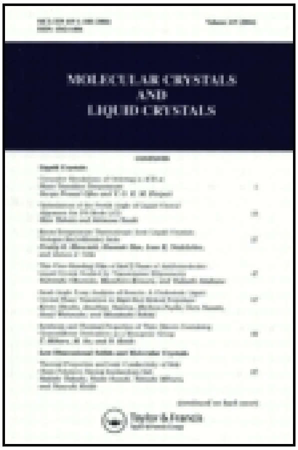

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HOLOGRAPHIC GRATINGS RECORDED ON A NEW PHOTOPOLYMER COMPOSED OF PHOTOSENSITIVE POLYMER BINDER

Dijon Feng [a] , Hanna Yoon [a] , Dong Hoon Choi [a] & Suk-Ho Choi [b]

[a] College of Environment & Applied Chemistry, Materials Research Center for Information for Display, Institute of Natural Science, Kyung Hee University, Yongin 449-701, Korea

[b] College of Electronics & Information, Materials Research Center for Information for Display, Institute of Natural Science, Kyung Hee University, Yongin 449-701, Korea

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HOLOGRAPHIC GRATINGS RECORDED ON A NEW PHOTOPOLYMER COMPOSED OF PHOTOSENSITIVE POLYMER BINDER

*Dijon Feng, Hanna Yoon and Dong Hoon Choi**
College of Environment & Applied Chemistry, Materials Research Center for Information for Display, Institute of Natural Science, Kyung Hee University, Yongin 449-701, Korea

Suk-Ho Choi
College of Electronics & Information, Materials Research Center for Information for Display, Institute of Natural Science, Kyung Hee University, Yongin 449-701, Korea

We suggested new photopolymer systems using polyacrylic acid (PAA), polyitaconic acid (PICA), and the photosensitive polymer (PP) as binders. The photochemical reaction of the photosensitive polymer binder and acrylamide monomers was studied by virtue of infrared spectroscopy. The holographic grating was elaborated by conventional optical interference method. The dynamic behaviors of the grating formation were studied with the change of exposure intensity. We observed the variation of the diffraction efficiency during post UV exposure. The surface topographical change of photopolymer layer was also observed by atomic force microscope (AFM).

Keywords: diffraction efficiency; holographic grating; photopolymer; temperature dependence

1. INTRODUCTION

Photopolymers have significant advantages making them suitable for application as holographic optical elements and data storage media. For example, self-development, high angular selectivity, and high resolution can be achieved in this photopolymer by holographic technique [1–5].

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*Corresponding author. E-mail: dhchoi@khu.ac.kr

Therefore, development of new photopolymers became quite an attractive research topic recently.

In general, the photopolymer typically consists of polymeric binders, vinyl or acrylic monomers, photo initiator, crosslinker, and sensitizing dyes [6,7]. The binders act as the support matrix containing the other additive components. The monomers serve as the Δn "carrier" induced by optical interference method. During holographic recording, the film sample is placed with an optical interference pattern formed by the intersection of two laser beams. The interference pattern consists of a sinusoidal variation of bright and dark fringes due to the constructive and destructive mode. In the bright fringes, the sensitizing dye absorbs light and interacts with the initiation system. Then the active intermediate initiates the monomer to induce sequential polymerization. As monomers are polymerized, concentration and density gradients occur, causing diffusion of monomer from the dark regions into the bright region. Index modulation arises from the density and compositional differences between the polymer binder region and polymer rich region. In most cases, UV exposure and heat treatment will be required to induce the polymerization of the unreacted residual monomer in overall regions.

In this paper, we present the diffraction properties of our photopolymer systems, which are investigated by real-time optical recording. The photopolymerization of acrylamide and photocrosslinking reaction in polymer binder were confirmed by infrared spectroscopy. The topographical change of the surface of photopolymer film with photosensitive polymer binder was also investigated by atomic force microscope.

2. EXPERIMENT

2.1. Sample Preparation

We selected polyacrylic acid (PAA, Mw = 2,100), polytechnic acid (PICA) and the photosensitive polymer (PP) as the binder for three kinds of photopolymer. Photosensitive polymer binder was synthesized to be the methacrylate homopolymer bearing a chalcone group in the side chain. All the other chemicals used for the preparation of the photopolymer film samples were acrylamide (AA), N,N′-methylenebisacrylamide (BAA), triethanolamine (TEA), and tetrabromofluorescein (TBF) derivative. The solvent was deionized water for PAA and PICA system, and tetrahydrofuran/cyclohexanone solvent for PP system. The composition of formula is as follows: Polymer binder: monomer: crosslinker: TEA: TBF = 1: 0.6: 0.04: 0.07: 0.0003. Photosensitive methacrylate polymer binder is composed of chalcone unit in the side chain. We used spin coating method to make the film samples on the leveled glass substrates. In our experiment, the thickness of the film sample was adjusted about 3.5 μm.

2.2. Optic Setup for Fabrication of Holographic Grating

The schematic diagram for recording the gratings and measuring the diffracted light intensity was illustrated in Figure 1(a). The Argon laser ($\lambda = 488\,\text{nm}$) was used in recording and the He-Ne laser ($\lambda = 632.8\,\text{nm}$) was used to probe the recorded grating. Two vertically plane polarized (s- & s-) light beams with equal intensity were obtained by adjusting the quarter wave plate and the polarizers appropriately, which was used for fabricating the holographic grating. The basic principle of recording gratings was based on optical interference. The intensity pattern consists of bright and dark planes throughout the region of the intersection. This leads a refractive index grating in the material. The refractive index grating can be shown as a periodic function, with the same period as the interference pattern see Figure 1(b). The angle between the interferential beams is approximately 14.6°, so we can calculate the grating period of 1.92 μm theoretically determined by the relationship of $\lambda = \lambda/2\sin\theta$.

The temporal variation of the first-order diffracted light intensity can be monitored in real-time with a probe light from a He-Ne laser (p-polarized). The grating diffracts the probe light with an efficiency η that is defined as the ratio of the 1st order diffracted light intensity to the incident light intensity.

3. RESULTS AND DISCUSSION

3.1. Diffraction Behavior of PAA Photopolymer

We prepared photopolymer containing PAA binder and the other low molecular additive components. All samples used in this study contain same concentration of the monomer, the crosslinker, the photoinitiator, and the photosensitizer. The photoinitiation could be performed from the mixture of TEA and eosin. TEA acts as a charge transporting molecules. The composition of the low molar mass compound was optimized preventing from phase separation and severe crystallization after drying the film samples.

We studied the diffraction properties of the PAA photopolymer under different exposure intensities to estimate the light sensitivity. Figure 2 shows the dynamic behavior of the diffraction efficiency under different exposure intensities. It is clear that the diffraction efficiency increases with the increase of the exposure intensity. However, the diffraction efficiency of this kind of grating mainly depends on several factors, such as the polarization states of the recording beams, the exposure intensities and the thickness of the film sample. Also, it is clear that increase of the diffraction

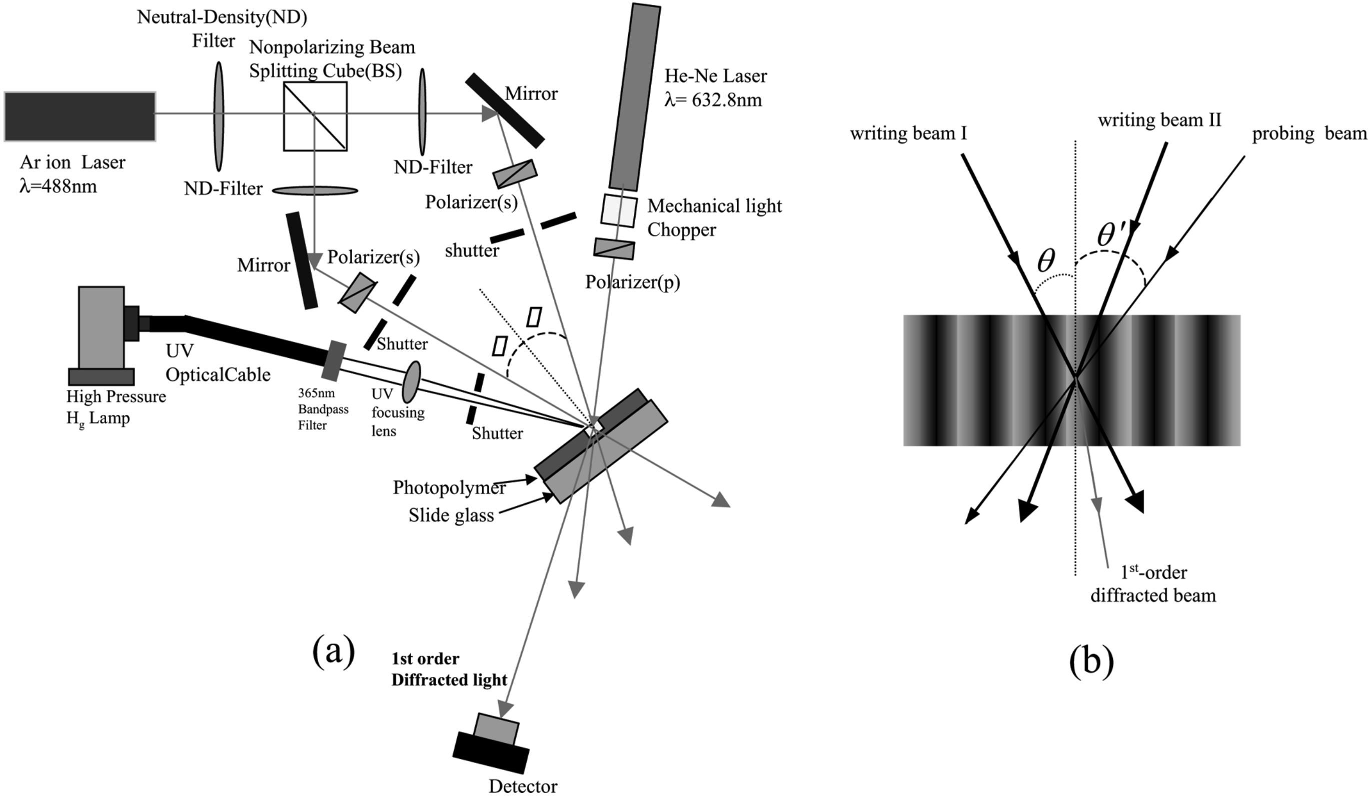

FIGURE 1 Optical setup for measuring the diffracted light intensity of the photopolymer (a) optical setup, (b) geometry of the pump beams and probe beam.

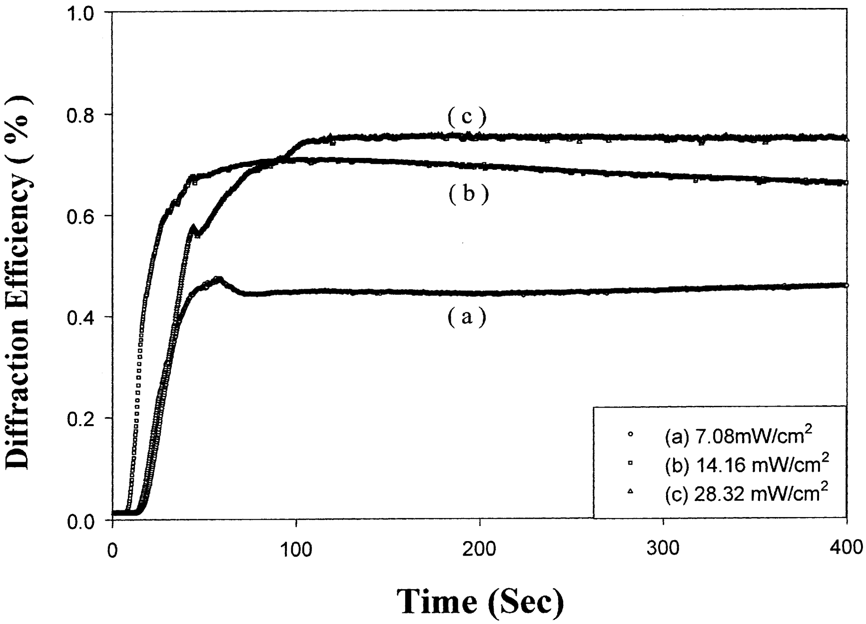

FIGURE 2 Variation of the diffraction efficiency with the change of the exposure intensity. *Sample: PAA photopolymer.

efficiency with respect to the pumping intensities is not uniform. It is believed that there should be optimum exposure intensity for the photopolymer, which will be reported elsewhere.

3.2. Diffraction Behavior of PICA Photopolymer

We prepared the photopolymer with PICA binder and the same additive components whose concentrations were identical as used before. The variation of diffraction efficiency under different exposure intensities was also studied to estimate the light sensitivity. Figure 3 shows the dynamic behavior of the diffraction efficiency under different excitation light intensities. It is clear that the diffraction efficiency increases with the increase of the exposure intensities in a certain range. At higher intensity (28.32 mW/cm^2), the diffraction efficiency showed lower value than that of 14.16 mW/cm^2, which is ascribed to the disruption of uniform gratings. The backward diffusion of the polymerized chain molecules may be owed to the Joule heat induced by the high intensity pumping beams. This experiment was performed under identical exposure dose used in the previous sample.

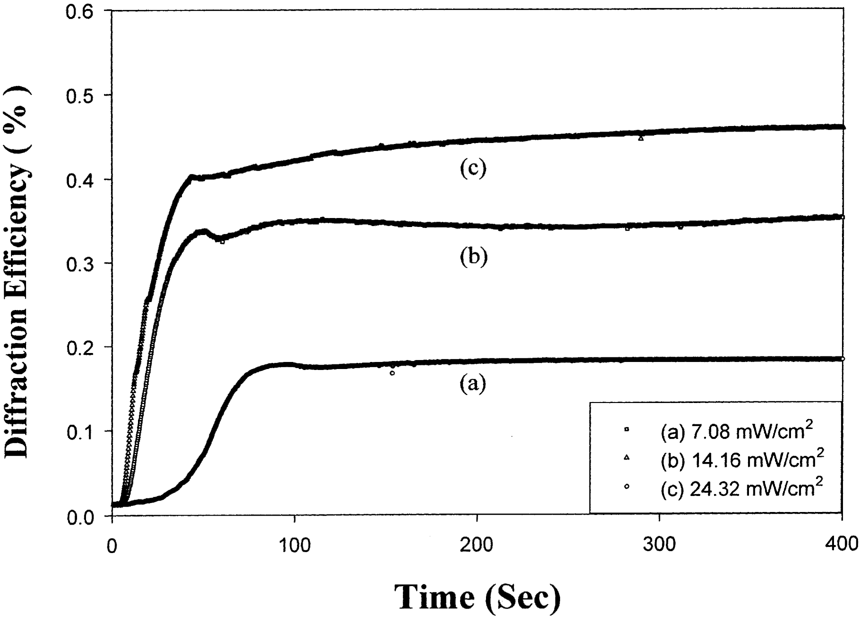

FIGURE 3 Variation of the diffraction efficiency with the change of the exposure intensity. *Sample: PICA photopolymer.

Compared to PAA binder system, this sample does not show that high diffraction efficiency. The reason is thought that self-association of acrylamide is dominant to retard the diffusion from dark to bright region. It also can be conjectured that the polymerized chains of acrylamide have some degree of freedom to be mobile inside the matrix since the glass transition of PICA polymer binder is inherently very low.

3.3. Diffraction Behavior of the Photopolymer with the Photosensitive Methacrylate Polymer Binder

We prepared another photopolymer along with the photosensitive polymer binder that is methacrylate homopolymer with chalcone group in the side chain. The distinct difference is that we selected organic solvent of tetrahydrofuran and cyclohexanone for fabricating this photopolymer film. First of all, we recorded the infrared spectra of the film sample before and after visible light irradiation ($\lambda = 488\,\text{nm}$) followed by UV light ($\lambda = 365\,\text{nm}$) irradiation in order to confirm the progress of radical polymerization of acrylamide and photo-cycloaddition of the chalcone groups, as shownin Figure 4.

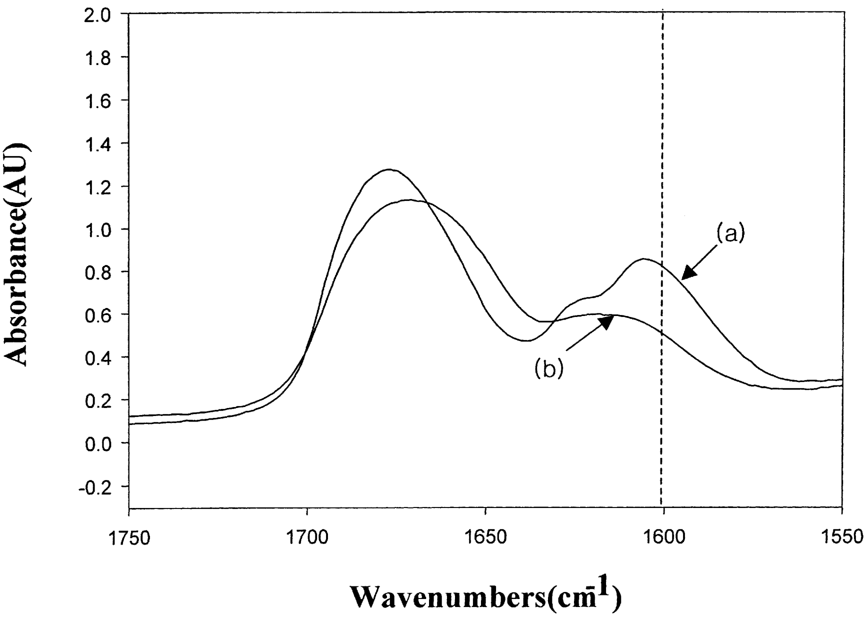

FIGURE 4 Infrared spectra of the photopolymer with the photosensitive methacrylate polymer binder before and after excitation light irradiation (1st exposure: $\lambda = 488\,\text{nm}$, 2nd exposure: $\lambda = 365\,\text{nm}$). (a) before irradiation, (b) after irradiation.

The double bond stretching band of acrylamide at 1605 cm^{-1} decreased significantly accompanying with the other combination bands. This indicates that acrylamide underwent the polymerization under irradiation of the visible light. At the same time we can expect that the double bond in chalcone group dispappeared due to cycloaddition reaction. This spectroscopic study helps quite effectively to optimize the irradiation time for saturating the diffraction efficiency, indicated by the stabilization of the absorbance at 1605 cm^{-1}.

We studied the response of the photopolymer under different exposure intensities to estimate the light sensitivity. Figure 5 shows the dynamic behavior of the diffraction efficiency under different exposure intensities. It is clear that the diffraction efficiency will increase with the increase of the exposure intensity.

The general process for producing holograms using the conventional photopolymer involves two steps: (1) holographic exposure, (2) UV irradiation. When the diffraction efficiency of the grating reaches its maximum value and becomes stable, we block the pump beams and start to irradiate the UV light source (High pressure H_g lamp with 365 nm filter) to induce

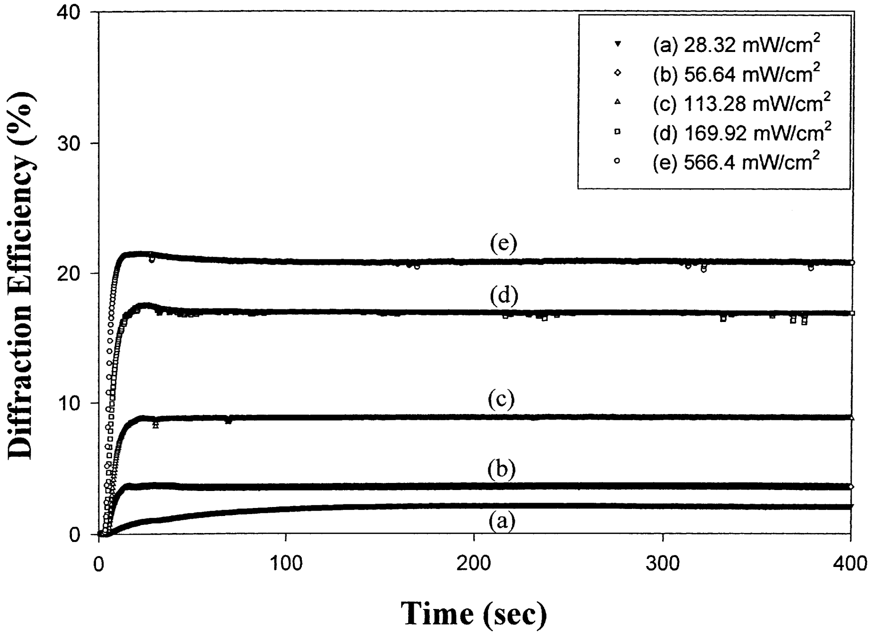

FIGURE 5 Variation of the diffraction efficiency with the change of the exposure intensity. *Sample: photopolymer with the photosensitive methacrylate polymer binder.

the polymerization of unreacted monomers for 25 minutes. UV irradiation is usually used to fix the grating and expose the recessed areas that are not exposed to laser light. In this case, when the concentration of the unreacted monomer is high, the index modulation decreases, resulting in decrease of the diffraction efficiency too. However, in Figure 6, we could not observe any decrement of the diffraction efficiency during UV irradiation. This indicates that the refractive index in the bright region also increased due to the molecular miscibility in an interpenetrating regime, accompanying with the increase of the refractive index in the dark region.

Figure 7 shows the surface topographic change of the grating area. The corresponding exposure intensity is 114 mW/cm^2. The depth of modulation is about 248 nm and the period of the grating is 2.12 μm. We compared the surface topography just after visible light irradiation (a) and visible /UV light irradiation sequentially (b). We could figure out that the grating resolution and the uniformity were greatly improved although there was a small degree of volume shrinkage. This mainly attributed that the matrix became rigid, resulting from polymerization of the residual monomers and photocrosslink of the chalcone group in the polymer binder.

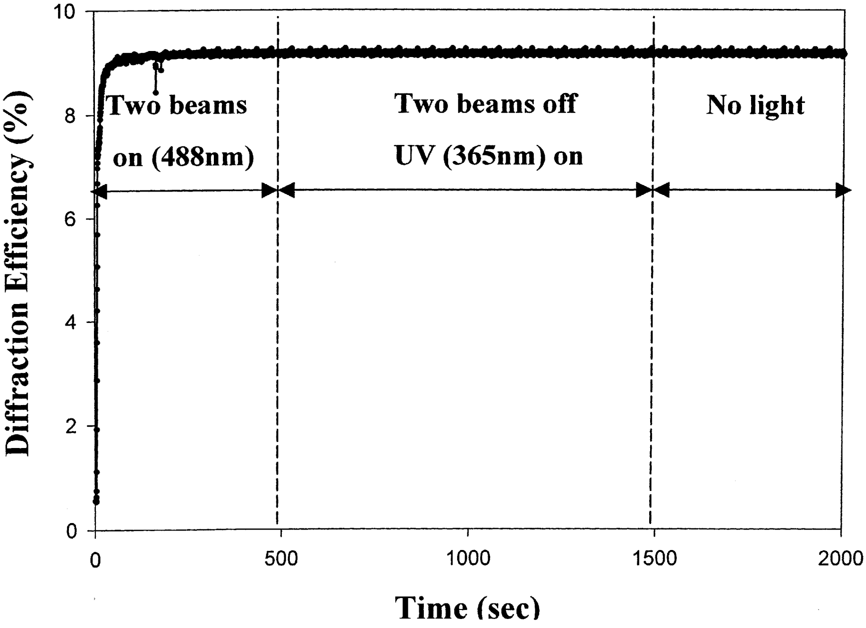

FIGURE 6 Variation of the diffraction efficiency during and after UV irradiation. *Sample: photopolymer with the photosensitive methacrylate polymer binder.

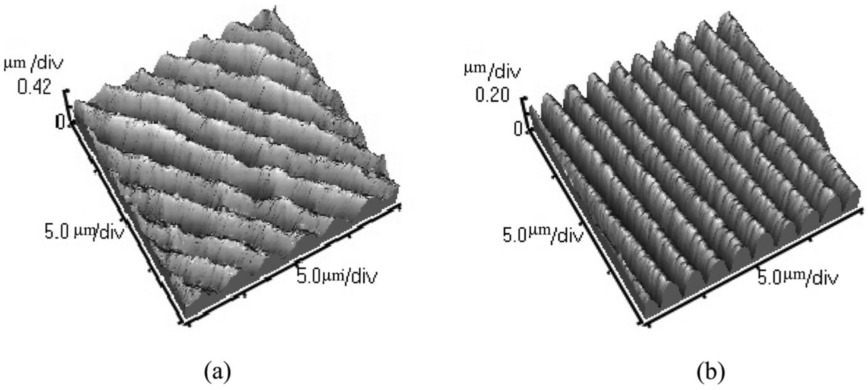

FIGURE 7 AFM images of the surface of the PP photopolymer. (a) after visible light irradiation ($\lambda = 488\,\text{nm}$), (b) after visible light irradiation ($\lambda = 488\,\text{nm}$) and UV light irradiation ($\lambda = 365\,\text{nm}$).

4. CONCLUSION

The dynamic holographic recording characteristics of the three photopolymers have been studied by optical interference method successfully. With the change of the exposure intensity in a certain range, the diffraction efficiency will change accordingly except the case of the very low T_g photopolymer. The photochemical reactions of the photosensitive binder and monomer were studied by IR spectra. Photopolymerization of the monomer and photocrosslink in polymer binder could be induced in the PP photopolymer. UV post-irradiation improves the grating resolution and the uniformity, confirmed by the surface topographical change.

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