000	130

From the table, it is clear that a variation in thickness was observed with variation in molecular weight. The maximum thickness of 130 μm was obtained for the film with highest molecular weight. The nominal thickness depends on the molecular weight used to fabricate the film. As the molecular weight increases, thickness also increases, because the rate of evaporation of water is inversely proportional to molecular weight; therefore, film with high molecular weight, water evaporation rate is low and this inturn increases the thickness of the film [13].

5.5 Comparison of optical absorption studies

For studying the effect of molecular weight on the absorbance of the photopolymer film, optical absorption spectra were taken and plotted (fig.5.6). From the spectra, it is observed that the characteristic peak of methylene blue was not affected by the molecular weight of PVA but the value of absorbance increased with increase in molecular weight. One possible explanation can be that, because of the lesser water content in low-molecular weight PVA films, the probability of dye molecules being reduced by the interaction with the –OH pendant groups in the neighbouring PVA chains is higher. This bleaching process is given during overnight water evaporation [13].

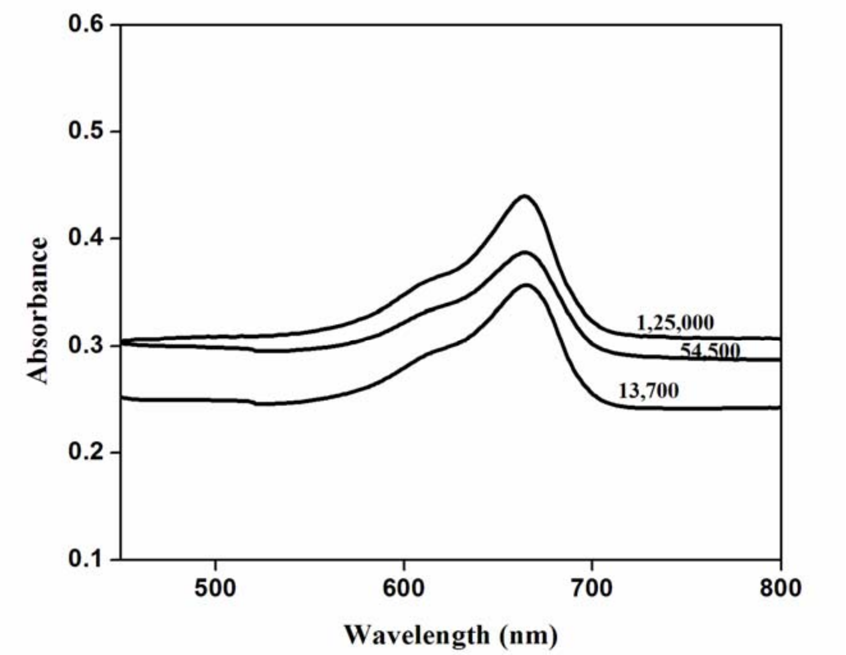

Fig. 5.6. Optical absorption spectra of the three photopolymer films

The optimized molecular weight of the photopolymer film was 54,500 and maximum DE of 83% was obtained at 1080 lines/mm with exposure energy of 20mJ/cm^2.Therefore other studies were done on this optimized film.

5.6 Calculation of RI modulation

The modulation in refractive index of the optimized sample before and after exposure was calculated using Kogelnik coupled wave theory;

$\Delta n = \mathrm{Sin}^{-1} (\eta^{1/2}) \times \lambda \cos\theta / \pi \times d$, where Δn-RI modulation, η-DE, λ - wavelength of reading beam, θ-angle inside the material measured from the normal to the surface and d-thickness of the film.

Using this equation a RI modulation of 1.69×10^{-3} was obtained.

5.7 DE on storage

For measuring the storage stability of the gratings recorded on the optimized film, DE was monitored at different time intervals and plotted (fig.5.7). From the graph, it can be seen that a sudden decrease in DE from 83% to 68% could be observed within first month of recording and it did not remain stable. After 4 months, DE was reduced to 62% and reached to 60% after 6 months of recording. In the photopolymer film, dye and monomer molecules get trapped within PVA chain. When the molecular weight of PVA is low, the trapped molecules can easily diffuse inside the PVA chain. Eventhough the easy diffusion causes an increase in material's sensitivity; it will reduce the efficiency of the recorded grating on storage.

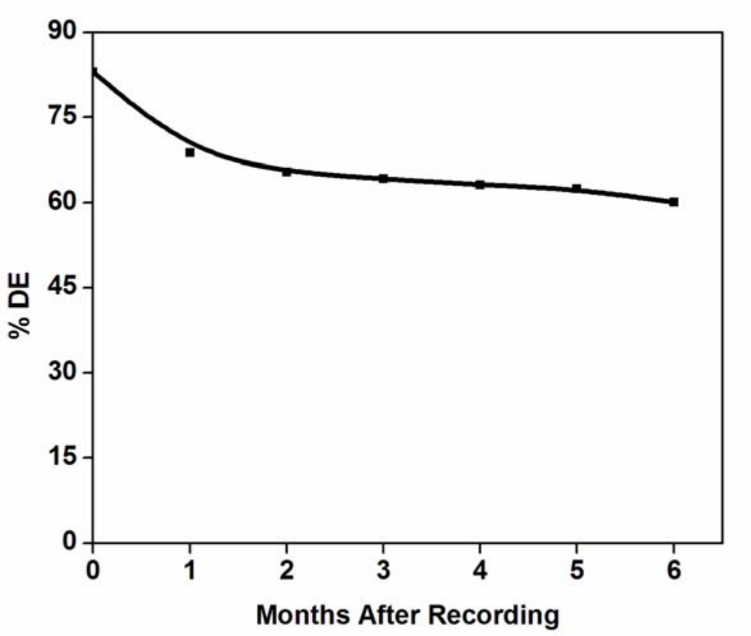

Fig. 5.7. DE on storage of MBPVA/AAm film with mol.wt. of photopolymer 54,500

5.8 Shelf life studies

The shelf life of the material after preparation or drying was studied by recording gratings on the dried films at different intervals of time. The DE was measured and plotted (fig.5.8). Gratings with a DE of 83% could be recorded for two weeks. After one month, gratings could be recorded with DE of 67% and after two months, a DE of 53% was obtained. After 3 months, DE was further reduced to 45% and after 6 months of film preparation, gratings could be recorded with a low efficiency of 13% only. The reduction in DE may be due to photopolymerization of residual monomer within the polymer network.

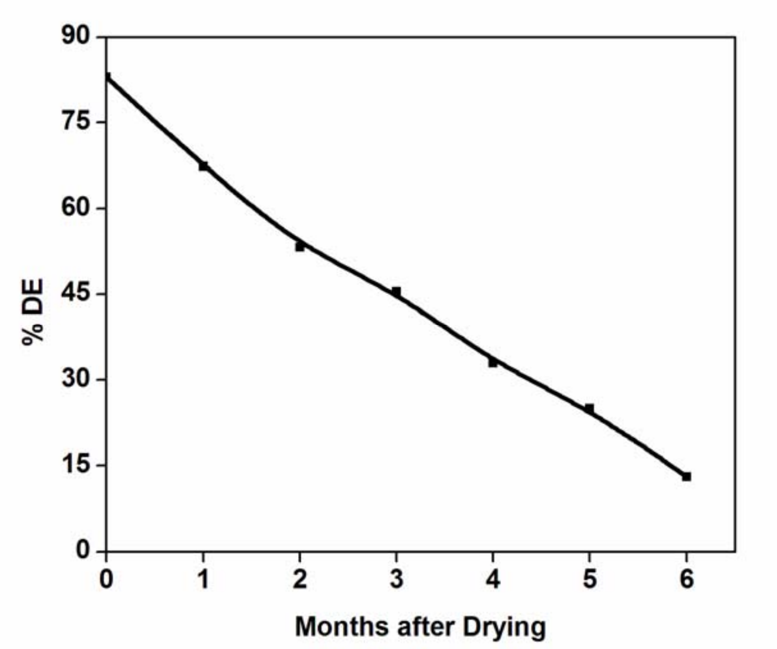

Fig. 5.8. Variation of DE with ageing of the optimized film

5.9 Effect of UV exposure on the storage life of gratings

In the case of MBPVA/AAm film with molecular weight 54,500, eventhough a DE of 83% could be obtained initially, it was reduced to 68% within one month after recording (section 5.7) and for obtaining stable DE, the recorded gratings were exposed to UV flood lamp for different time intervals. Fig.5.9 is the plot of optimization of UV exposure time. After exposed to UV, a small reduction in DE was observed in all the cases. With increase in time of exposure, DE was reduced because of crosslinking in PVA chain.

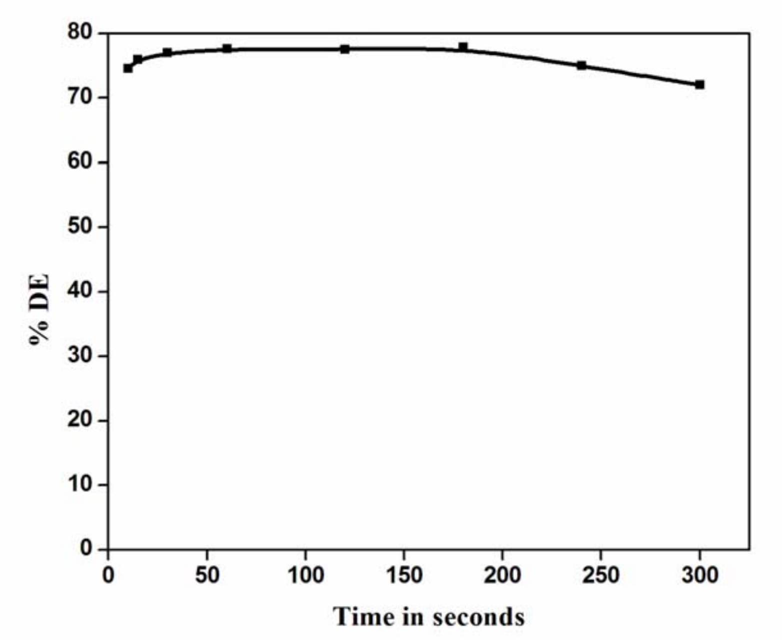

Fig. 5.9. Variation of DE with UV exposure

For studying the storage life of grating after UV exposure, DE was monitored in successive days after exposing to UV and a stable DE was obtained for the grating exposed to UV for 60 seconds as shown in (fig. 5.10). The figure shows DE on storage of the grating exposed to UV for 60 seconds. In this case, an initial DE of 77 % obtained after exposing to UV and this remained the same after one month of recording. After 3 months also, DE of 77% was obtained and after 4 months, a DE of 76% (for UV unexposed gratings, DE was reduced from 83% to 68% after one month of recording and after 4 months, DE was 62%, section 5.7.).When the film was exposed to UV, the dye molecules may get reduced and due to this, gratings with stable DE could be obtained.

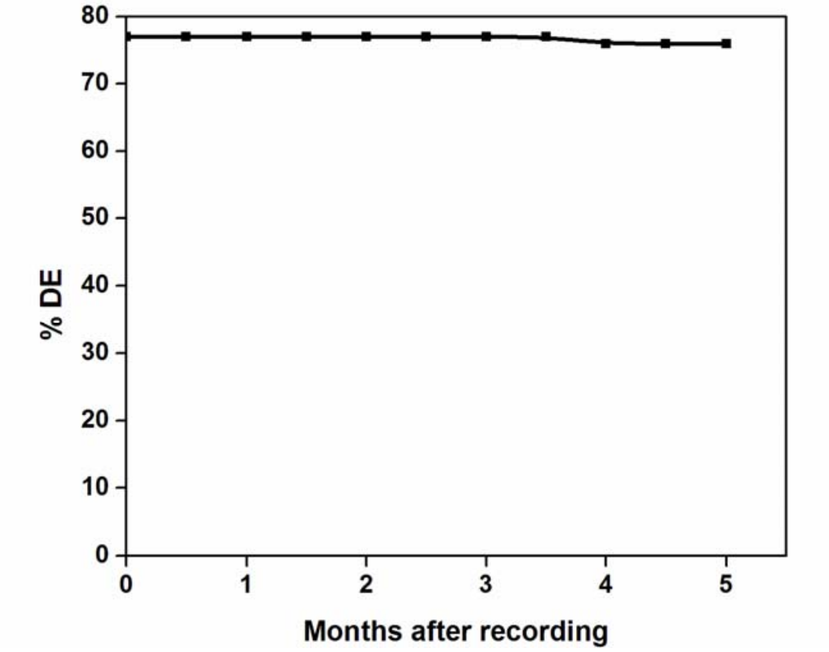

Fig. 5.10. DE on storage after exposed to UV for 60 seconds

5.10 Effect of BMA on the storage life and shelf life of grating

In chapter 4, the effect of BMA on the material's properties was studied and for that, the concentration of BMA was optimized. Here inorder to find the effect of BMA on storage life, the same concentration of BMA was used and gratings were recorded at 1080 lines/mm and DE was measured. Fig.5.11 is the plot of variation in DE with exposure energy of 5-60 mJ/cm^2. Maximum DE of 82% was obtained at 20 mJ/cm^2 and for the material without BMA also this was the optimized exposure energy. When the exposure energy was increased to 60 mJ/cm^2, DE was reduced to nearly 70%.

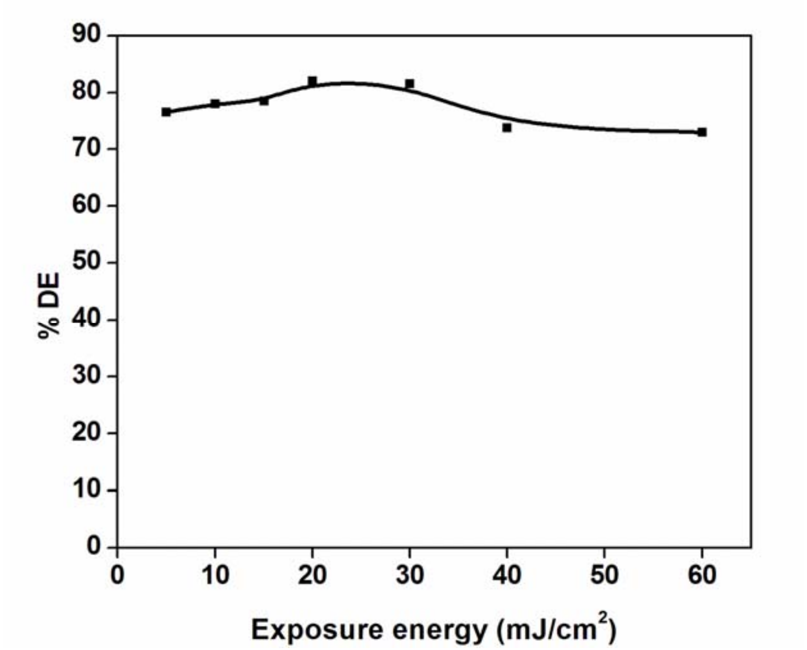

Fig. 5.11 Variation in DE with exposure energy

To study the effect of BMA on the storage life of the gratings, DE of the gratings was measured in different time intervals and plotted (fig.5.12). On the addition of BMA, DE of 82% could be obtained initially but on storage, it did not remain the same. After one month of recording, the DE was reduced to 77% (for uncrossliked film, it was 68%) and after 3 months, DE was again reduced to 71% and reached to 67% after 4 months. This may be due to the fact that in the case of low molecular weight polymer, eventhough the addition of BMA caused the formation of crosslinked polyacrylamide chains, the trapped dye molecules can easily diffuse from dark region to bright region and cause a slow decrease in DE of grating compared to the uncrosslinked film on storage.

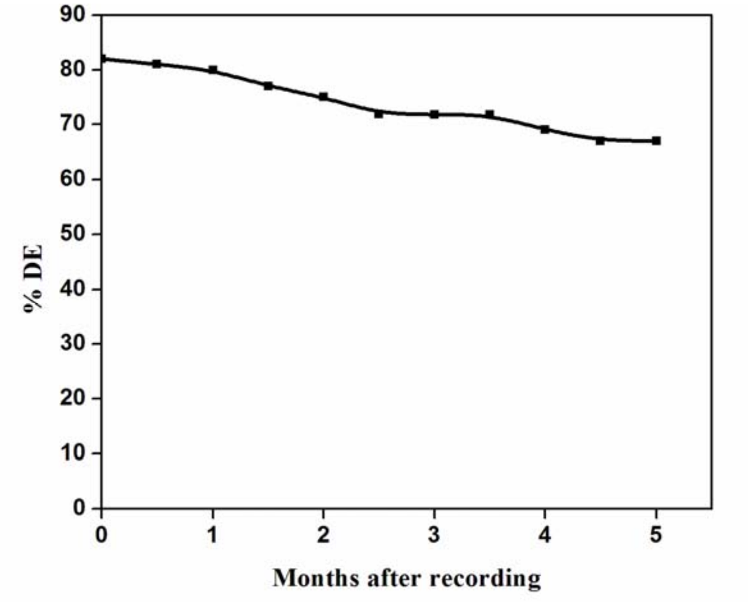

Fig. 5.12. DE on storage of MBPVA/AAm/BMA with mol wt of photopolymer 54,500

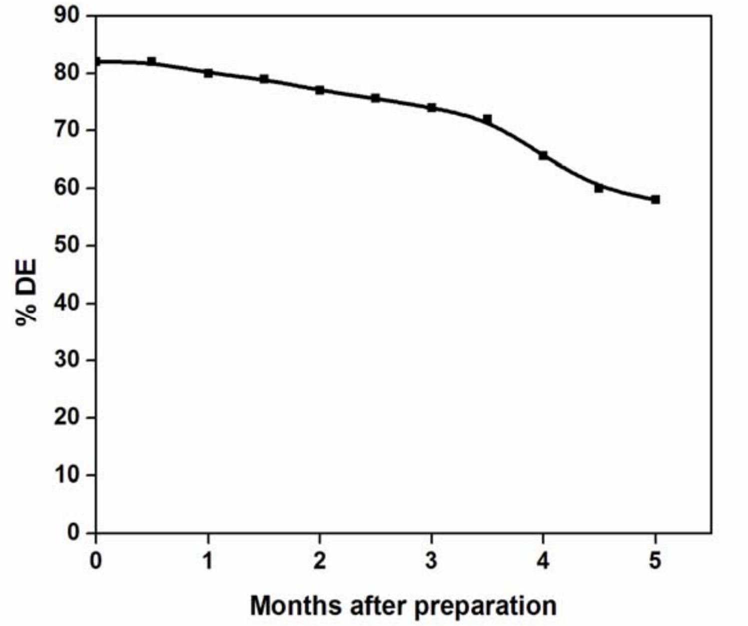

Fig.5.13. DE on ageing of MBPVA/AAm film with mol.wt of photopolymer 54,500

Shelf life of the film was also studied and for this, gratings were recorded at different time intervals and change in DE with ageing of the film is plotted (fig.5.13). Upto one month of sample preparation, gratings could be recorded with a DE of 79% and after 3 months of film preparation, gratings with DE of 72% could be recorded. When gratings were recorded on the films after 4 months of preparation, gratings with a DE of 60% was obtained (uncrosslinked film with low molecular weight PVA, DE of only 45% was obtained after 3 months, and after 4 months, DE of only 30% was obtained, section 5.8). The addition of BMA could improve the shelf life of the material.

5.11 Recording of Transmission Holograms

Transmission holograms were recorded using the optimized MBPVA/AAm films using the experimental setup described in section 2.3.(I). The photographs of the holograms recorded using He-Ne laser are shown in fig.5.14. The holograms were reconstructed with the recording wavelength itself.

Fig. 5.14. Photographs of transmission holograms recorded using He-Ne laser

5.12 Conclusion

For studying the effect of molecular weight of the polymer binder, 3 different molecular weights were used and maximum diffraction efficiency of 83% was obtained with 20 mJ/cm^2 exposure energy for PVA with molecular weight 54,500. By reducing the molecular weight, photosensitivity and diffraction efficiency of the material could be improved. Shelf life of the MBPVA/AAm film with low molecular weight PVA was slightly better than that with the high molecular weight polymer binder. For improving the storage life of gratings, UV exposure was used. Effect of BMA on the storage life and shelf life was also studied and on the addition of BMA, shelf life of the material could be improved.

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CORRECTIONS

Table 5.2: While comparing the effect of molecular weight of PVA, it would have been better to use same concentration of PVA for different molecular weights. Thus, it is desirable to furnish the results for either 12.5% concentration of 54,500 and 1,25,000 molecular weight samples or 10% concentration of 13,700 molecular weight sample.	In this chapter, the effect of molecular weight of PVA on DE was studied. It is observed that in addition to the molecular weight of the polymer, concentration of the polymer also affects the diffraction efficiency. So we have done experiments with PVA of different molecular weight keeping the concentrations same .The sample which gave maximum DE was selected as optimum. Table 5.2 given in the thesis reported the samples with different concentrations that gave maximum DE. The result of the three photopolymers with different molecular weights at 10% concentration is given as Table A (below).

Table A

Molecular weight of PVA	Concentration of PVA	Exp.Energy	Spatial frequency	Max. DE
13,700	10%	80mJ/cm^2	40^o	50%
54,500	10%	20mJ/cm^2	40^o	83%
1,25,000	10%	80mJ/cm^2	40^o	75%

Chapter 6

SUMMARY AND CONCLUSIONS

Holographic photopolymers are systems of organic molecules that rely on photoinitiated polymerization to record volume phase holograms. Characteristics such as good light sensitivity, real-time image development, large dynamic range, good optical properties, format flexibility, good image stability, and relatively low cost, make photopolymers promising materials for write-once, read-many times (WORM) holographic data storage applications. The thesis presents an attempt to make water soluble PVA/acrylamide photopolymer films with good energy sensitivity, good storage life and good efficiency. A summary of the results obtained from the experimental works are presented here.

An introduction to photopolymers, basic mechanisms of photopolymers used in various fields and applications of photopolymer technology was given in chapter 1. Requirements and different types of recording media, a brief review on photopolymers used as hologram recording media and mechanism of hologram formation in PVA/acrylamide system are also included in this chapter.

The experimental technique used for the fabrication of the films and different methods used for the characterization of the prepared films are given in chapter 2.

Photopolymer films were prepared with PVA as binder, methylene blue as sensitizer, acrylamide as monomer and triethanol amine as co-initiator. Gravity settling method was used to prepare the films. Concentration of each component was optimized by recording gratings and maximum diffraction efficiency of 75% was obtained for a dye concentration of 1.4 $x10^{-5}$M. For this, the exposure energy needed was 80 mJ/cm^2. The gratings recorded in these films could be stored for a long time. Effect of TEA on the T_g of PVA was studied by DSC analysis. The shelf life of the material could be improved by keeping the photopolymer mixture in solution form under controlled temperature. For further improving the storage of the gratings, UV exposure was employed and the gratings were exposed to UV for 180 seconds, a better storage life could be achieved. For protecting the films from external dust and contaminants, sealants were used and the storage life and shelf life of the material could be improved by sealing; in which, PMMA sealed films showed better results. These results are included in chapter 3.

Eventhough photopolymer films showed good diffraction efficiency, a decrease in DE could be observed on storage. For getting better storage life, usually, crosslinkers were incorporated. In the present study, the optimized film showed good DE and storage life compared to the earlier materials developed. But for getting photopolymer films with better storage life, two organic crosslinkers, glutaraldehyde and N-N’-methylene-bis-acrylamide were incorporated into the optimized MBPVA/AAm film and the effect of these have been given in chapter 4. The introduction of glutaraldehyde resulted in a lower diffraction efficiency and a decrease was observed on storage. Incorporation of N,N’-methylene-bis-acrylamide resulted in better stability of the recorded gratings without affecting sensitivity and resolution of MBPVA/AAm film. DE as high as 70% could be maintained for one year of recording for a particular concentration of N,N’-methylene-bis-acrylamide. For studying the crosslinking effect, DSC studies were performed on the optimized film. The thickness of the material was also measured and a thickness of 130μm was obtained. In addition to storage life of the material, shelf life of the sample was also checked and an improvement was observed, ie, even after 3 months of preparation, gratings could be recorded on the samples with a DE of 70%.

The effect of molecular weight of the polymer binder on the holographic properties was studied and the results are included in chapter 5. For this, 3 different molecular weights of PVA were used and maximum diffraction efficiency of 83% was obtained with 20 mJ/cm^2 exposure energy for PVA with molecular weight 54,500. The optical absorption spectra of the three photopolymer films were taken and the thickness of the films was also measured. By reducing the molecular weight, photosensitivity and diffraction efficiency of the material could be improved. Shelf life of the MBPVA/AAm film with low molecular weight PVA was also slightly better than that with the high molecular weight polymer binder. For improving the storage life of gratings, UV exposure was used. Effect of N-N'-methylene-bis-acrylamide, on the storage life and shelf life was also studied and on the addition of BMA, shelf life of the material could be improved and transmission holograms could be successfully recorded on the prepared films using He-Ne laser.

The importance of the photopolymer films developed in the present study is the easy fabrication method and good energy sensitivity with high diffraction efficiency. This material is also environmental friendly and economically favourable to industry and layman. Thus this material makes it a competent one in the field of holography.

Future work

For the fabrication of the photopolymer films used in the present study, gravity settling method was adopted and the prepared films have a problem with non-uniformity at the edges. For getting uniform films, spin coating method can be used.

Thickness plays an important role in the properties of the photopolymer films and therefore, photopolymer films should be prepared with varying thicknesses and here also, spin coating method can be used.

Incorporation of nano particles into the photopolymer film increases the spatial frequency of the film and therefore inorganic nano particles like metal oxides, zeolites and carbon nano tubes can be incorporated into the prepared films.

Effect of molecular weight of PVA on the holographic properties was studied and it could be seen that, low molecular weight PVA samples increased the sensitivity and diffraction efficiency of the film. In this case, all the PVA selected had the same degree of hydrolysis and studies can be extended to PVA with varying degree of hydrolysis also.

The property of the film was greatly affected by the environmental changes and therefore, effect of temperature and relative humidity has to be studied.

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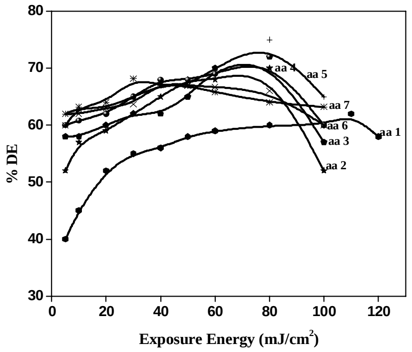
CORRECTIONS



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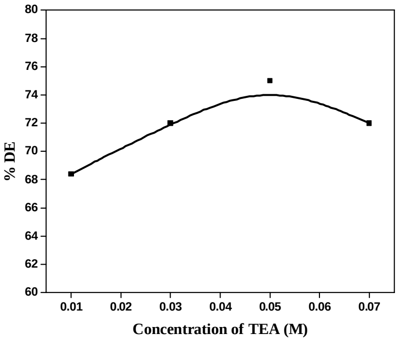

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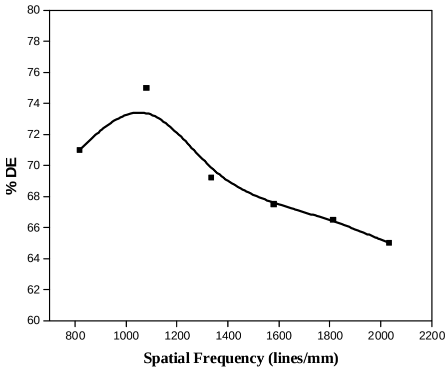

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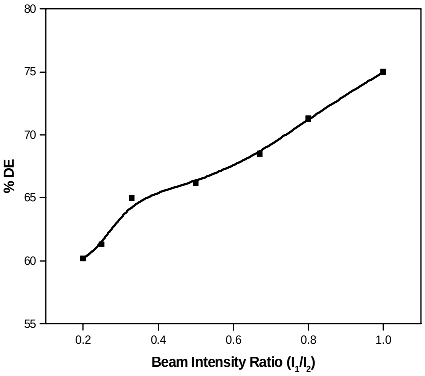

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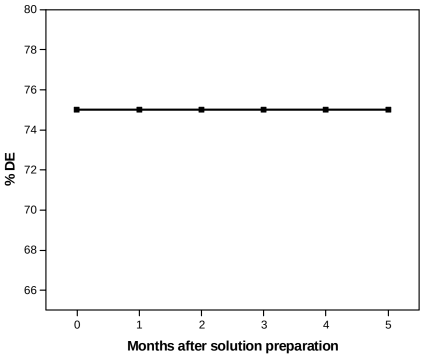

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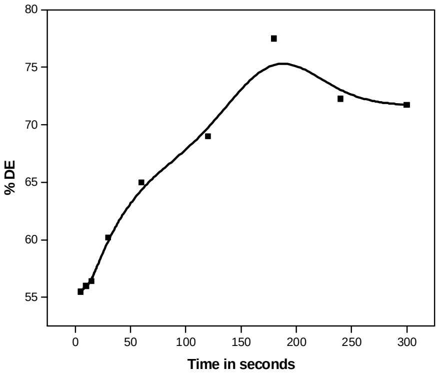

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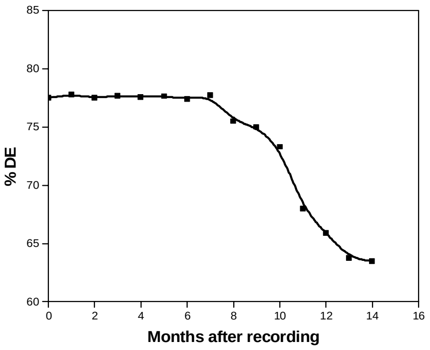

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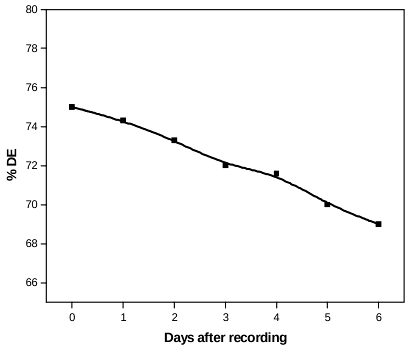

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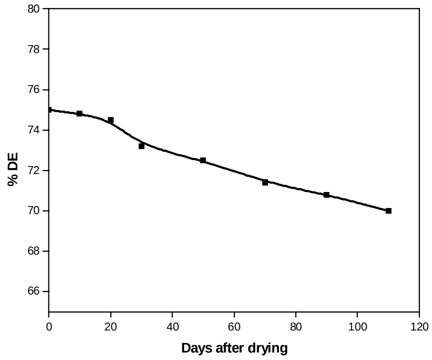

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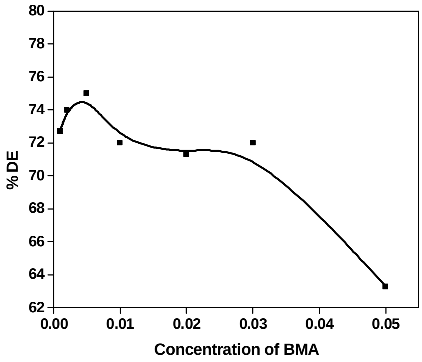

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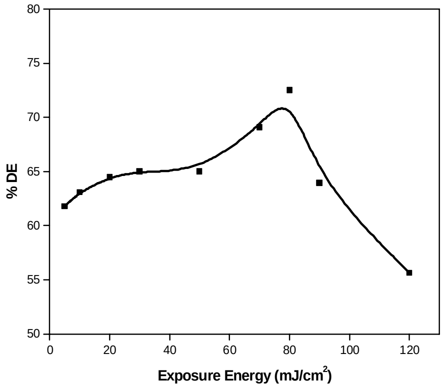


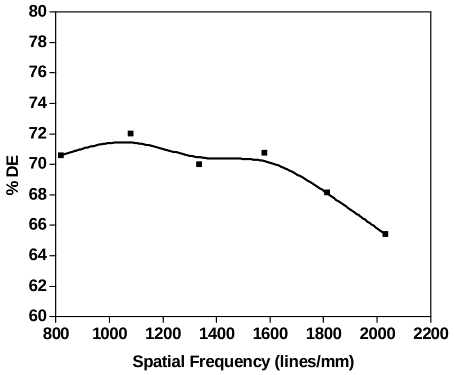
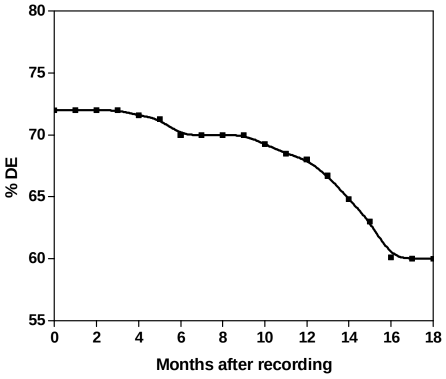


Fig.4.9 Fig.4.10



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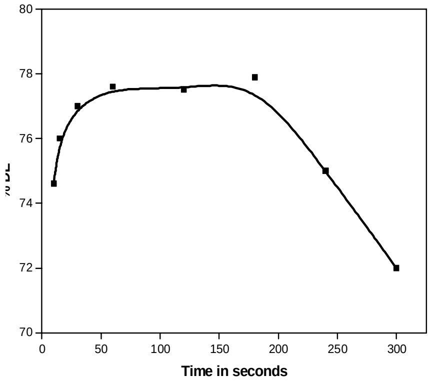
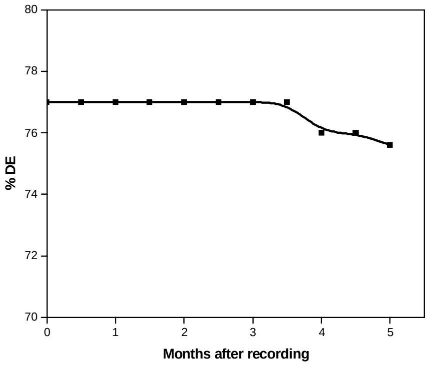


Fig.5.9



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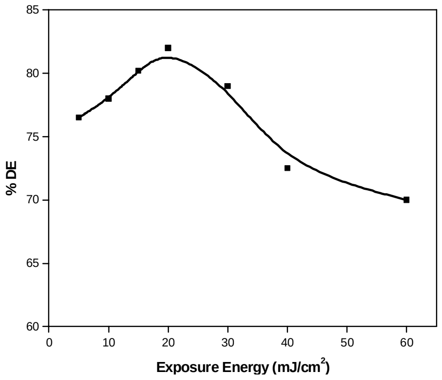

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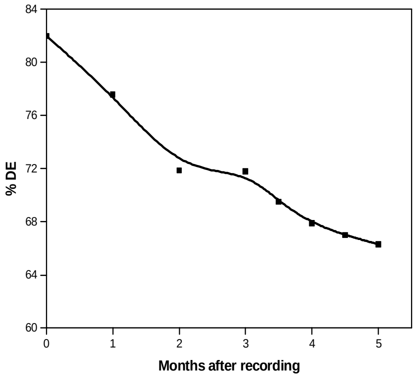

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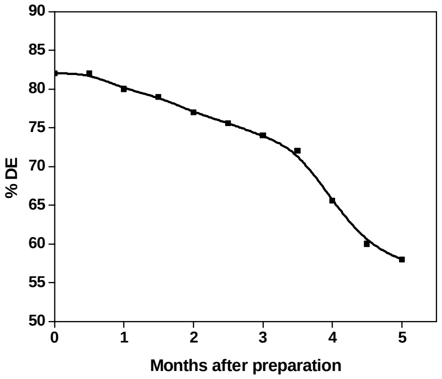

Fig.5.13

LIST OF PUBLICATIONS

Journal publications

- Effect of concentration of dye on the storage life of plane wave gratings on photopolymer film, **K. P. Nimmi,** V. Pramitha, K. Sreekumar, C. Sudha Kartha, Rani Joseph, Journal of Appl.Polymer Science (Accepted 2011)
- Silver-doped photopolymer media for holographic recording, V. Pramitha, **K. P. Nimmi**, N. V. Subramanian, Rani Joseph, K. Sreekumar and C. Sudha Kartha, Appl. Opt., 48, 2255-2261(2009)

Conference Publications

International conferences

- Effect of molecular weight of poly (vinyl alcohol) on the holographic properties of photopolymer film, **K. P. Nimmi**, V. Pramitha, C. Sudha Kartha, K. Sreekumar, Rani Joseph, POLYCHAR 2011, 20-24 March 2011, Kathmandu, Nepal, page no.230
- Performance of the grating's diffraction efficiency of the photopolymer film on the addition of crosslinker, **K. P. Nimmi**, V. Pramitha, K.Sreekumar, C.Sudha Kartha, Rani Joseph, APT 2010, Cochin University of Science & Technology, Cochin, 26-27 Feb 2010, page no. 83.
- Study on the effect of molecular weight of poly (vinyl alcohol) on the properties of photopolymer film, **Nimmi K. P**, Pramitha V, Sudha Kartha C, Sreekumar K, Rani Joseph , MATCON 2010, Cochin University of Science & Technology, Cochin, 11-13 Jan 2010, page no. 148.

- Peristrophic Multiplexing in a Methylene Blue Doped Acrylamide Polymer, Pramitha. V, **Nimmi. K. P**, Subramanyan. N. V, Rani Joseph, Sreekumar. K, Sudha Kartha. C, PHOTONICS 2008, 15-17 Dec 2008, IIT Delhi, New Delhi page no: 387
- Effect of Sealing on the diffraction efficiency of an Acrylamide based photopolymer, **K.P. Nimmi**, V. Pramitha, K. Sreekumar, C. Sudha Kartha, Rani Joseph, International Conference on Advances in Polymer Technology, Cochin University of Science and Technology, Cochin, 25-27 Sep 2008, page no: 109
- Silver Doped MBPVA/AA as an Efficient Holographic Recording Media, Pramitha. V, **Nimmi. K. P**, Rani Joseph, Sreekumar. K and Sudha Kartha. C, World Forum on Advanced Materials-POLYCHAR 16, 17-21 Feb 2008, Lucknow, page no: 213.

National Conferences

- Characterization of a Methylene Blue sensitized Poly (vinyl alcohol) /Acrylamide Photopolymer for Holographic Data Storage, Pramitha. V, **Nimmi. K. P**, Rani Joseph, Sreekumar. K, Sudha Kartha. C, NLS 08, LASTEC, New Delhi, 7-10 Jan 2009, page no: 51
- A Photopolymerizable holographic recording medium with spectral sensitivity in the entire visible region, Beena Mary John, Pramitha V, **Nimmi K.P**, K. Sreekumar, Rani Joseph and C. Sudha Kartha, 31st Optical society of India symposium on contemporary optics and applications(organized by OSI and M.S university), Baroda,1-3 March, 2007.

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LIST OF ABBREVIATIONS AND SYMBOLS

ASTM	-	American Society of Testing Materials
BMA	-	N, N'-methylene-bis-acrylamide
COI	-	Co-initiator
CRT	-	Cathode Ray Tube
DCG	-	Dichromated Gelatin
DCPVA	-	Dichromated poly (vinyl alcohol)
DE	-	Diffraction Efficiency
DHEBA	-	N,N-dihydroxyethylenebisacrylamide
2ISF	-	4,5,diiodosuccinylfluorescein
DMAA	-	Dimethyl acrylamide
DPI	-	Diphenyl iodonium chloride
DSC	-	Differential Scanning Calorimetry
ErB	-	Erythrosine B
T_g	-	Glass Transition Temperature
HEMA	-	2-hydroxyethylmethacrylate
IC	-	Integrated Circuit
LC	-	Liquid Crystal
LCD	-	Liquid Crystal Display
MB	-	Methylene Blue
MBPVC	-	Methylene blue sensitized poly (vinyl chloride)
MBPVA/AAm	-	Methylene blue sensitized poly (vinyl alcohol) acrylamide
mJ	-	millie Joule

µm	-	micro meter
µW	-	micro Watt
ND filter	-	Neutral Density filter
NLO	-	Non-Linear Optics
NP	-	Nano Particle
NPG	-	N- Phenyl Glycine
PA	-	Poly acrylamide
PAA	-	Poly (acrylic acid)
PMMA	-	Poly (methyl methacrylate)
PI	-	Photoinitiator
PPMs	-	Photopolymer Materials
PR	-	Photo Refractive
PVCi	-	Poly (vinyl cinnamate)
PVK	-	Poly (vinyl carbazole)
PWB	-	Printed Wiring Board
RB	-	Rose Bengal
RI	-	Refractive Index
SHSG	-	Silver Halide Sensitized Gelatin
SNR	-	Signal to Noise Ratio
TEA	-	Triethanolamine
TET	-	Trimethylolpropane ethoxylate triacrylate
UTM	-	Universal Testing Machine
UV	-	Ultra Violet
VAc	-	Vinyl acetate
WORM	-	Write Once Read Many

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