Photopolymer Materials for Holography

Zhang Cunlin, *Zhao Jia, He Jingsuo

Department of Physics, Capital Normal University, Beijing 100037, P.R. China

Li Lidong, Yang Yongyuan

Inst. of Photogra. Chem., the Chinese Academy of Sciences, Beijing 100101, P.R. China

The photopolymer holographic recording material is composed of a monomer, a binder, a photoinitiator system that contains a sensitizer, an initiator and a hydrogen donor. The photopolymer materials is sensitive to red light (633nm), the effective exposure sensitivity of the photopolymer plate can be increased by adding the third beam to expose the photopolymer plate simultaneously during the initial holographic exposure. Mechanisms of photoinitiating polymerization and hologram formation are discussed. More than 80% of reflection grating diffraction efficiency can be obtained. The holographic gratings have a good physical and chemical stability under ambient conditions.

Keywords: photopolymer, recording materials, holographic grating

1. Introduction

Progress in the field of holography to its fullest potential is largely dependent on the development of new recording materials with the required characteristics, namely (1) high energy and wavelength sensitivity, (2) high spatial resolution, (3) a simple processing method, (4) high diffraction efficiency, (5) erasability, and (6) physical and chemical stability under ambient conditions. Photopolymer systems have shown promise with regard to their capabilities as holographic recording media.^[1,2,3] One of the most important techniques is how to make the system sensitive to long-wavelength light and high energy sensitivity. Several visible light photoinitiating systems have been reported.^[4,5,6] In this paper, we further our study of photopolymer materials and provide a method to increase the effective energy sensitivity.

2. Experiment

2.1. Materials

The sensitizer, 2,4-bis[(1-methyl-3,3-dimethyl-2-indolinyliene)methyl]-cyclobutadienyl-1,3-diolate (Dye1) was synthesized after a revised procedure published by H. Schmidt^[7,8,9]. The initiator, 2-chlorohexaarylbiimidazole (o-cl-HABI) was prepared according to a known Procedure^[10]. The structure was confirmed by mass spectrometry (MS), nuclear magnetic resonance (NMR), infrared spectrometry (IR) and elementary analysis. The hydrogen-donor, 3-mercapto-4-methyl-4h-1,2,4-tiazole (MTA) was a product of Fluca, Swaziland. The binder, polyvinyl acetate was obtained from Beijing Organic Chemical Factory. The ethylenically unsaturated solid monomer, N-vinyl carbazole was obtained from Shanxi University. The ethylenically unsaturated liquid monomers were obtained from Beijing Chemical Store.

2.2. Sample preparation

The holographic photopolymer recording material is composed of a monomer, a binder, a photoinitiator system that contains a sensitizer, an initiator and a hydrogen donor. The coating solutions had the following composition: 0.1~0.2% sensitizer Dye1; 1~3% initiator o-cl-HABI; 2~3% hydrogen donor MTA; 28~46% monomers; 45~65% binder. The coating solutions were coated onto a glass plate and dried under the room temperature. After drying the photopolymer plates can be used in recording holographic diffraction gratings and determining their efficiency.

3. Results and discussion

3.1. Absorption Spectra

The absorption spectrum of Dye1 in trichloromethane displays a strong broad band in the visible region: $\lambda_{\max}=633\text{nm}$ and $\epsilon_{\max}=3.0 \times 10^4 \text{mol}^{-1} \cdot \text{L} \cdot \text{cm}^{-1}$, as shown in Fig. 1(a). O-cl-HABI has a very weak absorption in the visible region but absorbs strongly in the UV region: $\lambda_{\max}=265\text{nm}$ and $\epsilon_{\max}=2.82 \times 10^4 \text{mol}^{-1} \cdot \text{L} \cdot \text{cm}^{-1}$, as shown in Fig. 1(b). The bond energy of C-N in o-cl-HABI is very low which leads to the easy homolysis of HABI when exposed in UV light or heated^[3].

(a)Dye1, (b) o-cl-HABI

Fig.1 Absorption spectrum of Dye1 and o-cl-HABI in CHCl_3

3.2 Photosensitive initiating system

The photosensitive initiating system is composed of Dye1, o-cl-HABI and MTA, which act as sensitizer, initiator and hydrogen donor respectively.

Photopolymerization study with methyl methacrylate (MMA) was carried out in dilatometer ($\Phi=10\text{mm}$) at 30°C . The sample

tubes were rotated around the light source. A xenon lamp (400w) was used and its short wavelength light ($<300\text{nm}$) was removed by two Pyrex glass filters. The solution were deaerated by bubbling highly pure nitrogen for 30 minutes.

The solution of o-cl-HABI and MMA (monomer) in trichloromethane were exposed in the visible light ($\lambda > 510\text{nm}$). No polymerization occurred. The reason is that the absorption of o-cl-HABI is nearly all in the UV region, thus no free radicals can be produced with the visible light. When Dye1, the sensitizer, was added the photopolymerization occurred efficiently.

From Fig.1, we found that the maximum absorption band of o-cl-HABI and Dye1 (265nm and 633nm respectively) are too far away to have any overlay. It is difficult for energy transfer in this way. Therefore, we consider that the photopolymerization mechanism in this system was electron transfer: Dye1 was excited by visible light and then transferred an electron to o-cl-HABI (L_2). A dye cation radical and an o-cl-HABI anion radical ($L_2^{\cdot-}$) were produced. The latter soon dissociated and produced an anion (L^-) and a free radical ($L^{\cdot}$), which can initiate the photopolymerization of MMA. The following is the procedure:

3.3 Hologram Recording

Coated photopolymer plates were evaluated by recording holographic diffraction gratings. Gratings were obtained by actinic exposure at the intersection of two interfering collimated beams of a He-Ne laser operating at 633nm and TEM_{00} as illustrated in Fig.2. The beam intensity ratio was maintained at about 1:1. Exposure times ranged from 4-18 minutes, corresponding to 180-800 mJ/cm^2 total exposure. About one minute after the holographic exposure each grating was given a 2-3 minutes overall fixing exposure using one of the two 633nm laser beams, and then was heated in a thermostat at 130°C . More than 80% of reflection grating diffraction efficiency can be obtained as shown in Fig.3. The holographic gratings have a good physical and chemical stability under ambient conditions.

L₁-Objective Lens; L₂-Collimating Lens; M₁, M₂-Mirror; B-Beam Splitter; H-Photopolymer
Fig.2 Setup for recording reflection holographic gratings

3.4.Mechanism of Hologram Formation^[3,11]

The procedure of recording a hologram is divided into three steps. First, expose a coated photopolymer plate with holographic exposure. Second, expose the plate with overall fixing exposure. Third, heat the plate in a thermostat.

During the initial holographic exposure, monomer in light-struck region is polymerized. Because holographic exposure selectively polymerizes monomer in the light-struck regions, changing its refractive index, thus a initial hologram is formed prior to the second overall exposure. Monomer is depleted in the light-struck regions but not depleted in the non-light-struck regions. The resulting concentration gradient causes monomer to diffuse from non-light-struck regions to light-struck regions. Diffusion occurs both during and after exposure and continues until the hologram is fixed by overall exposure, which polymerizes the remaining monomer. Because of monomer diffusion, the density of monomer-derived polymer is greater in the light-struck regions than in the non-light-struck regions. Monomer migration creates density differences and corresponding refractive index differences between adjacent regions, which forms a holographic grating. The mechanism of hogram formation is shown in Fig.5.

3.4 Method to Shorten the Exposure Times

The energy sensitivity of the photopolymer plate was relatively low. In order to reduce the exposure times we propose to add a beam to

expose the photopolymer plate simultaneously during the initial holographic exposure. The third added beam can not interference with

Fig.3 Diffraction efficiency of a grating.

other two holographic exposure beams, it is irradiated from other laser or non-coherent light sources. In this way, the initial hologram would not be destroyed according to above mechanism of hologram formation, however, the effective exposure sensitivity of the photopolymer plate is increased. In other words, without any chemical modification of the photopolymerizable material, the energy input required to cause photopolymerization is reduced. The exposure times of the photopolymer plate was shortened obviously as shown in Fig.4.

(a) two interfering beam(as shown in Fig.2)
(b) added a third non-coherent beam

Fig.4 Increase Effective Exposure Sensitivity

Fig.5. Mechanism of Hologram Formation

4. Conclusion

The photopolymerization mechanism in this system was electron transfer, the effective exposure sensitivity of the photopolymer plate can be increased by adding the third beam to expose the photopolymer plate simultaneously during the initial holographic exposure. The holographic gratings have a high diffraction efficiency (>80%), a good physical and chemical stability under ambient conditions. The diffraction efficiency of a hologram had no change after the hologram had been immersing in water for 24 hours.

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*Zhao Jia is working at Beijing Light Industry Institute.

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