PQ-based derivatives doped PMMA photopolymers for holographic data storage

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We report our investigation on several poly(methyl methacrylate)(PMMA) photopolymers doped with different 9,10-phenanthrenequinone based derivatives for holographic data storage. By introducing different kinds of the functional groups on the doped elements, we could tailor the holographic characteristics of the materials.

I. INTRODUCTION

Due to the advantage of facile fabrication, flexibility and high diffraction efficiency, photopolymer materials have recently been attractive candidates of recording media for holographic data storage.[1] In our laboratory, we have investigated on the syntheses and analysis of 9,10-PhenanthreneQuinone doped Poly(Methyl MethAcrylate) (PQ/PMMA) photopolymer[2]. The results demonstrate that the PQ/PMMA photopolymers not only possess high optical quality but also invulnerability to the shrinkage effect under light exposure and then are particularly useful for the volume holographic recording. It allows the holographic data storage system has the capability of pushing up to the upper limits of the geometries of the set up. However, comparing with other photo-polymerized polymers, the dye-doped polymer system is relatively less sensitive and has lower dynamic range (M#). Therefore, it turns out an important issue to improve our PQ/PMMA photopolymers. We have investigated the physical mechanism of the holographic recording in our material, and found that the o-quinone double bond on the carbonyl functional groups of PQ molecule plays an important role of photo-chemical reaction[3]. During light exposure, photons excite PQ molecules to become radicals, which attach with the vinyl groups on MMA molecules to form a new compound. The new compound provides the refractive index change for holographic recording. These investigations suggest that changing the side functional group around the carbonyl group on PQ molecules may change its combination ability with MMA and then the holographic recording behavior of the samples can be modified. In this paper, we demonstrate that by using PQ-based derivatives with different functional groups, including electron-donor, electron-withdrawing, aromatic structure, the characteristics of the photopolymers have been successfully manipulated. We also show that by selecting the molecule with the electron-donor functional group, the recording sensitivity of material has been improved.
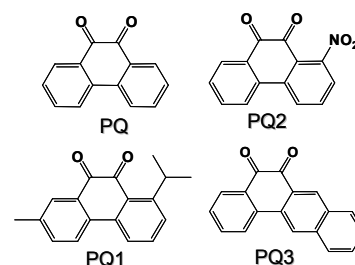

Fig.1. The chemical formulas of four photosensitive molecules

II. EXPERIMENTS

We select three different kinds of PQ-based derivatives molecules: 1-isopropyl-7methyl-9,10-phenanthrenequinone (named as PQ1) with an additional electron-donor functional group, 2-nitro phenanthrenequinone (named as PQ2) with an additional electron-withdrawing functional group, and 11,12-Dihydrochrysene-11,12-Dione (named as PQ3) with another aromatic structure. Their chemical formulas are shown in Fig. 1. In comparison, the PQ molecule is also shown.

In material fabrication, four different PQ-based derivatives: PQ, PQ1, PQ2, PQ3 are chosen. One of them and thermal -initiator azobisisobutyronitrile (AIBN) are dissolved into the purified methyl methacrylate (MMA) solution. The solution was poured into a glass cell with dimensions of 10cm x 10cm and thickness of 2mm. By controlling synthesis temperature and time conditions of sample, the solution can be transformed into well-polymerized bulk. The sample can then be removed from glass container for optical experiments. All samples appear to be yellowish color, with a clear optical transmission.

To characterize the material for volume holographic storage, we have performed multiple-hologram recording experiment at a single location by using peristropherical multiplexing technique. In experiments, we recorded a series of plane wave holograms by using 514-nm argon laser until the material got exhausted and no more holograms can be

recorded. The diffraction efficiency of each hologram was measured after recording. Then, the summation of the square root of the diffraction efficiency of the current hologram with that of previously recorded holograms can form a running curve of the cumulative grating strength, i.e $C = \sum_{i=1}^{n} \sqrt{\eta_i}$; where η_i is diffraction efficiency and n is the total number of holograms that have been recorded. The running curve is plotted as a function of total exposure energy that has been illuminated on the material during recording. When the material got exhausted, C tends to be saturated, and its saturation value is equal to the dynamic range or M/# of recording material. In addition, if we perform a curve fitting by the function $C = C_{sat}[1\text{-exp}(-E/E_\tau)]$, where E is exposure energy, then the saturation value C_{sat} gives the dynamic range or M/#, and E_τ gives the characteristic exposure energy of the material. The material sensitivity S, which describes the speed at the initial state of material, can be written by the expression, $S = C_{sat} / E_\tau = M\# / E_\tau$. The experimental results for four different samples with same doping concentration (ca. 155μmol.) are shown in Fig. 2. By exponentially curve fitting of the running curves, the material M#, E_τ and sensitivity of each sample are estimated. It is seen that PQ2 possesses a slightly larger M/# than that of PQ (from 0.32 to 0.36), whereas the sensitivities is only half value. We can also found that PQ1 sample is the fastest among the four samples. This can be attributed to the aliphatic (R-) electron-donor group on PQ1 molecules, which provides more electrons and accelerates the photoreaction. On the other hand, the nitro (NO2-) electron-withdrawing group on PQ2 makes the electron diffusely distributed and decelerate the photoreaction, thus the speed of photoreaction has been slowed down. However, the NO2-group provides larger refractive index birefringe. Same behavior as PQ2 occurs for the PQ3 sample, which arises because of aromatic structure on the PQ3 molecules. In fact, the different molecular structures of quinone-based molecules possess different solubility in PMMA matrix. In order to further enhance the photochemical reaction of the photopolymer, we fabricated samples with saturation concentrations of photosensitizers. Then, the holographic characteristics of each sample were measured by using the same optical setup. The calculated results of the material M#, E_τ and sensitivity of each sample are listed in Table 1. We can see that the PQ1/PMMA sample is the most sensitive one among the four samples (4.4 times faster than PQ/PMMA) and best performance of M/# can be achieved to 5.18.

In conclusion, we have fabricated four doped PMMA photopolymers with different PQ-based derivatives. The holographic characteristics have measured and compared. The experimental results show that by changing the electron-donor functional group on photosensitive molecules, the recording properties of photopolymers can be manipulated. These results provide us useful information to improve our recording materials.

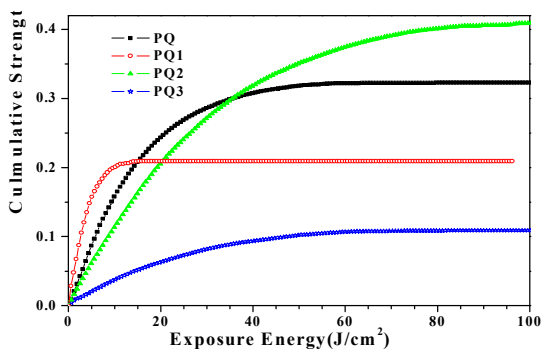Fig. 2. The running curves for four different doped PMMA samples.

	PQ	PQ1	PQ2	PQ3
Doping conc. (wt%)	0.7	0.7	0.26	0.25
M#	3.23	5.18	0.82	0.22
E_τ (J/cm^2)	9.07	3.23	17.5	26.9
S (cm^2/J)	0.36	1.6	0.047	0.008

Table 1. The characteristics of the holographic recording on the four samples

III. REFERENCES

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