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Characterization and Applications of Crosslinkable Materials

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Crosslinkable photosensitive materials have been studied for many years and they are widely used for optical recording of information. After investigating the photochemical process in various systems, it appears that the chemical structure of the polymeric matrix plays an essential role in the process of the reaction that takes place upon irradiation by a laser beam. The results of experiments that were conducted to investigate the possible use of different sensitizers and different mixtures of polymers are presented in this paper. Also, some applications that were studied using such crosslinkable systems as volume hologram as well as surface relief structure recording material are presented.

Keywords: Optical Materials; Polymers; Holography; Photophysics; Photochemistry

INTRODUCTION

Photocrosslinkable systems constitute a major class of materials for many applications. There are two kinds of photocrosslinkable systems: those made of gelatin and those made of polymers. These sub-systems are also called biopolymers and synthetic polymers respectively. Photocrosslinkable systems are attractive since polymers are excellent materials for many applications due to their interesting properties. They are being used as substrates, as well as media, in standard information storage systems. Due to the increase of importance of optical communication, an important increase in the demand of

optical devices is also appearing. Consequently, the demand for better materials with desired characteristics such as high resolution, better energy sensitivity, broad wavelength sensitivity, simpler processing procedure and erasability arises due to increased optical applications. The increased emphasis on compactness, speed of operation and wavelength selectivity has also focused a great deal of attention on the solutions offered by all-optic devices and by hybrid electro-optic systems, as partial replacements for electronic systems. Examples of such devices are optical components, which include switches, modulators, 3-D storage devices, holographic optical elements, scanners and wavelength division multiplexers. The performance of these optical devices depend to a great extend on the performance and the survivability of the employed optical materials.

PHOTOCROSSLINKABLE SYSTEMS

Photocrosslinkable systems such as dichromated gelatin, dichromated poly(vinyl alcohol) (DCPVA), dichromated poly(acrylic acid) (DCPAA), ferric chloride doped poly(vinyl alcohol) (FePVA), DCPVA with dimethylformamide (DMF), and DCPAA-DMF have been widely investgated for applications in the field of optics. Those different metal ion and dye sensitizers were employed to sensitize the polymer matrix. On exposure to appropriate light source the sensitizer undergoes photochemical changes leading to refractive index modulation and the hologram formation. Most of these materials are used in the form of dry films.

PHOTOCHEMICAL ACTION

Cr(VI) doped polymer systems

The photochemistry of Cr(VI) has been investigated over decades. It was found that the photoreduction of Cr(VI) leads to Cr(III) in presence of organic reducing agents [1]. To understand the primary photoprocess of Cr(VI) in PVA matrix, ESR spectroscopic measurements were performed in polymer films[2-3]. Thermal and photochemical evolution of Cr(V) was identified from the

characteristic ESR signal and the formation of photoproduct Cr(III) has also been monitored in aqueous solution and in polymer films. Involvement of polymer matrix in the electron transfer process was also confirmed by spin-trapping experiments. The significant influence of electron donors on the holographic efficiency of the recording materials also strongly favours the involvement of an electron transfer mechanism. Then it was suggested a reaction scheme in which the Cr(V) is the primary species formed from Cr(VI) by the irradiation leading to the hologram formation through an electron transfer mechanism involving polymer matrix. The reduction of Cr(V) into final Cr(III) can be either photochemically, chemically or thermally (in the dark at room temperature) achieved according to the nature of the polymeric matrix. Figure 1 shows another interpretation as which the interference pattern is created in polymer matrix through the photocrosslinking reaction due to the removal of three electrons from the polymer matrix for the conversion of Cr(VI) to Cr(III)

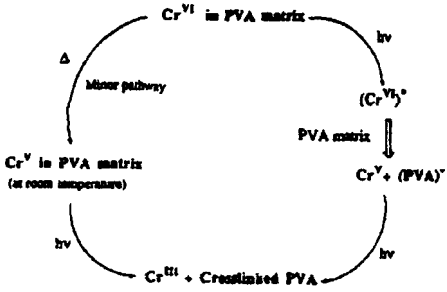


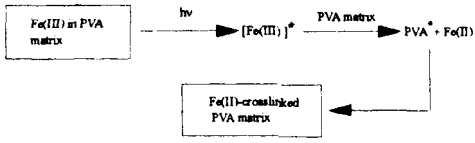
FIGURE 1: Mechanism of holographic recording for dichromated polymer systems.

Recently, Bolte et al. [4,5] reported a comparative study of the primary photochemical process observed in dichromated gelatin, in dichromated poly(vinyl alcohol) and in dichromated poly(acrylic acid). Spectral evolution of a dichromated gelatin film gave evidence for the presence of chromium (V) and showed that chromium (V) is highly stable in gelatin and that the rate of chromium (V) disappearance is very low ; the light only slightly accelerates the

process. The spectral features of a dichromated poly(vinyl alcohol) film are similar to that of a dichromated gelatin film. The chromium (V) formation was also confirmed by ESR spectroscopy. The reduction into chromium (III) is again a very slow process. By performing ESR experiments on dichromated poly(acrylic acid) films, the presence of two different chromium signals according to their origin has been detected : thermal origin and photochemical origin. The formation of a macroradical was also evidenced by ESR spectroscopy upon irradiation of a dichromated poly(acrylic acid) film. From all those recent results, it appears that only poly(acrylic acid) is unable to stabilize chromium (V) in a dichromated poly(acrylic acid) film. On the contrary, dichromated gelatin and dichromated poly(vinyl alcohol) present a different photochemical behavior : chromium (V) is highly stable in a poly(vinyl alcohol) or gelatin matrix.

Fe(III) doped polymer systems

The photo transformation in a Fe(III)-PVA system at low temperature in thin films has been studied by Bulkevich *et al.* [6] who suggested the reduction of Fe(III) to Fe (II) with the removal of one chlorine radical. Also, studies of electron paramagnetic resonance indicated that 5 to 10% of the chlorine radical leaves the intermediate and reacts with polymer. Different techniques offered complimentary data to conclude the involvement of a charge transfer mechanism[7-8]. Then a general mechanism for the photochemical changes during the holographic recording was proposed[9]. The Fe(III) doped in polymer matrix undergoes excitation upon irradiation and removes the needed one electron from the polymer matrix which undergoes photocrossslinking in the form of holographic gratings as shown below:



APPLICATIONS

Dichromated gelatin

Dichromated gelatin has been the most widely used polymer for applications such as the fabrication of holographic optical elements, head-up displays, laser scanners, fiber-optic couplers and optical interconnects. Some organic dyes can also be used to render the film sensitive to a selected wavelength. A good review of this system can be found in many books [10-13]. Although this particular recording systems is making a class by itself, the addition of an appropriate dye can accelerate the process and alter the recording wavelength [14-17].

Metal doped polymers

Metal ions such as Cr(IV) and Fe(III) have been doped into different polymer matrices such as poly(vinyl alcohol) and poly(acrylic acid) to realize various holographic recordings

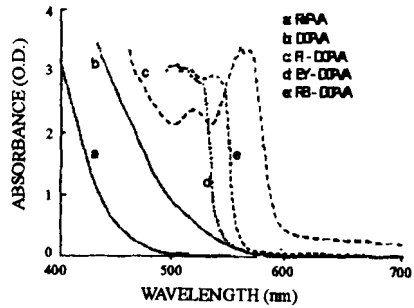


FIGURE 2. The absorption spectra of the Ferric Chloride poly(vinyl alcohol) (FePVA), Dichromated poly(vinyl alcohol) (DCPVA) and Dye sensitized DCPVA systems: Fl-DCPVA, Fluorescein-DCPVA; EY-DCPVA, Eosin Y-DCPVA and Rose-Bengal-DCPVA.

Fabrication of metal ion doped polymer films has been described in Ref.9. The absorption spectra of FePVA and DCPVA doped with various dyes such as Fluorescein, Eosin Y and Rose Bengal are shown in Fig. 2 as an indication that these systems can be made sensitive to a particular wavelength.

Reflection holograms have been recorded in DCPVA films using the Lippmann configuration [18]. A typical profile of the diffraction efficiency of DCPVA reflection holograms is shown in Fig. 3 where one can see that the peak diffraction efficiency is approximately 35 % at an exposure of 500 mJ/cm^2. The angular selectivity response of those holograms is also shown in Fig. 4.

The wavelength selectivity of reflection holograms recorded in DCPVA films has been evaluated and the transmission spectrum of a typical grating is shown in Fig. 5. The bandwidth of the filters as seen from this figure is around 3 nm. Thus DCPVA polymer films can be used for the fabrication of very narrow band wavelength filters. Volume transmission holograms have been recorded in DCPAA polymer

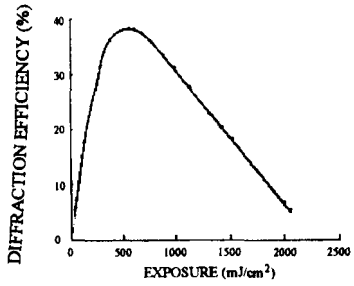


FIGURE 3: Diffraction efficiency of DCPVA reflection holograms as a function of exposure energy.

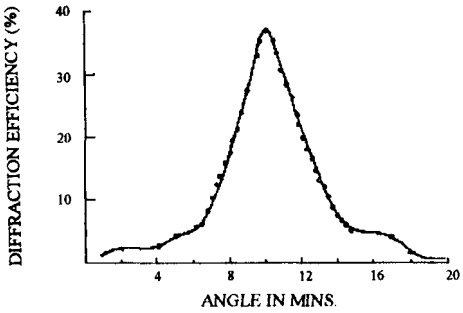


FIGURE 4 : Angular selectivity of the recorded reflection grating.

films[19]. Also, using an angular multiplexing technique, twenty holograms with equal diffraction efficiencies have been stored in one specific area of those films. As an application in optical

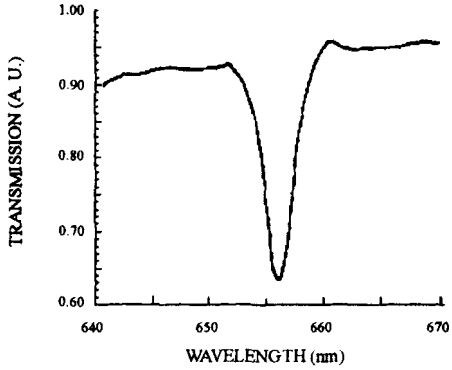


FIGURE 5 : Wavelength selectivity curve of the reflection grating.

computing, multiple holograms were recorded in DCPAA polymer films[19]. Figure 6 shows the angular selectivity profile of those holograms. The interesting and significant feature of this profile are the absence of side lobes on both sides of the main peak and the sharpness of the profile. Consequently, it is possible to record multiple holograms without any overlap with each other. Fig. 7 shows the angular selectivity of twenty multiplexed DCPAA holograms.

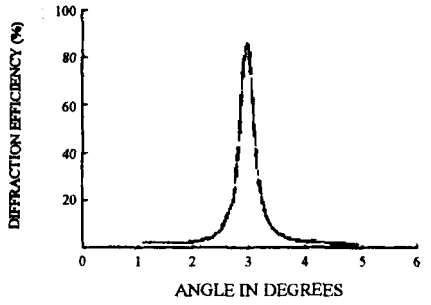


FIGURE 6: Angular selectivity of a DCPAA hologram.

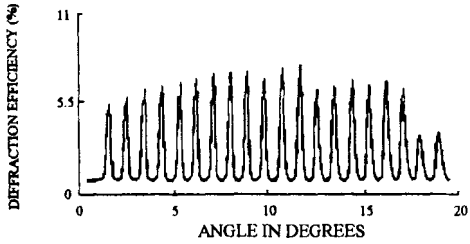


FIGURE 7: Angular selectivity of 20 multiplexed holograms.

Ferric chloride doped PVA is a very simple system that can be used in many applications. As for DCPVA, FePVA can be doped with dyes to select the writing wavelength. FePVA can also be used in real-time as well as after development. PVA systems represent a very simple and non expensive technique for those who want to make their own holographic media. These systems can be spin-coated as well as made by levelled deposition. They can be used as thin and thick films. The good diffraction efficiency obtained, their high resolution make those films very attractive[20]. Figures 8, 9, and 10 illustrate the results of our study.

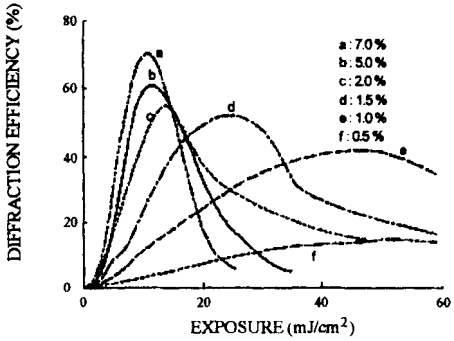


FIGURE 8 : Diffraction efficiency as a function of exposure energy of FePVA holograms for various concentrations of $FeCl_3$.

Metal ion-electron donor doped polymers

It was found that like for dye doped dichromated gelatin, electron donors influence significantly the diffraction efficiency of the recorded holograms.

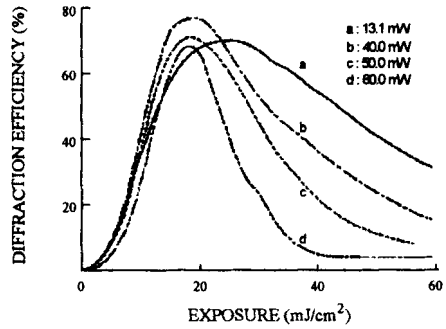


FIGURE 9: Diffraction efficiency as a function of exposure energy for different recording powers.

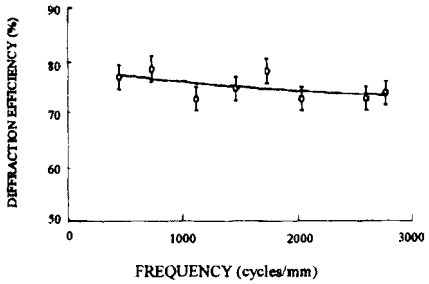


FIGURE 10 : Diffraction efficiency as a function of spatial frequency of FePVA holograms.

From all different nitrogen containing compounds, dimethyl formamide (DMF) showed the best performance. Figure 11 depicts the influence of this compound, it portrays the comparative picture of real-time diffraction efficiency profiles of DCPVA with and without DMF. One can see from this figure that the diffraction efficiency of 45% without DMF is increased to ~65% when DMF is added.

It was also found that using PVA doped with xanthene dyes permit higher diffraction efficiencies. Figure 12 shows that the real-time diffraction efficiency of DCPVA doped with Fluorescein permits can reach about 60%. So, those xanthene dyes serve as wavelength selectors and as electron donors increasing the crosslinking of the materials and contributing to an enhancement of the diffraction efficiency.

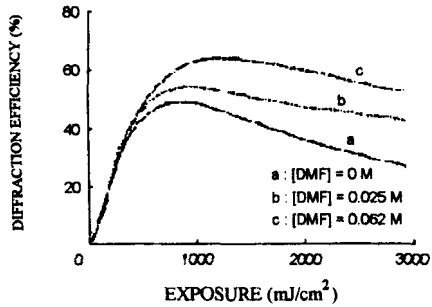


FIGURE 11: Real-time diffraction efficiency profiles of DCPVA with and without dimethyl formamide (DMF) as a function of the exposure energy.

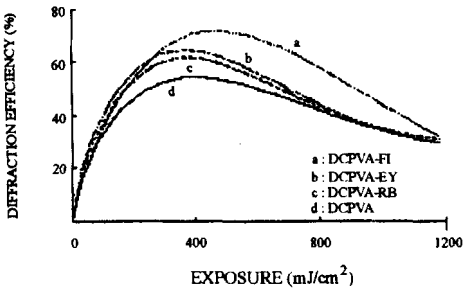


FIGURE 12: Real-time diffraction efficiency profiles for Xanthene dyes doped with DCPVA. PVA= 7 wt%; $(NH_4)_2Cr_2O_7$ = 1.4 wt%; fluorescein = $5x10^{-4}$ M; eosin Y = $5x10^{-4}$ M and Rose bengal = $2.4x10^{-4}$M.

This efficiency can still be improved if a very simple developing process is used. In effect, after exposure, by immersing the hologram in 100% ethanol at 70°C for 10 minutes and drying with an air blower the diffraction efficiency goes up to 72% (See Fig. 7 in Ref. 9). In this case, development represents a constraint but for some applications it might be seen as a good process permitting to render the film insensitive to light radiation.

Another synthetic polymer which is very attractive is the poly(acrylic acid) (PAA) doped with metal ions and organic dyes. Different DCPAA films have been prepared with different weight percentage of PAA ranging of 5-25%, keeping constant the amount of ammonium dichromate (2,0 wt%). It was found

that films with the higher concentration of PAA showed the maximum diffraction efficiency of 28% with a 25wt% of polymer but the energy requirement was fairly high (4 J/cm^2). Incorporating dimethyl formamide (DMF), the selected electron donor, into a typical film made of 20.0 wt.% of PAA and 2.0 wt.% of ammonium dichromate permitted to obtain a diffraction efficiency of more than 80% at an energy density of about 250 mJ/cm^2 for a concentration of 2.2 M of DMF. This result showed that this recording system can also be easily used in many applications.

Conventional volume transmission holograms of a 3D scene have been recorded on DCPAA-DMF films under 488 nm light[21]. The recorded holograms can be efficiently reconstructed either with red light or with a low energy beam in the blue region without any post thermal or chemical processing. Those experiments have clearly added another dimension for the versatile applications demonstrated by the photocrosslinking polymer material for holographic imaging.

Cr(VI) and Fe(III) doped PVA and PAA polymer films have been used to fabricate planar waveguides. Experimental results strongly suggest that those films can find successful applications in areas such as integrated optics and planar optical interconnects[22].

Computer Generated Holograms (CGH) with a sinusoidal amplitude profile have been copied onto DCPAA-DMF films by a simple technique namely Contact Copying [23]. By placing CGH over the recording film and exposing it with white light, contact copying was done. For thick and thin films, diffraction efficiencies of 16 % and 1.2 % have been achieved respectively.

Photoinduced holographic surface relief gratings have been fabricated in dichromated poly(acrylic acid) films[23-25]. These gratings are formed in darkness subsequent to the illumination at 442 nm and they are obtained without any chemical treatment or wet processing. Gratings with large modulation depth at low spatial frequencies have been obtained as one can see by looking at Fig. 13. This figure shows experimental data relating to a typical

cross-sectional profile of a grating as measured with a Sloan Dektak profilometer where it can be seen that the depth of modulation is approximately 520 nm and the pitch of the grating is ~ 6.2 μm.

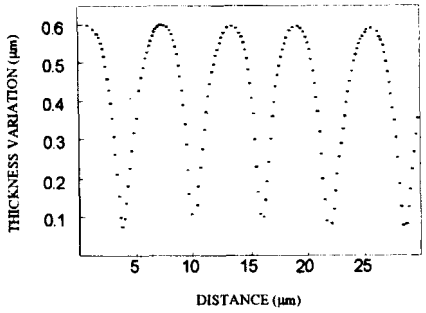


FIGURE 13. Surface profile of a section of a grating.

The influence of chemical parameters on the holographic properties of these films has been investigated [26]. This investigation allowed us to determine the optimal mixture concentration for maximizing the performance of the gratings evaluated at a spatial frequency of approximately 1200 cycles/mm. Figures 14-17 illustrate the results of this investigation. At the recording, the average power density was in order of 10 mW/cm^2.

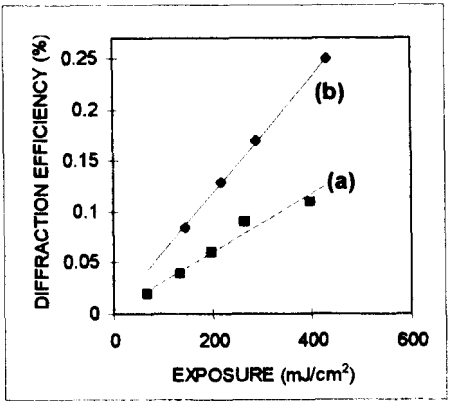


FIGURE 14. Diffraction efficiency as a function of exposure at a solution of 1.5 mol/L of dimethylformamide and at a concentration of (a) 1 wt. % and (b) 2 wt. % of ammonium dichromate.

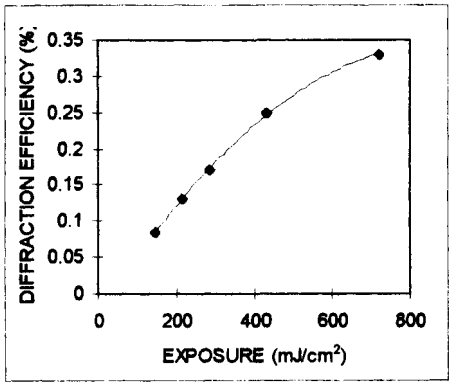


FIGURE 15. Diffraction efficiency vs exposure at a solution of 1.5 mol/L of dimethylformamide and at a concentration of 2 wt. % of ammonium dichromate.

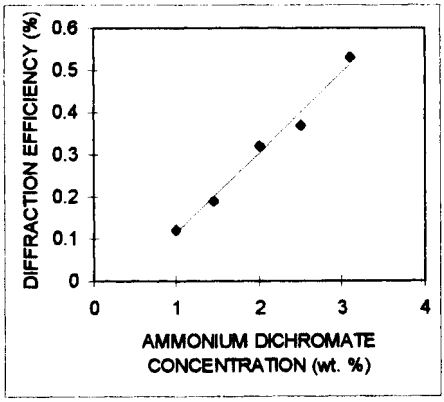


FIGURE 16. Diffraction efficiency vs the ammonium dichromate concentration at a mixture of 3 mol/L of dimethylformamide.

In summary, all these results showed that the diffraction efficiency is low even if the concentrations of ammonium dichromate and dimethylformamide are chosen to maximize the sensitivity of the films. Dichromated poly(acrylic acid) films with dimethylformamide have been used to fabricate surface relief gratings as multiple beam splitters[28]. These gratings can be recorded interferometrically and are generated in a self- developing photopolymer system

They can be used in a variety of applications that necessitate moderate beam uniformity.

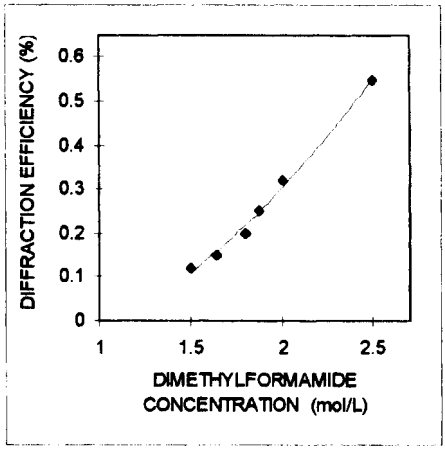


FIGURE 17. Diffraction efficiency vs the dimethylformamide concentration at a mixture of 2 wt. % of ammonium dichromate.

Typical experimental values of the diffraction efficiencies at a wavelength of 543.5 are presented in Fig. 18. These results indicate that the ratio of the maximum to the minimum diffraction efficiency and the total usefull energy fraction are approximately 6.0 and 78 % respectively.

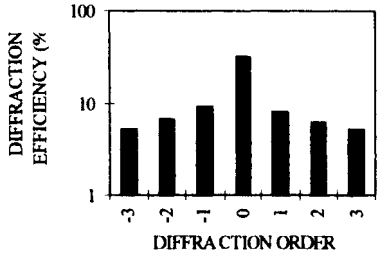


FIGURE 18. Experimental diffraction efficiency as a function of the diffraction order.

Also, these films have been used to photofabricate surface relief gratings as microlens arrays. Fig. 19 shows a typical AFM view of two sets of gratings recorded orthogonally to each other on the same spot on the DCPAA-DMF film. This AFM view shows very regularly spaced surface relief structures with a depth modulation of approximately 0.3 μm. The experimental set-up shown schematically in Fig. 20 has been used to observe the focusing properties of this microlens array. Those focusing properties are demonstrated in Fig. 21.

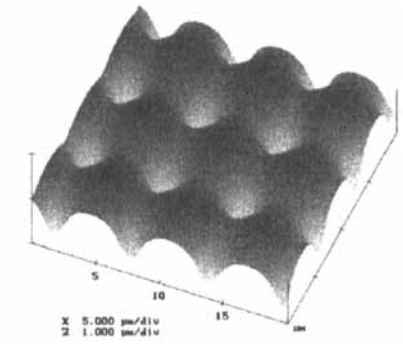


FIGURE 19. AFM view of a surface relief structure photofabricated in a DCPAA-DMF film.

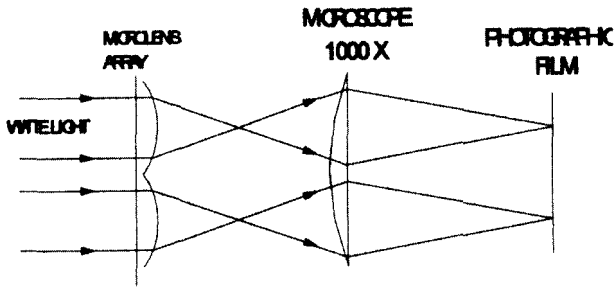


FIGURE 20. Schematic diagram of the optical set-up for observing the focusing properties of a microlens array.

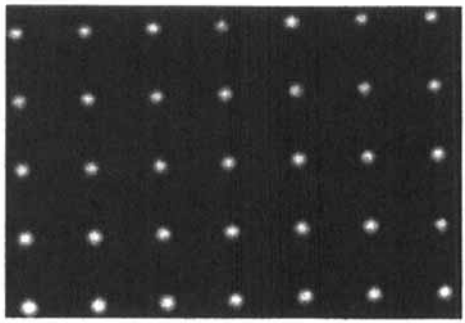


FIGURE 21. Photograph of images of the focal spots formed by the microlenses

CONCLUDING REMARKS

Experimental studies on the performance of metal ion doped polymers and metal ion-electron donor doped polymers have been carried out. These photocrosslinkable systems have demonstrated their versatility in many applications. Volume transmission holograms, reflection holograms, computer generated holograms, narrow band wavelength selective filters, holographic multiplexing, surface relief diffraction gratings, and beam dividers are some of the demonstrated applications. Indeed, one can conclude that those polymer materials are good candidates for specific applications. Also, the mechanism of information storage on these photocrosslinkable systems has been investigated and general mechanisms for the photochemical changes during the holographic recording have been proposed.

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