Preparation and Holographic Recording of Diarylethene-Doped Photochromic Films

Eunkyoung Kim, Jiyoung Park, Song Yun Cho, Nam Kim, and Jung Hoi Kim

This study investigated the photochromic properties and characterization of acetyl-substituted diarylethene (DAMBTF6)-doped fluoroacrylates media for holographic storage. For the rewritable holographic recording media, we prepared photochromic polymer films using an acrylate matrix by simple photocuring methods. Switching light sources from a visible (532 nm) to an ultraviolet (365 nm) produced transparent films that changed from pale yellow to red. Holographic recording was performed on the photochromic films by two interfering collimated plane wave beams. Excitation with a visible or ultraviolet light completely erased the records, and the film was rewritable either by 532 nm laser or by 325 nm laser within 2 seconds. Images were recorded onto a pixelated spatial light modulator with rectangular pixel apertures and reconstructed on the photochromic films to show recovery of the original images with high resolution.

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Eunkyoung Kim (phone: +82 42 860 7200, email: ekkim@krict.re.kr), Jiyoung Park (email: jypark@krict.re.kr) and Song Yun Cho (email: scho@krict.re.kr) are with Advanced Materials Division, Korea Research Institute of Chemical Technology, Daejeon, Korea.

Nam Kim (email: namkim@cbucc.chungbuk.ac.kr) and Jung Hoi Kim (email: jhkim@osp.chungbuk.ac.kr) are with the Department of Computer & Communication Engineering, Chungbuk National University, Chungbuk, Korea.

I. Introduction

Polymeric materials are becoming more important for application in information processing [1], [2], and one of the most challenging areas for the polymeric materials is holographic recording. Holographic optical storage is a unique method for achieving high-density data storage in three dimensions. Several organic and inorganic materials for holographic storage have been widely explored in the last few years. Among the proposed holographic materials, photorefractive [3], [4] and photopolymer [5], [6] materials have been considered for their good holographic properties. Photorefractive materials show diffraction efficiency of 100% and a refractive index change (Δn) as high as 7×10^{-3}. However, these materials require poling under a high external electric field to align the chromophores within the film. Photopolymer systems are quite attractive because of their high sensitivity, ease of preparation, and self-development capability. However, their application to data storage is severely restricted by their limited thickness, high shrinkage during holographic exposure, and need for solvent processing. Furthermore, it is difficult to use photopolymer systems in various types of holographic recording other than "write once read many" because of the irreversibility of the photoreaction in photopolymers.

Because of the limitations of photorefractive and photopolymer materials, rewritable holographic recording materials based on photochromic conversion have attracted strong interest for three-dimensional optical recording [7]. Although the ideal materials seem to be lacking, photochromic materials are promising candidates because no electric field is required to write or read the information. Moreover, the recorded information can be either permanently stored or erased for repeated recordings. For example, due to their

photochromic nature, the recording layers may first be recorded by coloration with UV irradiation and then erased with visible light or heat, or vice versa.

The following properties are required of photochromic materials that are to be employed as optical memory media: i) thermal stability of both isomers, ii) resistance to fatigue during cyclic write and erase processes, iii) fast response, iv) high sensitivity, and v) nondestructive readout capability [8]-[10]. For those requirements, diarylethene derivatives are exceptionally promising photochromic compounds because of their high thermal stability and photochromic conversion efficiency. Here we report on our investigation of the photochromic properties and characterization of acetyl-substituted diarylethene (DAMBTF6)-doped fluoroacrylates media for holographic storage.

II. Experimentals

1. Materials

We synthesized BTF6 from benzothiophene in three steps [8], [11]; 1,2-Bis(6',6''-(acetyl)-2'-methylbenzo[b]thiophene-3'-yl)hexafluorocyclopentene (DAMBTF6) from BTF6 in one step [12]; and fluorinated acrylates from corresponding alcohols or isocyanates in the presence of catalysts [13]. Other chemicals and solvents were purchased from either Aldrich or Tokyo Kasei and purified according to the literature [14].

2. Preparation of Photochromic Polymer Films

We added DAMBTF6 (10 wt%) to a mixture containing fluorinated acrylate monomers (85 wt%) and photoinitiator (Darocur 1173, 5 wt%) and stirred it well to obtain a transparent and homogeneous solution. The solution was filtered using membranes of 0.45 μm pore size attached to a Teflon syringe and casted on a substrate (silicon wafer, fused silica, or slide glass) with a 200 μm spacer. After covering the substrate with glass and photopolymerizing it with a UV light (365 nm) for 10 min, we obtained either coated film or free standing film with a thickness of 200 μm by removing the cover glass. We used the film obtained from this process for holographic recording. For UV spectral change measurements, a photochromic film with a thickness of 3.6 μm was prepared by spin coating the above mixture and then exposing the film to a UV source.

3. Instruments

UV absorption spectra were obtained on a SCINCO model S-2100 (SCINCO, Inc., Korea). The light sources for the UV spectral change and data erasure were a He-Cd laser (325 nm, 10 mW) and a UV lamp (365 nm, Spectronics Corp.). Thickness measurements were performed on an alpha-step (Tencor instruments, 500 surface profiler).

4. Holographic Set-up

Figure 1 shows the schematic diagram of the experimental setup. We used two-wave-mixing techniques to obtain optical absorption grating in thick films and a diode laser at 532 nm for the laser writing. The light beam was then split between two beams, which were spatially overlapped at the recording medium. The power of the light in each beam after splitting was 20 mW. The beam diameters were 1 cm, and the two beams intersected at an angle of 20°. We studied the grating growth during and after the holographic exposure by diffraction of the readout beam. A Bragg-matched 633 nm probe beam was used to read out the holograms and the diffraction beam was collected on the detector.

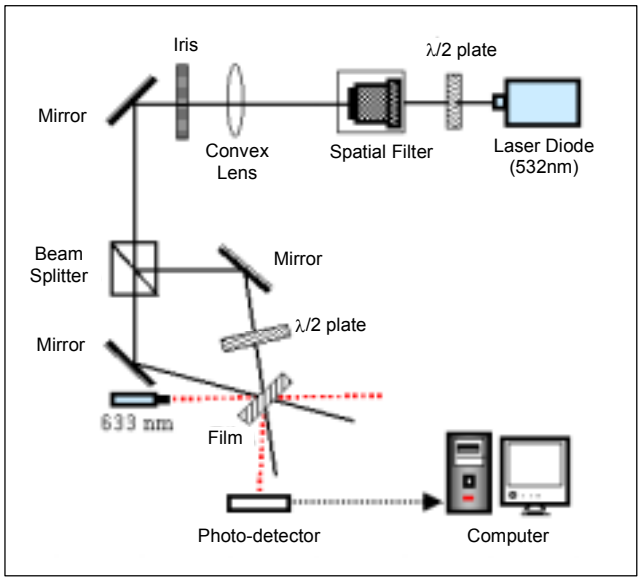


Fig. 1. Experimental setup for holographic recording.

Another experimental setup was used to monitor the image of the holographic data storage (Fig. 2). The laser source for these experiments was coherent frequency-doubled Nd:YAG at 532 nm. The reference beam and signal beams were incident at ±30° with respect to the recording materials surface normal and the optical powers of the signal and the reference beams were 0.66 mW/cm^2 and 2.1 mW/cm^2, respectively. In this holographic data storage set up, a spatial light modulator (SLM) converted data to an optical signal. Readout of the stored data page involved illuminating the films and the reference beam and imaging the diffracted optical signal onto a

charged coupled device (CCD) array, an MVOS CMOS camera, which converts the optical signal back into an electronic signal. For this purpose, we used a motorized and computer-controlled linear stage for spatial multiplexing and electronic-shutter. The SLM was based on 640 × 480 pixel liquid crystal (EPSON VGA LCTV), and pixel matching of SLM-CCD was 1:3 over sampling.

For all these experiments, we determined the power of the writing beam with a power meter and kept the thickness of the films for holographic recording constant at 200 μm.

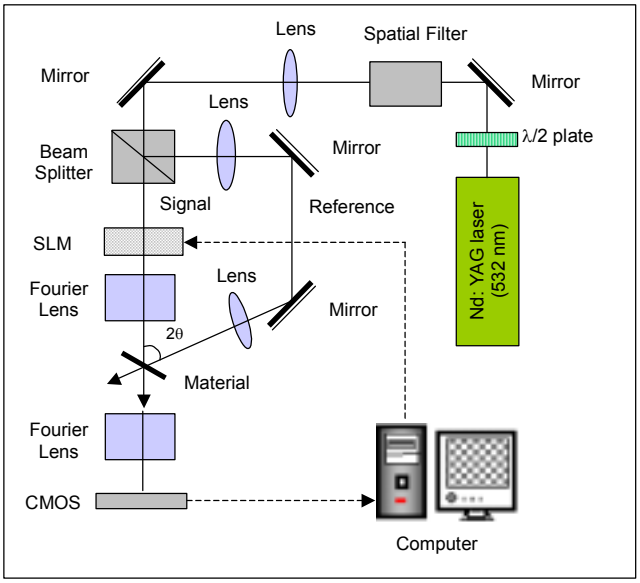
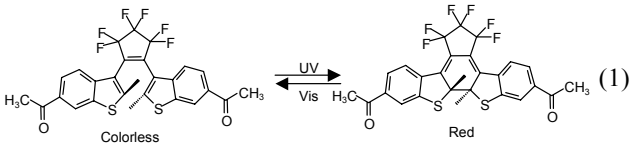


Fig. 2. Experimental setup for holographic data storage with a spatial light modulator.

III. Results and Discussion

Fluoroacrylates media containing DAMBTF6 was prepared by a photocuring method using a mixture of fluoroacrylate monomers and DAMBTF6 in the presence of a photoinitiator. The photocuring reaction was efficient and the conversion of liquid phase monomers to a solid phase polymer film was over 60%, as determined by a differential scanning calorimetry. Transparent red colored films were obtained upon exposure to a UV light but bleached to a colorless film when the film was under room light or exposed to a visible light. Such a color change could be attributed to the photochromic conversion of the DAMBTF6 during the photocuring of the fluoroacrylates under UV irradiation. This photochromic property of DAMBTF6 is based on the reversible ring cyclization by UV and a ring opening by visible light, as summarized in (1) [15].

Figure 3 shows the spectral change of DAMBTF6-doped fluoroacrylates film upon UV exposure. Before irradiation with



(1)

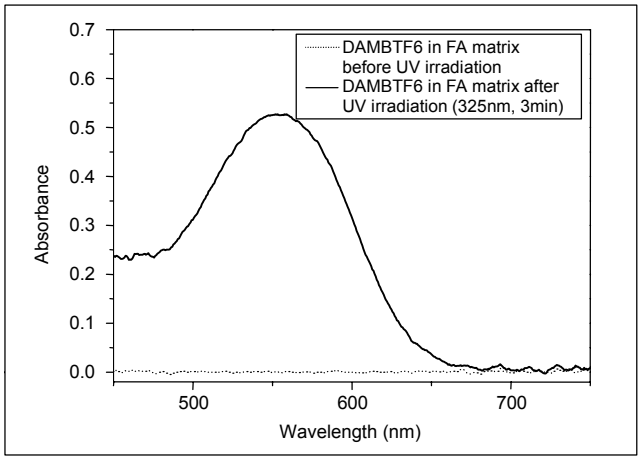


Fig. 3. UV spectral change of diarylethene polymer films by a light 325 nm.

UV light, the absorbance of the film corresponded to the absorption by the ring open isomer and the maximum absorption of the open isomer was below 320 nm. Thus, in the visible region of the spectrum, there was no absorption band corresponding to the open isomer. Upon excitation with UV light, the open isomer changed to a closed isomer and the absorption peak at λ_{max} (554 nm) was composed of the absorption for closed isomers. This spectral change was accompanied by a color change in the photochromic film. Thus, a pale yellow film changed into a red colored film by irradiation with 325 or 365 nm light. The color was completely bleached to the original color upon excitation with a visible light (532 nm). Color intensity and optical intensity at the visible region of the diarylethene polymer film can be cycled using two light sources of UV (erasing) and visible light (writing). Figure 4 shows the cyclability of polymer films by 325 nm and 532 nm lasers, indicating that the cyclability is longer than 1000 cycles even in air. Typically, the ring closure/opening reaction cycle can be repeated more than 10^4 times without any significant loss of photochromic performance.

These reversible photochromic properties induced by DAMBTF6 can be applied to a rewritable holographic memory. The holographic recording was made using the diarylethene-doped photochromic films. Figure 1 schematically shows a typical optics setup for recording and readout in realtime holographic gratings.

To prepare for the writing with a 532 nm laser, we initially

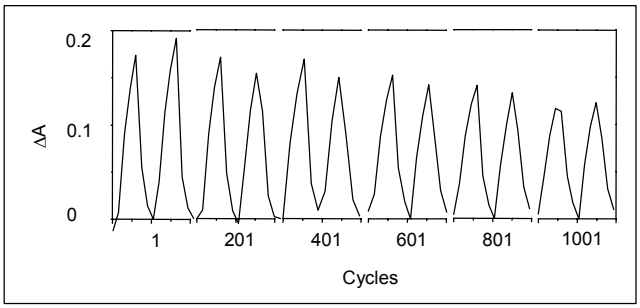


Fig. 4. Photochromic cyclability.

exposed the DAMBTF6-doped photochromic film to a homogeneous and incoherent excitation beam from a UV lamp at 365 nm until maximal coloring occurred. The holographic recording was performed with a 532 nm laser using the colored film. The two-wave mixing of 532 nm light formed a sinusoidal interference pattern on the photochromic film. In the bright region of the interference pattern, a ring opening reaction of DAMBTF6 occurred and a phase grating formed according to the difference of the refractive index. The angle between the two beams determined the grating period. This sample grating formed with two 532 nm laser beams had a fringe spacing of 0.99 microns. The interference pattern suggested that the photochromic conversion of DAMBTF6 in a fluoroacrylates matrix by the two-beam coupling method was effective.

This photochromic film did not exhibit any apparent fatigue or shrinkage, even after 1000 write/erase cycles. Such stability is attributed to the chemical inertness of the diarylethene molecules. Since the holographic recording was based on the photochromic conversion of DAMBTF6, the volume change was much less than in typical photopolymer media, in which cross-linking of photoactive monomers by the writing beam results in significant volume change [6].

Since the reverse ring opening reaction (toward a colorless state) can occur with 532 nm, the measurement for diffraction power and efficiency must be carried out under non-destructive conditions with a monitoring light having a longer wavelength (> 700 nm). We characterized the holographic recording property in a real time reading method by determining the light intensity of the diffracted light from the photopolymer film, using a low powered 633 nm laser (2 mW). The experimentally measured diffraction efficiency was 2%, leading to Δn between the colored and colorless state. The diffraction efficiency was determined by the ratio of the intensity of the diffraction beam to the intensity of the recording beam. Figure 5 shows the intensity of the diffracted light measured at every 1 ms for the photochromic films over 120 seconds. Within 2 seconds, the diffracted light was detected and the intensity of the diffracted light was maximized

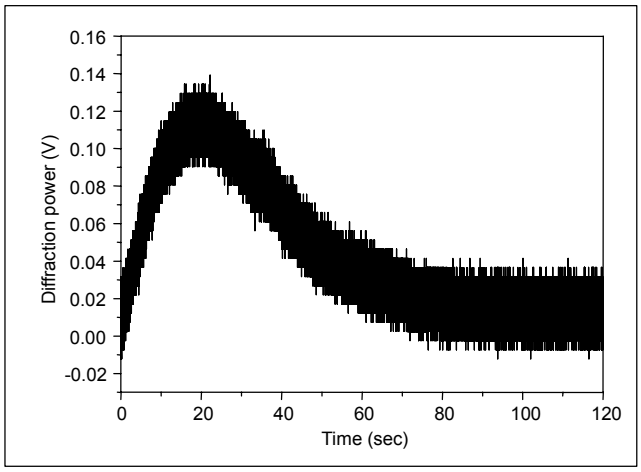


Fig. 5. Intensity change of diffraction light during the holographic recording.

after 20 seconds. After prolonged exposure, the diffracted light was reduced because the recorded image by two-beam coupling was erased by the monitoring light (633 nm). Similarly, the coupling efficiency increased and reached a maximum value at about 20 seconds; then it decreased to the initial zero point upon prolonged exposure.

Images were recorded onto a pixelated spatial light modulator with rectangular pixel apertures and reconstructed on the photochromic film. Figure 6 shows the reconstruction of an image (letter "KRICT/광변색 (광변색 means photochromic in Korean)") stored in the photochromic film. The original letter image with rectangular pixel apertures was completely reconstructed on the photochromic film with high resolution. We were able to completely erase the holographic images by illumination of a reference beam alone.

Fig. 6. Reconstruction of an image stored by spatial light modulator in the photochromic film.
(pixel size : 42 μm)

IV. Conclusion

Preparing photochromic films with a thickness of 200 μm using a mixture of DAMBTF6 and a fluorinated acrylate matrix for a rewritable holographic memory, we successfully achieved a rewritable holographic recording with UV and visible light sources. Future work based on these results is in progress and will explore a non-destructive method of reading and characterizations for diarylethene containing photochromic polymer films.

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Eunkyoung Kim received her BS degree in chemistry from Yonsei University in Seoul (Korea) in 1982, a master's degree in chemistry from Seoul National University in Seoul (Korea) in 1984, and PhD in chemistry from University of Houston in 1990. Since 1992 she has been working at the Korea Research Institute of Chemical Technology in Daejeon, Korea. Her work has primarily focused on the development of functional polymers, including photochromic polymers, photoconductive polymers, and charge transport issues.

Jiyoung Park received the BS degree in chemistry from Chungnam National University, Korea, in 2001. Since 2001 she has been working at the Korea Research Institute of Chemical Technology in Daejeon, Korea. She is working on the development of functional polymers based on photochromic materials and holographic recording material.

Song Yun Cho received his BS and MS degrees in polymer science and engineering from Inha University, Korea in 1996 and 1998, respectively. His research was on the design and synthesis of dendritic polymers. In 2000, he joined Korea Research Institute of Chemical Technology in Daejeon, Korea, where he is working on the development of functional polymers based on photochromic materials and polymeric photonics materials.

Nam Kim received the BS, MS, and PhD degrees in electronic engineering from Yonsei University, Korea, in 1981, 1983, and 1988, respectively. He was a Visiting Professor of the Dr. Goodman's group in Stanford University from 1992 to 1993 and of the Dr. Psaltis group in Caltech from 2000 to 2001. Since 1989, he has been a Professor in the Computer and Communication Department at Chungbuk National University, Korea. His research interests include holographic recording material, diffractive optical element, non-linear optics, holographic data storage, and optical information processing.

Jung Hoi Kim received the BS degree in electronics engineering from Sunchon National University, Korea, in 1997 and the MS degree in computer and communication engineering from Chungbuk National University, Korea, in 1999. Now, he is working on the PhD course at Chungbuk National University from 1999. His research interests are holographic material, digital holographic memory, optical security, and optical information processing.