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A new photopolymerizable holographic recording material based on acrylamide and N-hydroxymethyl acrylamide*

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A new polyvinylalcohol-based photopolymeric holographic recording material has been developed. The recording is obtained by the copolymerization of acrylamide and N-hydroxymethyl acrylamide. Diffraction efficiencies near 50% are obtained with energetic exposure of 80mJ/cm^2. N-hydroxymethyl acrylamide can improve the optical quality of the film. With the increase of the concentration of N-hydroxymethyl acrylamide, the flatness of the film increases, scattering reduces and the straight image is clearer with a small distortion. The postexposure effect on the grating is also studied. The diffraction efficiency of grating increases further during postexposure, gradient of monomer exists after exposure.

Keywords: photopolymer, holographic storage, sensitivity, diffraction efficiency
PACC: 4240E

1. Introduction

Holographic data storage is a three-dimensional data storage technology that processes high storage density and fast readout rate. In addition, unlike conventional technologies which record data bit by bit, an entire page of information is stored and read out at once in holographic storage, enabling data transfer rates as high as a billion bits per second (fast enough to transfer a DVD movie in about 30 seconds), and storage densities as high as 100Gbit/in^2.[1]

The primary components of such a system consist of a spatial-light modulator (SLM), which formats the data to be stored into a "page" of pixels, an array of charge-coupled devices (CCD), which "read" the data stored in the hologram, and the recording medium itself. The recording medium itself is part of the imaging system and must exhibit the high degree of optical quality. Very high standards of optical homogeneity and fabrication must be maintained over the full area of the storage medium. For this reason the development of new photopolymerizable materials has focused on improving the optical quality of photopolymer films.

One of the best and most widely used holographic recording photopolymers currently available are the acrylamide-photopolymers.[2,3] They exhibit high dynamic range and photosensitivity, real-time image development, good optical properties, format flexibility, and can be easily processed. In this paper we present a new composition based on polyvinyalcohol and acrylamide where N-hydroxymethyl acrylamide has been added to improve the properties of the initial material. N-hydroxymethyl acrylamide is a highly soluble monomer. By adding N-hydroxymethyl acrylamide in the materials, the necessary optical quality of materials has been achieved. The postexposure effect on the grating is also studied. This is useful for optimizing the recording schedule in holographic data storage applications.

2. Experiment

The photopolymer is composed of erythrosin B (ErB) as a dye, triethanolamine(TEA) as an electron donor, acrylamide (AA), and N-hydroxymethyl acrylamide (HMA) as monomers, and a polymeric binder

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(7%w.v. polyvinyalcohol PVA) is used for this study. Erythrosin B is ideally suited for holographic recording with an Ar^+ laser as it displays a broad absorption spectrum at about 528nm. This mixture was homogenized to a viscous solution by a magnetic stirring device. Photopolymeric film was prepared by depositing the solution on a clean glass substrate, then it was dried under normal laboratory conditions(22°C and relative humidity 60%) for 24–36h. Finally, we obtain the dry photopolymer film that would be used in the following experiment. Preparation, mixing, and transfer of the photopolymeric solution onto the glass slides were done in the dark as the material is sensitive to light.

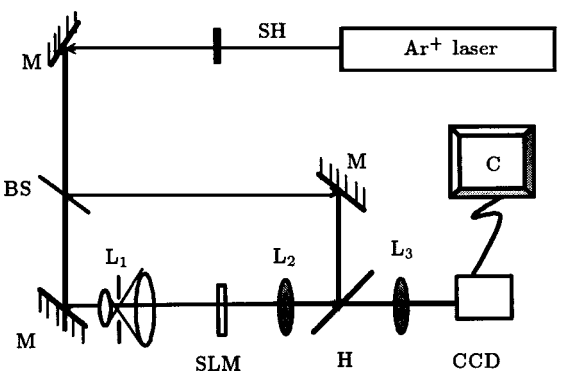


Fig.1. Schematic of a holographic storage system. SH: electronic shutters; M: mirror; BS: beam splitter; H: holographic recording material; L_1: beam expander system; L_2, L_3: Fourier Lens; SLM: spatial light modulator; CCD: charge-coupled device; C: computer.

The experimental setup of holographic grating forming has been described previously.[4] Diffraction gratings were obtained by means of Ar^+ laser of 514nm wavelength with a spatial frequency of 2275lines/mm. The recording beams were symmetrically interfering with and at an angle to the holographic material normal of 45° in air and the beam ratio was 1/1. The diffracted intensity was monitored with a He-Ne laser positioned at the Bragg's angle for avoiding the absorption of the material. Figure 1 is the experimental setup of holographic storage. It is 4f system. Data are imprinted onto the object beam through spatial light modulator(SLM). A pair of Fourier lenses images the data though the storage material onto a charge-coupled device(CCD) and a computer is used to capture the images. A reference beam intersects the object beam in the storage material, allowing the holograms to be stored and retrieved later.

3. Results and discussion

Hologram formation in the photopolymer has been discussed previously by several researchers.[4,5] The material consists of a photopolymerizable monomer, an initiator and a binder to secure the monomer. Neill *et al*[6] have studied the mechanism of hologram formation in acrylamide-photopolymer. When exposed to an interference pattern, in the bright fringes, ErB absorption results in an excited singlet state followed by intersystem crossing to the triplet state. The ErB triplet undergoes an electron-transfer reaction in which TEA functions as an electron donor, producing a TEA radical. Free radical polymerization is then initiated by the TEA radical. The monomer polymerization occurs in the bright fringes area. Then a gradient of monomer concentration produces between the bright regions and the dark regions. So monomer molecules diffuse from dark fringes to lighted ones. As a result the exposed and the bright regions contain high levels of polymerized monomer, whereas the dark regions have high binder content. The index difference between these two regions results in a phase grating. In this case the most possible termination process in the polymerization reaction is a unimolecular termination. Because we are working with a dry film which has a high viscosity, the bimolecular termination is more difficult due to the dependence of this constant on diffusion.[7]

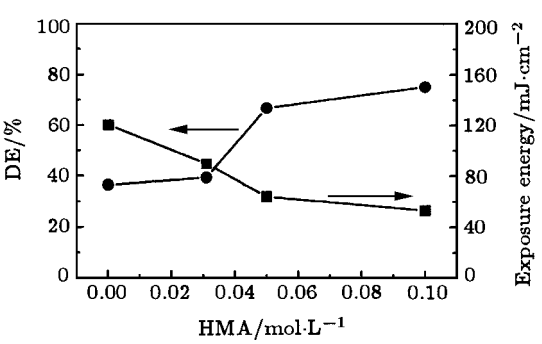


Fig.2. Effect of the concentration of HMA on the holographic parameters. The basic composition is: AA: 0.33 mol·L^{-1}; TEA: 0.3 mol·L^{-1}; ErB: 2.0×10^{-4} mol·L^{-1}; PVA: 7%. The power density was 28 mW/cm^2. DE: diffraction efficiency.

To improve the quality of the material, we add N-hydroxymethyl acrylamide to the photopolymer. N-hydroxymethyl acrylamide is a monofunctional monomer and its reactivity is quite different from the multifunctional acrylamide derivatives. N-hydroxymethyl acrylamide has a hydroxyl groups that favour the solubility in polar and protic solvents such as water and of course polyvinylalcohol of aqueous

solutions.[3] In Figure 2 the variation of the diffraction efficiency is shown in materials with different concentrations of HMA. With the increase of HMA, the diffraction efficiency reduces and exposure energy increases. Especially, for high concentration of HMA($0.10\,\mathrm{mol\cdot L^{-1}}$), diffraction efficiency reduces to 25%, and the exposure energy increases dramatically. However, the diffraction efficiency does not reduce very much when a few HMA is added into the photopolymer.

When the exposure of grating is stopped after the maximum diffraction efficiency is reached, the grating is illuminated with one of the writing beams. The photopolymers doped with different concentrations of HMA are expressed with a group of curves of diffraction efficiency, produced by measuring the diffraction intensities with different illumination times (Fig.3). There is a significant increase in diffraction efficiency. In ten minutes, the diffraction efficiency varies from 20% to 50%.

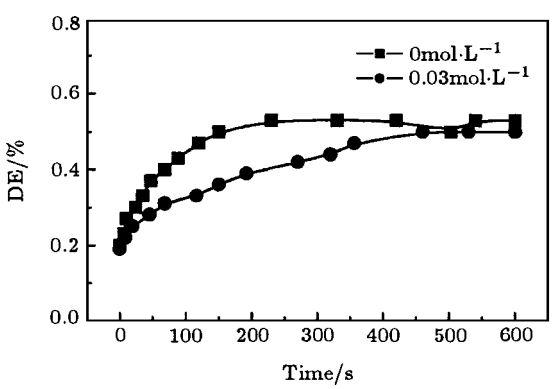


Fig.3. Diffraction efficiency versus read time after hologram recording. The basic composition is: AA: $0.33\,\mathrm{mol\cdot L^{-1}}$; TEA: $0.3\,\mathrm{mol\cdot L^{-1}}$; ErB: $2.0\times10^{-4}\,\mathrm{mol\cdot L^{-1}}$; PVA: 7%.

The same phenomena can be observed in DuPont's photopolymer in which the dye is sensitive to UV light.[8] After hologram recording, the photopolymer is exposed to UV light, thus the residual free monomers are polymerized and the diffraction efficiency can increase. In our study, after recording, exposure to recording beam may bleach the residual dye and complete the photopolymerization of the residual free monomers. In other words, this indicates that the photopolymerization process proceeds faster than the diffusion process, since a concentration gradient between polymer-rich and monomer-rich regions remain after the exposing beam is shut off. From Fig.4, the increasing rate of diffraction efficiency in the photopolymer with AA as monomer is faster than in the photopolymer with AA and HMA as monomer. The rate of polymerization of AA is faster than that of HMA, and the concentration gradient is bigger in photopolymer with AA as monomer. It may be that the diffusion rate of acrylamide is greater than that of N-hydroxymethylacrylamide, because the acrylamide molecule is smaller so that it is easier to diffuse.

To complete the characterization of the material, the effects of this component on transmittance curves measured with one He-Ne laser beam in normal incidence have also been studied. For this purpose, temporal variations of the transmittance $T(t)$ have been fitted with a photobleaching model:[9]

$$T(t) = \frac{T_{\mathrm{sf}}}{1 + (\mathrm{e}^{\varepsilon d[D]_0} - 1)\mathrm{e}^{-\varepsilon\phi I_0 t}}, \qquad (1)$$

where T_{sf} is a parameter related to scattering losses, d the thickness of the film, $[D]_0$ the initial concentration of the dye, ε the natural molar absorption coefficient, ϕ the quantum yield of generation of radicals, and I_0 the exposure intensity. By applying a nonlinear procedure based on Levenberg–Marquardt's algorithms, the values of the quantum yield, the molar absorption and T_{sf} is obtained.

Figure 4 shows a good correspondence between the experimental data and the model with a regression coefficient of 0.99. The effect of N-hydroxymethylacrylamide on these parameters is shown in Table 1. As the concentration of HMA is raised, it is observed that the molar coefficient decreases. High values of the quantum yield of generation of radicals are observed at concentrations lower than $0.065\,\mathrm{mol\cdot L^{-1}}$ of HMA, which are greater than the quantum yield obtained in the absence of this compound. The scattering factor reduces with the increase of concentration of HMA. It proves that HMA improves the optical quality of materials.

Table 1. Values of the parameters obtained from the nonlinear fit of the transmittance curves shown in Fig.4 in materials with different concentrations of HMA according to Eq.(1).

Conc./$\mathrm{mol\cdot L^{-1}}$	$\varepsilon/(10^8\mathrm{cm^2/mol})$	$\Phi/(10^{-9}\mathrm{mol/J})$	T_{sf}
0	7.91	5.39	0.483
0.031	6.76	6.16	0.492
0.065	5.42	6.12	0.524
0.10	5.25	5.86	0.528

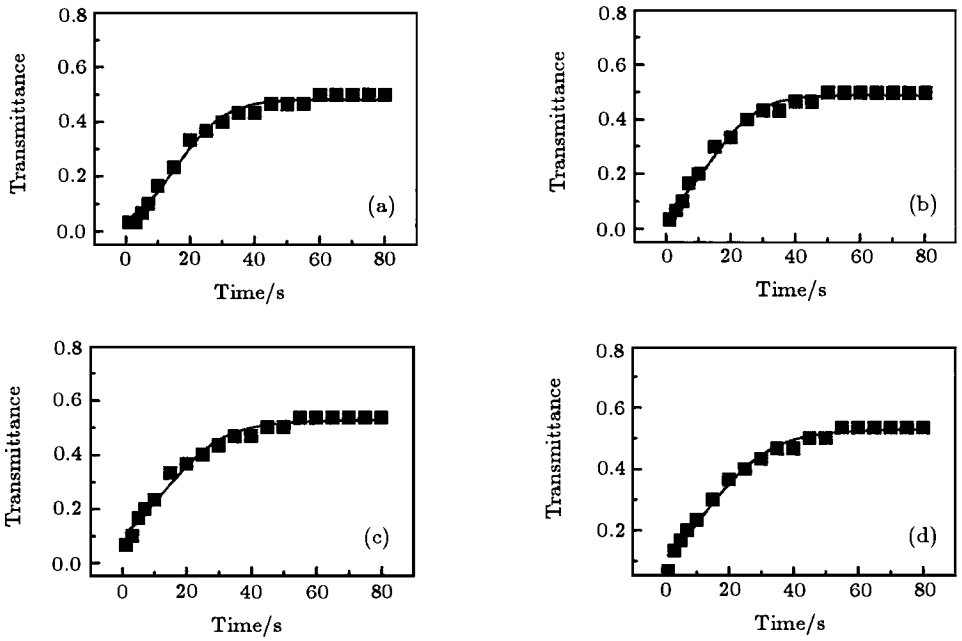


Fig.4. Experimental and fitted transmittance curves for the materials with composition: AA: 0.33 mol·L^{-1}, TEA: 0.3 mol·L^{-1}, ErB: 2.0×10^{-4} mol·L^{-1}, and concentration of HMA: (a) =0 mol·L^{-1}, (b) =0.031 mol·L^{-1}, (c) = 0.065 mol·L^{-1}, (d) =0.10 mol·L^{-1}.

On the other hand, the baseline performance of an optical system is measured by the straight-through image and data page imaged through the storage medium and the optics of the object arm. Figure 5 is the straight-through image obtained utilizing a 150μm thick photopolymer sample. Figure 5(a) shows the direct image of the mask from the object beam with no sample placed in the beam path. Figures 5(b)–(e) are the straight -through mask images with the sample film in the object beam path. By comparing the qualities of straight-through mask images with different HMA concentration films, it can be seen that with the increase of HMA concentration, the quality of straight-through mask image becomes better, the fidelity of image is higher. As shown in Fig.5, with the increase of concentration of N-hydroxymethylacrylamide, the optical quality of film increases. The image storage in the film becomes clearer and clearer. When the concentration of HMA is 0.065 mol·L^{-1}, the image has a clear fidelity similar to the direct data mask image, indicating negligible light scattering in the film. The ability to obtain high-fidelity straight-through images reflects the high optical quality and low level of scattering in our material.

In addition, using the photopolymers prepared,

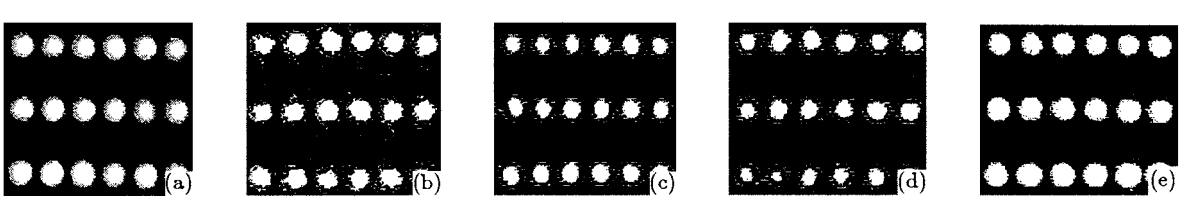


Fig.5. (a) Original mask image; (b)–(e) straight -through mask image. The basic chemical composition: AA: 0.33 mol·L^{-1}, TEA: 0.3 mol·L^{-1}, ErB: 2.0×10^{-4} mol·L^{-1}, and concentration of HMA: (b) =0 mol·L^{-1}, (c) =0.031 mol·L^{-1}, (d) =0.065 mol·L^{-1}, (e) =0.10 mol·L^{-1}.

we successfully stored some holograms. The reconstructed and the original images are shown in Fig.6. We can see that the signal/noise ratio (SNR) of the images is good and the distortion is small. This demonstrates that our current material preparation and film formation procedures can produce homogeneous and uniform photopolymer films for high-density holographic data storage.

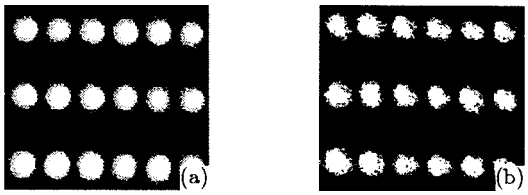


Fig.6. (a) Original mask image; (b) reconstructed mask image.

4. Conclusion

From all these results it can be concluded that the new photopolymer described here presents interesting properties for use as holographic recording materials. At HMA concentrations higher than 0.065 mol·L^{-1} the values of diffraction efficiency and sensitivity are too low; however, the optical quality of straight through image improve with the increase of HMA. In addition, we successfully realize holographic recording in our photopolymer material. The postexposure effect on the grating is studied too. The diffraction efficiency of grating increase furthermore during postexposure, gradient of monomer exist after exposure. Improved modelling of these effects will be required for fully optimizing recording scheduling for holographic data storage applications.

Ongoing work is focused on the long-term archival life of stored data and on the effects of changes in temperature of the polymer media on the fidelity of data readout. With these considerations, we believe the results described here greatly enhance the promise of photopolymer materials for holographic data storage.

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