

This article was downloaded by: [National Chiao Tung University 國立交通大學]

On: 24 April 2014, At: 18:11

Publisher: Taylor & Francis

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Modern Optics

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/tmop20>

Co-doping with polysquaraine enhances the holographic optical data storage of PMMA/PQ photopolymers

Cheng-Jung Ko ^a, Yeh-Lu Chang ^a, Yi-Nan Hsiao ^b, Po-Lin Chen ^b, Shiu-an-Huei Lin ^c, Wha-Tzong Whang ^a, Ken-Y. Hsu ^b, Mei-Hui Tsai ^d & Wen-Yen Tsang ^d

^a Department of Materials Science and Engineering, National Chiao Tung University, Hsin-Chu 300, Taiwan, ROC

^b Department of Photonics and Institute of Electro-Optical Engineering, National Chiao Tung University, Hsin-Chu 300, Taiwan, ROC

^c Department of Electrophysics, National Chiao Tung University, Hsin-Chu 300, Taiwan, ROC

^d Department of Chemical and Materials Engineering, National Chin-Yi University of Technology, Taichung 411, Taiwan, ROC

Published online: 04 Aug 2011.

To cite this article: Cheng-Jung Ko, Yeh-Lu Chang, Yi-Nan Hsiao, Po-Lin Chen, Shiu-an-Huei Lin, Wha-Tzong Whang, Ken-Y. Hsu, Mei-Hui Tsai & Wen-Yen Tsang (2011) Co-doping with polysquaraine enhances the holographic optical data storage of PMMA/PQ photopolymers, *Journal of Modern Optics*, 58:14, 1215-1219, DOI: [10.1080/09500340.2011.581765](https://doi.org/10.1080/09500340.2011.581765)

To link to this article: <http://dx.doi.org/10.1080/09500340.2011.581765>

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the "Content") contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms & Conditions of access and use can be found at <http://www.tandfonline.com/page/terms-and-conditions>

Co-doping with polysquaraine enhances the holographic optical data storage of PMMA/PQ photopolymers

Cheng-Jung Ko^a, Yeh-Lu Chang^a, Yi-Nan Hsiao^b, Po-Lin Chen^b, Shiu-an-Huei Lin^c, Wha-Tzong Whang^{a*}, Ken-Y. Hsu^b, Mei-Hui Tsai^d and Wen-Yen Tsang^d

^aDepartment of Materials Science and Engineering, National Chiao Tung University, Hsin-Chu 300, Taiwan, ROC;

^bDepartment of Photonics and Institute of Electro-Optical Engineering, National Chiao Tung University,

Hsin-Chu 300, Taiwan, ROC; ^cDepartment of Electrophysics, National Chiao Tung University,

Hsin-Chu 300, Taiwan, ROC; ^dDepartment of Chemical and Materials Engineering,

National Chin-Yi University of Technology,

Taichung 411, Taiwan, ROC

(Received 6 January 2011; final version received 12 April 2011)

In this study, we synthesised poly(3-octylpyrrole-*co*-squaric acid) (PSQ3), a polysquaraine, through the reaction of 3-octylpyrrole and squaric acid, and then co-doped it with phenanthrenequinone (PQ) into poly(methyl methacrylate) (PMMA) to improve the holographic data storage characteristics of the photopolymer. The photopolymers co-doped with relatively small amounts of PSQ3 exhibited greatly improved holographic recording characteristics, including superior diffraction efficiency and dynamic range ($M\#$). Among the samples co-doped with PQ and PSQ3, the maximum diffraction efficiency reached 54.8% (cf. 9.0% for PMMA/PQ) without further downgrade and the value of $M\#$ reached 1.05 (cf. 0.46 for PMMA/PQ). Therefore, the holographic data storage characteristics of the photopolymer PMMA/PQ were improved through co-doping with PSQ3.

Keywords: polysquaraine; phenanthrenequinone; poly(methyl methacrylate); holographic recording; optical data storage

1. Introduction

Holographic data storage is one of the most promising next-generation data storage technologies because it combines large storage capacities with fast data access rates. Photopolymer recording materials are particularly attractive for holographic recording applications [1–6]; compared with inorganic materials, photopolymers can provide larger refractive index modulation, higher sensitivity and better flexibility in terms of composition. In previous studies, we found that 9,10-phenanthrenequinone (PQ)-doped poly(methyl methacrylate) (PMMA) serves as a good recording material for holographic data storage [6–9]. During such a holographic recording process, the PQ molecules absorb energy to form an excited state, which undergoes further transfer to a radical state that reacts with residual MMA monomer to form the photoproduct; at the same time, a modulated refractive index change occurs [10]. Faster photoreaction processes and larger modulated refractive index changes of the photopolymer are expected to result in superior holographic recording characteristics.

Polysquaraines are π -conjugated polymers that possess consecutive donor/acceptor repeating units in the polymer chain [11,12]; they feature considerable charge-transfer interactions, which could be used to affect the photoreaction between PQ and MMA and, thereby, improve the holographic characteristics. In this study, we synthesised poly(3-octylpyrrole-*co*-squaric acid) (PSQ3) and co-doped it with PQ into PMMA as the photopolymer. We used a UV-visible (Vis) spectrometer and an Abbe refractometer to measure the optical absorption and refractive index data, respectively. From a study of the holographic recording characteristics of the photopolymer incorporating different doped concentrations of PSQ3, we found that the co-doped polysquaraine improved the dynamic range and sensitivity of the photopolymer.

2. Experimental

2.1. Materials

High-purity 3-octylpyrrole and squaric acid were obtained from Tokyo Chemical Industry and Acros

*Corresponding author. Email: wtwhang@mail.nctu.edu.tw

Organics, respectively. Benzene was acquired from Showa Chemical. Butyl alcohol, ethyl ether and CH_2Cl_2 were purchased from Echo Chemical Company. PMMA powder (average molecular weight: 120,000) was obtained from Sigma–Aldrich. PQ was acquired from Tokyo Chemical Industry and used as received.

2.2. Poly(3-octylpyrrole-co-squaric acid) (PSQ3)

3-Octylpyrrole (0.5 mmol) and squaric acid (0.5 mmol) were heated under reflux in benzene (10 ml) and butyl alcohol (20 ml) under a N_2 atmosphere with stirring for 24 h, with azeotropic removal of water in a Dean–Stark apparatus [11,13]. After cooling, the mixture was concentrated under vacuum and the product poured into ethyl ether. The precipitate was collected by filtration, dissolved in CH_2Cl_2 and re-precipitated from ethyl ether to provide the final product, which was dried in a vacuum oven at 30°C for 24 h prior to use.

2.3. Photopolymer fabrication

PMMA powder (20 wt%) and polysquaraine powder were dissolved in CH_2Cl_2 by stirring at room temperature for 2 h; the dissolved PSQ3 concentrations within the PMMA matrix were ca. 0.05, 0.07, and 0.1 wt%. PQ (5 wt%) was then added into the solution, which was stirred for 2 h [14]. This precursor solution was coated on a dust-free glass plate using a $650\ \mu\text{m}$ wide doctor blade. The gel film was further heated at 35°C for 30 min to remove the CH_2Cl_2 , providing PMMA/PQ/PSQ3 photopolymer films having an average final thickness of $110\ \mu\text{m}$.

2.4. Measurements

Fourier transform infrared (FTIR) absorption spectra were recorded between 4000 and $500\ \text{cm}^{-1}$ using a PerkinElmer 100 spectrophotometer. To identify the photoreactions occurring in our photopolymer, the samples were measured in unexposed and exposed states. UV–Vis spectra of the photopolymer were recorded using a Shimadzu UV-1800 instrument. Refractive indices were measured using an Abbe refractometer (ATAGO-DR-M2) and a sodium light source ($589\ \text{nm}$) at room temperature.

A typical four-wave mixing optical setup was constructed to measure the holographic characteristics (Figure 1). A collimated light beam from an Ar laser (wavelength: $514\ \text{nm}$) was s-polarised and divided into two beams with an intensity ratio of 1:1 (intensity of each beam: $6\ \text{mW}/\text{cm}^2$; diameter: $0.7\ \text{cm}$). The intensity of the diffraction beam was detected when the shutter

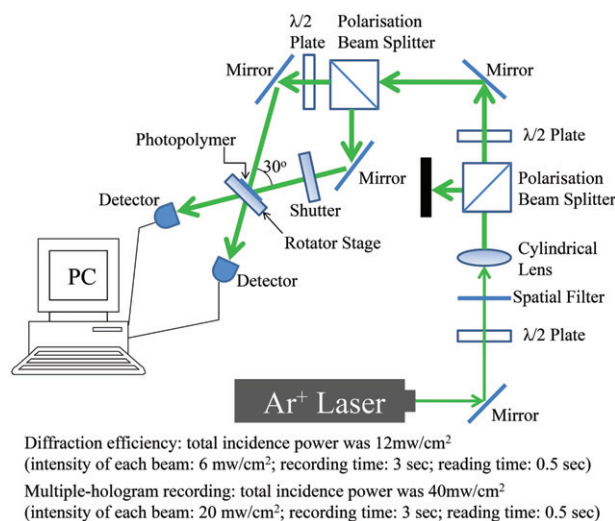


Figure 1. Optical setup for measuring holographic data recording characteristics. (The colour version of this figure is included in the online version of the journal.)

blocked one of the beams. The light beams were aligned incident and symmetrically to the sample with an intersection angle of 30° outside of the sample. The diffraction efficiency was defined as the ratio of the intensity of the diffracted beam to the sum of the intensities of the diffracted and transmitted beams. To measure the dynamic range, the photopolymer was placed on a rotational stage to allow multiple hologram recordings using a peristrophic multiplexing technique. The exposure energy of each hologram was $0.312\ \text{J}/\text{cm}^2$.

3. Results and discussion

3.1. FTIR spectra

We prepared PSQ3 through the reaction of 3-octylpyrrole and squaric acid and characterised its chemical structure using FTIR spectroscopy (Figure 2). The signals at 1610 and $1730\ \text{cm}^{-1}$ represent the C–O and C=O stretchings of the cyclobutenediylum-1,3-diolate moiety, respectively [11,15,16]. The strong C–H stretching of the C_8H_{17} units appeared as absorption bands at ca. 2800 – $3000\ \text{cm}^{-1}$ [16]. The broad absorption band at $3300\ \text{cm}^{-1}$ was produced as a result of intramolecular hydrogen bonding of the PSQ3 structures. These spectral features were consistent with the proposed structure of PSQ3.

3.2. Optical chemical measurements

Figure 3 presents typical optical absorption spectra of the various photopolymers before and after exposure. PSQ3 itself exhibited its maximum

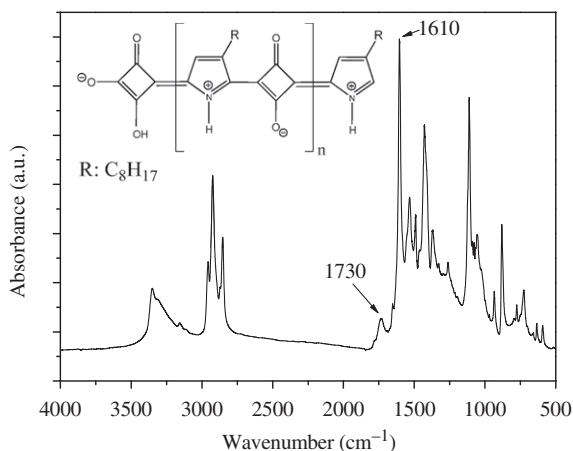


Figure 2. FTIR spectra of PSQ3.

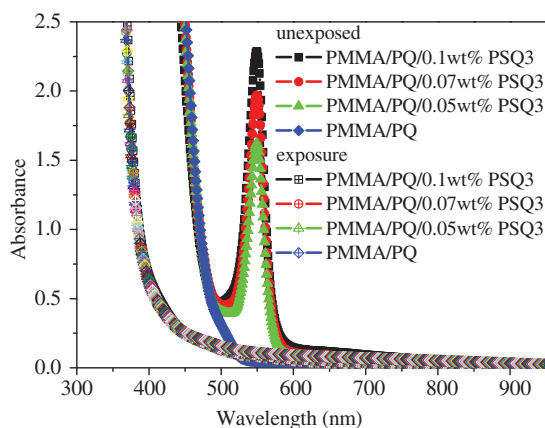


Figure 3. UV-Vis absorption spectra of the unexposed and exposure photopolymers. (The colour version of this figure is included in the online version of the journal.)

absorption at 549 nm. Prior to exposure, the photopolymers co-doped with PSQ3 all provided similar absorption curves. All of the samples had lower absorbance at 514 nm than they did at 532 nm. Notably, the absorption coefficients at 514 and 549 nm increased upon increasing the doped content of PSQ3. After exposure to green light (514 nm), the entire absorption band of the each photopolymer underwent a blue shift. At the same time, the absorption peak of PSQ3 disappeared, predictably because PSQ3 reacted with PQ and PMMA to form various photoproducts [10,17,18]. This substantial variation in absorbance was clearly different from that of the unmodified PMMA/PQ photopolymer. To monitor the effect of co-doping PSQ3 in the PMMA/PQ photopolymer in terms of the holographic data storage characteristics, we selected 514 nm as the recording wavelength for our subsequent studies.

Table 1 reveals that the refractive indices of the photopolymers increased upon increasing the content of PSQ3. The change in refractive index after exposure of the co-doped PMMA/PQ photopolymer to radiation increased when the concentration of PSQ3 increased from 0 to 0.1 wt%. For the PQ-only and PSQ3-only doped photopolymers, the refractive index changes were much lower. These results suggested that the holographic data storage characteristics of the PMMA/PQ photopolymer might be enhanced after co-doping with PSQ3.

3.3. Holographic data storage characteristics

Figure 4 presents the diffraction efficiencies of the photopolymers plotted as a function of the exposure energy. The co-doped PMMA/PQ/PSQ3 photopolymers all exhibited higher holographic diffraction efficiencies than did the PMMA/PQ photopolymer. The maximum diffraction efficiencies at PSQ3 co-doping levels of 0.1, 0.07, 0.05 and 0 wt% reached 54.8, 44.9, 19.9 and 9.0%, respectively. For the PMMA/0.1 wt% PSQ3 photopolymer prepared without PQ, the diffraction efficiency was very low (ca. 0.2%). These variations are consistent with the changes in refractive index.

The two most important parameters for holographic data storage materials are their dynamic range and sensitivity. The dynamic range of a holographic material provides an estimate of the recording capacity; the larger the dynamic range of a material, the larger its storage capacity. The sensitivity is a gauge of the recording data rate; because a material with high sensitivity allows faster recording, less energy is required when recording each hologram.

We applied a peristrophic multiplexing technique to record 200 holograms in a single location of each photopolymer. The sum of the square roots of the diffraction efficiency forms a running curve of the cumulative grating strength, expressed as

$$C(E) = \sum_{i=1}^n \sqrt{\eta_i}, \quad (1)$$

where n is total number of holograms that have been recorded for a total exposure energy density of EJ/cm^2 . By curve fitting with the function

$$C(E) = C_{\text{sat}}[1 - \exp(-E/E_\tau)], \quad (2)$$

where E is total exposure energy, the saturation value C_{sat} ($M\#$) of the curve gives the dynamic range of the material, and E_τ gives the exposure energy constant of the material [7,19]. The material sensitivity (S) is an increment in cumulative grating strength with respect to the amount of exposure energy. When the sample

Table 1. Refractive indices of PSQ3/PQ-doped PMMA photopolymers.

Sample	Unexposed refractive index	Exposed refractive index	Refractive index change (Δn)
PMMA/PQ	1.4925	1.4901	0.0024
PMMA/PQ/0.05 wt% PSQ3	1.4969	1.4921	0.0048
PMMA/PQ/0.07 wt% PSQ3	1.4983	1.4930	0.0053
PMMA/PQ/0.10 wt% PSQ3	1.5030	1.4962	0.0068
PMMA/0.10 wt% PSQ3	1.4984	1.4978	0.0006

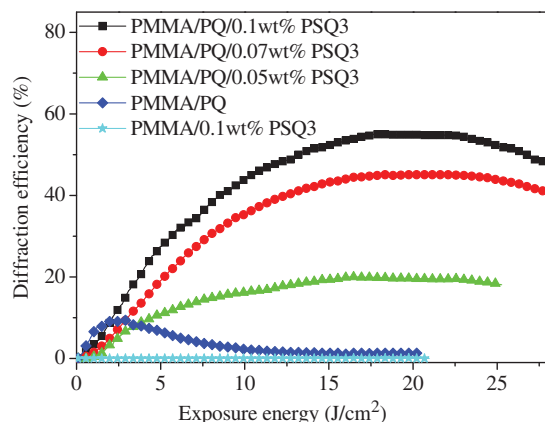


Figure 4. Holographic diffraction efficiencies of the photopolymers. (The colour version of this figure is included in the online version of the journal.)

is unexposed, $S = dC/dE|_{E \rightarrow 0}$. According to the running curve function, the sensitivity can be written as

$$S = C_{\text{sat}}/E_{\tau} = M\#/E_{\tau}. \quad (3)$$

Figure 5 displays the running curves for multiple-hologram recording in PMMA/PQ photopolymers co-doped with PSQ3. Each curve reached saturation when the exposure energy exceeded a certain value. Using the formulae above for curve-fitting, we obtained the values of $M\#$, E_{τ} and S listed in Table 2. All of the photopolymers co-doped with PSQ3 had higher values of $M\#$ and S than did the PQ-only doped photopolymer. The PMMA/PQ/0.1 wt% PSQ3 photopolymer exhibited the highest value of $M\#$ (1.05) among all of the tested samples (cf. 0.47 for PMMA/PQ). Moreover, the value of S of the PMMA/PQ/0.1 wt% PSQ3 system was 2.6 times greater than that of the PMMA/PQ photopolymer.

These experimental results reveal that co-doping with PSQ3 enhanced the holographic data storage characteristics of the PMMA/PQ photopolymer system. Upon exposure to light, the π -conjugated structure of PSQ3 predictably changed or was destroyed; the absorption peaks of PSQ3 disappeared, consistent with it having undergone photochemical reactions with PQ and PMMA, in which the PSQ3 was

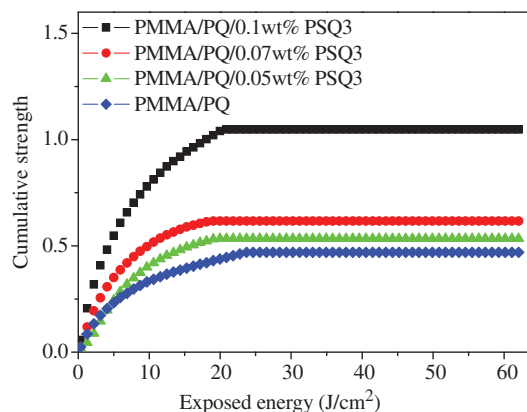


Figure 5. Running curves for multiple-hologram recording in the photopolymers. (The color version of this figure is included in the online version of the journal.)

Table 2. Characteristics of multiplexed volume holographic recording in PSQ3/PQ-doped PMMA photopolymers.

Sample	$M\#$	E_{τ} (J/cm ²)	Sensitivity (cm ² /J) ^a
PMMA/PQ	0.47	8.33	0.056
PMMA/PQ/0.05 wt% PSQ3	0.53	7.69	0.069
PMMA/PQ/0.07 wt% PSQ3	0.62	5.88	0.105
PMMA/PQ/0.10 wt% PSQ3	1.05	7.14	0.147

^aSensitivity (S) = $M\#/E_{\tau}$.

reacted with the residue monomer of PMMA [17,18] and the C=C of PSQ3 was furthermore reacted with the C=O group of PQ [10]. These new photoproducts would be different from those in the PMMA/PQ sample, providing a larger refractive index change and superior holographic recording performance.

4. Conclusions

Co-doped PMMA/PQ/polysquaraine photopolymers exhibit superior holographic performance relative to

that of the corresponding PMMA/PQ photopolymer. Single-hologram recording revealed that the diffraction efficiency of the PMMA/PQ/0.1 wt% PSQ3 photopolymer was higher than those of any of the other tested photopolymers. Furthermore, in a multiple-hologram recording scheme, the PMMA/PQ/0.1 wt% PSQ3 photopolymer also exhibited the greatest value of $M\#$ and sensitivity. The refractive index change of the PMMA/PQ photopolymer was enhanced after copolymerizing with the polysquaraine, providing greater holographic recording characteristics.

Acknowledgements

We thank the National Science Council Republic of China, Taiwan, for supporting in this research financially under Grant NSC97-2221-E009-012-MY3.

References

- [1] Dhar, L.; Hale, A.; Katz, H.E.; Schilling, M.L.; Schnoes, M.G.; Schilling, F.C. *Opt. Lett.* **1999**, *24*, 487–489.
- [2] Ono, H.; Tamoto, T.; Emoto, A.; Kawatsuki, N. *Jpn. J. Appl. Phys.* **2005**, *44*, 1781–1786.
- [3] Mahilny, U.V.; Marmysh, D.N.; Stankevich, A.I.; Tolstik, A.L.; Matusevich, V.; Kowarschik, R. *Appl. Phys. B: Lasers Opt.* **2006**, *82*, 299–302.
- [4] Xue, S.S.; Manivannan, G.; Lessard, R.A. *Thin Solid Films* **1994**, *253*, 228–232.
- [5] Pham, V.P.; Manivannan, G.; Lessard, R.A. *Thin Solid Films* **1995**, *270*, 295–299.
- [6] Lin, S.H.; Chen, P.L.; Hsiao, Y.N.; Whang, W.T. *Opt. Commun.* **2008**, *281*, 559–566.
- [7] Hsiao, Y.N.; Whang, W.T.; Lin, S.H. *Opt. Eng.* **2004**, *43*, 1993–2002.
- [8] Sukhanov, V.I. *J. Opt. Technol.* **1994**, *61*, 49–56.
- [9] Steckman, G.J.; Solomatine, I.; Zhou, G.; Psaltis, D. *Opt. Lett.* **1998**, *23*, 1310–1312.
- [10] Horspool, W.M.; Song, P.S. *CRC Handbook of Organic Photochemistry and Photobiology*; CRC Press: Boca Raton, FL, 1995.
- [11] Chenthamarakshan, C.R.; Eldo, J.; Ajayaghosh, A. *Macromolecules* **1999**, *32*, 251–257.
- [12] Eldo, J.; Ajayaghosh, A. *Chem. Mater.* **2002**, *14*, 410–418.
- [13] Lu, H.C.; Whang, W.T.; Cheng, B.M. *Synth. Met.* **2010**, *160*, 1002–1007.
- [14] Hsiao, Y.N.; Whang, W.T.; Lin, S.H. *Jpn. J. Appl. Phys.* **2005**, *44*, 914–919.
- [15] Silva, C.E.; Diniz, R.; Rodrigues, B.L.; de Oliveira, L.F.C. *J. Mol. Struct.* **2007**, *831*, 187–194.
- [16] Sant'Ana, A.C.; de Siqueira, L.J.A.; Santos, P.S.; Temperini, M.L.A. *J. Raman Spectrosc.* **2006**, *37*, 1346–1353.
- [17] He, Y.; Zhou, W.; Wu, F.; Li, M.; Wang, E. *J. Photochem. Photobiol., A* **2004**, *162*, 463–471.
- [18] Mohr, G.J. *Sens. Actuators, B* **2005**, *107*, 2–13.
- [19] Pu, A.; Psaltis, D. *Appl. Opt.* **1996**, *35*, 2389–2398.