

Nitroanilines Enhancing the Holographic Data Storage Characteristics of the 9,10-Phenanthrenequinone-Doped Poly(methyl methacrylate) Photopolymer

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ABSTRACT: This article describes an approach toward improving the characteristics of a photopolymer for holographic data storage application. The maximum diffraction efficiency (η_{max}) and dynamic range (M#) of 9,10-phenanthrenequinone (PQ)-doped poly (methyl methacrylate; PMMA) both improved significantly after co-doping with one of three nitroanilines—*N*,*N*-dimethyl-4-nitroaniline (DMNA), *N*-methyl-4-nitroaniline (MNA), and 4-nitroaniline (pNA). In particular, the value of η_{max} increased from 38% for the PMMA/PQ system to 72% for the PMMA/PQ/DMNA system (a 1.89-fold improvement) and the value of M# increased accordingly from 2.7 to 7.3 (a 2.70-fold improvement). Thus, the holographic data storage characteristics of PMMA/PQ photopolymers can be improved through co-doping with nitroaniline compounds. We also investigated the mechanism of the nitroaniline-induced improvement in optical storage performance using proton nuclear magnetic resonance and X-ray photoelectron spectroscopy. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

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INTRODUCTION

Because it provides excellent storage capacity with rapid data access, holographic data storage is a promising technology for next-generation data recording. The development of suitable recording media plays a key role in the technical realization of holographic data storage. A good holographic recording material requires high optical sensitivity, simple fabrication, uniform spatial-frequency response, large diffraction efficiency, and long-term stability.^{1–3} Recently, many experimental studies have revealed that photopolymers are attractive materials for holographic recording applications.^{1,4–10} Among the various photopolymers that have been tested, poly(methyl methacrylate; PMMA)-based polymers and the ability to modify their characteristics through chemical doping.

In previous studies, we have found that 9,10-phenanthrenequinone (PQ)-doped PMMA serves as an excellent holographic recording material.^{3,10–12} The grating in such systems is formed through photoreactions, with the photoproduct featuring one methyl methacrylate (MMA) unit attached to one PQ derivative³; notably, however, the limited availability of PQ in the PMMA/PQ system restricts the dynamic range (M#) of holographic data storage. A previous approach toward overcoming this obstacle has involved doping PQ-based derivatives for holographic data storage.¹⁰ The presence of an electron donor group accelerates the photoreaction and, thereby, increased the recording sensitivity. For example, the nitro (NO₂) group (electron acceptor) on 2-nitrophenanthrenequinone distributes the electron density diffusely and increases the birefringence effect of the sample, thereby improving the holographic characteristics of the sample.

In this present study, we tested the effects of three different nitroaniline compounds—4-nitroaniline (pNA), *N*-methyl-4-nitroaniline (MNA), and *N*,*N*-dimethylaniline (DMNA)—on the holographic recording characteristics of a PQ-doped PMMA

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system. These nitroaniline compounds, which can be regarded as simple nonlinear optical (NLO) materials,13-15 feature both electron donor and electron acceptor groups in their structures. We expected the co-doping of these nitroaniline compounds in the PMMA/PQ photopolymer to induce larger birefringence effects and, thereby, improve the holographic characteristics. We examined the holographic recording characteristics of the codoped PMMA/PQ photopolymers in terms of their maximum diffraction efficiencies (η_{max}) and values of M#. We have used UV-Vis spectra, a prism coupler, ¹H nuclear magnetic resonance (NMR) spectroscopy, and X-ray photoelectron spectroscopy (XPS) to investigate the resulting recording mechanism. Our results indicate that the co-doping of the nitroaniline compounds into the PMMA/PQ photopolymers improved the dynamic range and sensitivity because of the presence of the electron donor units.

EXPERIMENTS

Materials

The monomer, methyl methacrylate (MMA), was obtained from Showa; the stabilizer was removed through distillation under low pressure; the purified MMA was refrigerated until required for use. 2,2-Azobisisobutyrolnitrile (AIBN) was purchased from Showa and purified through recrystallization from EtOH (99.5%). The photosensitizer dye PQ was obtained from Tokyo Chemical Industry and used as received. DMNA (98%) was obtained from Tokyo Chemical Industry. MNA (97%) and pNA (98%) were purchased from Alfa Aesar. The chemical structures are displayed in Figure 1.

Photopolymer Fabrication

AIBN (1 wt %) was dissolved in the MMA monomer and stirred at room temperature for 3 h. PQ (0.7 wt %) and a nitroaniline compound (molar ratio of PQ to nitroaniline: 1:1) were added and then the solution was stirred for 6 h before being filtered through a membrane (pore size: $0.2 \ \mu$ m). The mixed solution was stirred at 35°C for 12 h until the solution turned highly viscous. The viscous solution was finally poured into a glass cell and baked at 45°C for 3 days. The resulting yellowish



Figure 1. Chemical structures of the compounds used in this study.

bulk photopolymer had a thickness of 2 mm, good optical quality, and exhibited negligible photochemical shrinkage.¹⁶

Measurements

To identify the mechanism behind the recording characteristics of the various nitroaniline-modified PMMA/PQ materials, analyses (UV-Vis spectroscopy, prism coupler, ¹H NMR spectroscopy, XPS) were performed both before and after light exposure. For measurement of holographic characteristics, a collimated light beam from a DSSP laser (wavelength: 532 nm) was divided into two s-polarization beams with an intensity ratio of 1:1. Two incident beams entered the samples symmetrically with an intersection angle of 30° outside the sample. The intensity of the diffraction beam was detected when a shutter blocked one of the writing beams. The intensity of each beam was 7 mW/cm²; the beam diameter was 0.7 cm. The diffraction efficiency is defined as the ratio of the intensity of the diffracted beam to that of the summation of the diffracted beam and the transmitted beam. To measure the dynamic range, photopolymers placed on a rotational stage underwent multiple-hologram recording using the perstrophic multiplexing technique. The exposed energy of each hologram was 5.66 J/cm².

To reach the exposed state, the photopolymer was illuminated with light from a 532-nm laser (intensity: 40 mW/cm²) until it changed from yellow to transparent. UV-Vis spectra of the photopolymer were recorded using a Hitach-U2000 spectrometer. The transverse electric (TE) and transverse magnetic (TM) refractive indices of the prepared photopolymers were measured at a wavelength of 632.8 nm using a prism coupler (Metricon Model 2010). The change in birefringence (Δn) was calculated as the difference between the refractive indices $n_{\rm TE}$ and $n_{\rm TM}$. To identify the variation of the structures of the photoproducts, Fourier transform infrared (FTIR) absorption spectra were recorded between 4000 and 500 cm⁻¹ using a PerkinElmer 100 spectrophotometer. It provides information about functional groups of the molecule structure. Before measurement, the unexposed and exposed solutions (MMA/PQ, MMA/PQ/pNA, MMA/PQ/MNA, MMA/PQ/DMNA) were dipped on KBr plates. The plate samples were baked at 45°C under vacuum condition for 24 h such that the unreacted MMA molecules were removed and the samples were left on the KBr plates. ¹H NMR spectra of the samples were recorded using a Unity Inova-500 spectrometer. XPS spectra of the nitrogen and oxygen elements in the exposed photopolymers were recorded using a Microlab 350 instrument, operated in constant analyzer energy mode (pass energy: 40 eV) with Mg K α (1253.6 eV) radiation as the excitation source. XPS analysis was performed at room temperature under vacuum (pressure: $<10^{-8}$ torr).

RESULTS AND DISCUSSION

Optical Properties

Figure 2 presents typical optical absorption spectra of the photopolymer incorporating the various doping components in both the unexposed and exposed states. Here, the "unexposed" samples were tested immediately after fabrication; the "exposed" samples were those that had been illuminated with laser light having a wavelength of 532 nm for a length of time. Figure 2(a) reveals that the spectral features of all of the photopolymers



Figure 2. UV–vis absorption spectra of the unexposed and exposed (a) PMMA/PQ/nitroaniline and (b) PMMA/nitroaniline photopolymers.

(PMMA/PQ, PMMA/PQ/pNA, PMMA/PQ/MNA, and PMMA/ PQ/DMNA) underwent a blue shift to shorter wavelength upon irradiation. Figure 2(b) indicates that the nitroaniline-only doped photopolymers exhibited identical absorption responses in both their exposed and unexposed states, implying that 532nm illumination did not induce any photochemical reactions in these samples. Comparing Figure 2(a,b), we note that in the unexposed state all of the photopolymers provided similar absorption spectra, but after illumination at 532 nm the absorption bonds of the PMMA/PQ photopolymers co-doped with pNA, MNA, and DMNA shifted to the positions of the absorption bands of the corresponding nitroaniline-only doped photopolymers (PMMA/pNA, PMMA/MNA, and PMMA/DMNA,

 Table I. Birefringence of Light-Exposed PMMA/PQ/Nitroaniline

 Photopolymers

Sample	n _{te} (632.8 nm)	п _{тм} (632.8 nm)	Δn (n_{TE} – n_{TM})
PMMA/PQ/DMNA	1.4892	1.4913	-0.0021
PMMA/PQ/pNA	1.4890	1.4904	-0.0014
PMMA/PQ/MNA	1.4888	1.4898	-0.0010
PMMA/PQ	1.4837	1.4843	-0.0006

respectively. Thus, in the absence of PQ, nitroaniline-doped PMMA was incapable of undergoing photoreactions; in addition, PQ served as the only major photosensitizer in the codoped photopolymers.

Table I lists the refractive indices (n_{TE} , n_{TM}) and birefringence ($\Delta n = n_{\text{TE}} - n_{\text{TM}}$) of the nitroaniline-doped PMMA/PQ photopolymers. Each of the nitroaniline-doped photopolymers exhibited higher birefringence than that of the PMMA/PQ photopolymer. Among these systems, the PMMA/PQ/DMNA photopolymer exhibited the greatest improvement in birefringence. A large birefringence will enhance reliability in holographic recording applications. Moreover, a photopolymer with a higher birefringence will also increase the holographic storage capacity.

Holographic Recording

To observe the effect of nitroaniline doping on the PMMA/PQ photopolymer, we measured the sensitivity and dynamic range of holographic recording at a wavelength of 532 nm.

Figure 3 presents the holographic diffraction efficiency plotted with respect to time. The PMMA samples co-doped with PQ and DMNA, pNA, and MNA exhibited maximum diffraction efficiencies of 71.2, 56.6, and 47.6%, respectively. In contrast, the maximum diffraction efficiency of the PQ-only doped photopolymer was 38.2%. Therefore, co-doping nitroaniline compounds into PQ significantly improved the maximum diffraction efficiency this system.

For each of the co-doped photopolymer systems, the diffraction efficiency reached a maximum value at a particular time, thereafter decreasing upon further exposure. Such decreases in diffraction efficiency are typically caused by noise gratings.^{16,17} The noise gratings result in scattering of the beams from scattering centers (e.g., microscopic air bubbles) and/or the nonuniformity of the refractive index of the photopolymer.

We employed perstrophic multiplexing to record 190 holograms at a single location of the photopolymer. The summation of the square roots of the diffraction efficiency as a function of the



Figure 3. Holographic diffraction efficiencies of the PMMA/PQ/nitroaniline photopolymers.





Figure 4. Running curves of multiple-hologram recordings in PMMA/PQ photopolymers doped with different nitroaniline compounds.

exposed energy forms a running curve of the cumulative grating strength (Figure 4). It can be expressed as

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

where *n* is total number of holograms recorded for a total exposed energy density of E (J/cm²).^{3,11,12,18} By curve fitting with the function

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

the saturation value C_{sat} (M#) of the curve gives the dynamic range of the material, and E_{t} gives the exposed energy constant of the material.^{3,18} The material recording sensitivity (*S*) is defined as the increment in cumulative grating strength with respect to the amount of exposed energy.¹⁸ When the sample is fresh,

$$S = dC/dE|_{E \to 0} \tag{3}$$

According to the running curve function, the sensitivity can be written as

$$S = C_{\text{sat}} / E_{\tau} = M \# / E_{\tau} \tag{4}$$

Taken together, the values of M# and S indicate the information storage capability of a material for volume data storage.^{3,18}

 Table II. Characteristics of Multiplexed Volume Holographic Recording in

 Nitroaniline/PQ Co-Doped PMMA Photopolymers

Sample	M#	E _τ (J/cm ²)	Sensitivity (cm²/J)ª
PMMA/PQ/DMNA	7.30	142.86	0.0511
PMMA/PQ/pNA	5.68	165.77	0.0343
PMMA/PQ/MNA	5.04	143.46	0.0351
PMMA/PQ	2.72	166.67	0.0163

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

By curve-fitting the data in Figure 4, we obtained the values of M#, E_t , and S for the various co-doped PQ photopolymers. Table II reveals that all of the nitroaniline-doped photopolymers exhibited higher values of M# and S than those of the singly doped PMMA/PQ sample. Among them, the PMMA/PQ/DMNA photopolymer provided the largest improvement, with the value of M# increasing from 2.7 for the PMMA/PQ sample to 7.3 and the value of S increasing accordingly from 0.0163 to 0.0511 cm²/J. Table I also reveals that doping with the nitroaniline compounds increased the birefringence of the photopolymer, thereby causing its dynamic range to increase.¹⁰

Photopolymer Chemical Characterization

Upon light exposure, PQ in its excited state reacts with the MMA monomer. Four different routes (I, II, III, and IV; Figure 5) are available for photoreactions between one PQ molecule and one MMA molecule.^{3,19,20} The Figure 5 show that during light exposure of the photopolymer material the o-quinones on the PQ molecules may bond to the olefins on the MMA molecules. Under photoreactions, four different routes might be taken in the form of one PQ molecule to one MMA molecule bonding structure. These four routes all lead the PQ molecules to become less conjugated, so that the birefringence effect of the photopolymer can be changed via photo-induced chemical reaction. However, these four photoproducts have different chemical properties such that the stability and change of the birefringence effect change of the photopolymer samples after light exposure are different. Nitroaniline compounds act as NLO materials because they feature both electron donor and acceptor functional groups in their molecular structures. The amino group of nitroaniline behaves as an electron donor group, thereby contributing to the acceleration of the photoreaction; consequently, the recording sensitivity is enhanced.¹⁰ On the other hand, the NO₂ group of the



Figure 5. Four different ways to combine PQ with an olefin.



Figure 6. The FTIR absorption spectra of unexposed and light exposed photopolymers: (a) PQ molecules, (b) unexposed, and (c) exposed MMA/ PQ photopolymer.

nitroaniline derivative is an electron acceptor that is responsible for increasing the birefringence of the photopolymers, thereby improving the dynamic range of the photopolymers.¹⁰ To understand the chemical characteristics and mechanism of the photoinduced reactions, we performed several types of chemical analyses of the nitroaniline-doped samples.

The chemical structure of unexposed and exposed samples was characterized by FTIR. Before measurement, the unexposed and exposed solutions (MMA/PQ, MMA/PQ/pNA, MMA/PQ/ MNA, MMA/PQ/DMNA) were baked at 45°C under vacuum condition for 24 h to remove the unreacted MMA molecules. Figure 6 shows the FTIR spectra of unexposed and exposed MMA/PQ sample. In Figure 6(a), the standard PQ spectrum, shows the PQ weak absorption peak spreads between wave numbers 3000 cm⁻¹ to 3100 cm⁻¹, indicating the existence of C-H on an aromatic function group.^{3,21} The signals at 1675 and 1593 cm⁻¹ represent the C=O and C=C stretchings of the PO molecules, respectively.³ Unexposed MMA/PO sample was show in Figure 6(b), the C=O and C=C stretchings of the PQ molecules at 1675 and 1593 cm⁻¹. However, the C=O stretchings of the MMA molecules was not discovered in Figure 6(b), which the MMA molecules were removed by vacuum condition. This result shows unexposed state the MMA molecules unreacted with PQ molecules. Moreover, after light exposure the o-quinone double bond C=O of the carbonyl group on the PQ molecule becomes radical and attaches with the double bond C=C of the vinyl group on the MMA molecule, as shown in our previous studies.³ Figure 6(c) shows FTIR spectrum of the exposure MMA/PQ samples. The peak at 1737 cm⁻¹ is due to the absorption of C=O in the acrylate part of the photoproduct. The absorption band at 1634 cm⁻¹ is produced by absorption of either C=O in the carbonyl group or C=C in the aromatic ring of the photoproduct.³ Two peaks at 1254 and 1081 cm⁻¹, which are produced by the light exposure, indicate that light exposure has turned the carbonyl group on the PQ molecule and the vinyl group on the MMA molecule to form C-O-C group. The results suggest that by



Figure 7. The FTIR absorption spectra of nitroaniline compounds: (a) pNA, (b) MNA, and (c) DMNA.

light exposure, PQ and MMA molecules react to form the photoproduct.

Figure 7 shows the FTIR spectra of nitroaniline compounds. The pNA FTIR spectrum show in Figure 7(a), the NH₂ of pNA molecules stretching vibration is observed at 3476 and 3360 cm⁻¹ and the C–N of 1° amines groups stretch is observed at 1444 cm^{-1.21-24} Figure 7(b) shows the MNA FTIR spectrum. The two peaks at 3366 cm⁻¹ and 2900 cm⁻¹ were N–H and CH₃ groups stretching vibrations, respectively.²⁵ The 2° amines groups C–N stretch is observed at 1455 cm^{-1.24-29} However, the CH₃ groups and C–N of 3° amines groups of DMNA molecules stretching vibration are observed at 2923 cm⁻¹ and 1482 cm⁻¹²⁹⁻³¹ in Figure 7(c). As for NO₂, the asymmetric and symmetric stretching vibration of NO₂ group of these three nitroaniline compounds generally gives rise to bands in the regions 1500–1570 cm⁻¹ and 1300–1370 cm⁻¹ and the C–N stretch of NO₂ group is shown at 836 cm^{-1.21-30,32}

Figure 8 shows the FTIR spectra of unexposed MMA/PQ/nitroaniline samples. No MMA-related peaks were found and these



Figure 8. FTIR absorption spectra of the unexposed PMMA/PQ/nitroaniline photopolymers: (a) MMA/PQ/pNA, (b) MMA/PQ/MNA, and (c) MMA/PQ/DMNA.



Figure 9. FTIR absorption spectra of the light exposed PMMA/PQ/nitroaniline photopolymers: (a) MMA/PQ/pNA, (b) MMA/PQ/MNA, and (c) MMA/PQ/DMNA.

spectra are just the combination of the FTIR spectra of pristine PQ and nitroaniline. These results indicated unexposed state the MMA molecules were removed by vacuum condition and the nitroaniline compounds didn't reaction with MMA and PQ molecules.

Figure 9 presents the FTIR spectra of the light exposed MMA/ PQ/nitroaniline samples. After light exposed, the samples, shows weak peak at 1737 cm^{-1} is due to the absorption of C=O in the acrylate part of the photoproduct. The signals at 1675 cm⁻¹ represent the C=O stretchings of the PQ molecules. The peak at 1634 cm⁻¹ was C=O in the carbonyl group or C=C in the aromatic ring of the photoproduct. Two peaks at 1254 and 1081 cm⁻¹ are due to the C-O-C groups of the photoproducts of carbonyl group on the PQ molecule reacting with the vinyl group on the MMA molecule. In Figure 9(a) for the PMMA/ PQ/pNA samples, the 1444 cm⁻¹ [1° amines groups C-N, Figure 8(a)] peak disappeared but a new shoulder occurring at 1482 cm⁻¹. Furthermore, the 2° amines groups C-N [1455 cm⁻¹, Figure 8(b)] peak was disappear and a new shoulder appears at 1482 cm⁻¹ in Figure 9(b). These results indicated the C-N group of 1° amines groups of pNA and 2° amines groups of MNA predictably react with PQ to form new photoproducts (3° amines). These new photoproducts would be different from those in the MMA/PQ sample, providing a larger birefringence change and superior holographic recording performance. On the other hand, in Figure 9(c), the 3° amines groups peak at 1482 cm⁻¹, it did not shift compared with Figure 8(c). This result proved the DMNA did not react with either MMA or PQ to form new photoproducts when exposed to light. In the PMMA/PQ/DMNA system, the coexisting DMNA molecules affected the polarizability of PQ during the recording process,^{33,34} which induces larger birefringence effects, thereby, improves the holographic characteristics.

Figure 10(a) displays the ¹H-NMR spectrum of the MMA/PQ/ DMNA sample prior to irradiation. The protons of the phenyl groups of PQ appear as signals at 7.45, 7.71, 8.01, and 8.17 ppm. The methyl and phenyl protons of DMNA appear as peaks

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located at 3.10 ppm and 6.57 and 8.08 ppm, respectively. The peaks at 1.94, 3.75, 5.56, and 6.10 ppm represent the protons of the MMA functional groups. In addition, one peak appears at 2.17 ppm, which we ascribe to PMMA (i.e., from polymerization of MMA). Figure 10(b) presents the ¹H NMR spectrum of the exposed sample of MMA/PQ/DMNA. The signals a1 (5.20 ppm), b1 (2.94 ppm), b2 (3.04 ppm), and b3 (8.06 ppm) correspond to the hydrogen atoms of the products formed through photoproducts III and IV in Figure 5. The signals for the protons of DMNA are also evident in Figure 10(a). Thus, only two photoproducts coexisted after exposure of the MMA/PQ/DMNA sample to light, and DMNA molecules were not involved in the photochemical reaction.

Next, we used XPS to analyze the environments of the nitrogen and oxygen atoms in the exposed photopolymer. Figure 11 presents the N 1s and O 1s XPS spectra of the exposed PMMA/ PQ/DMNA photopolymer. In Figure 11(a), we attribute the peaks at 399.9 and 406.2 eV to -N= and NO₂ units, respectively^{35–38}; these signals are typical for such functional groups in XPS spectra displaying the N 1s energy level. In Figure 11(b), the XPS spectrum of the O 1s energy levels displays overlapping peaks that we separated into four peaks through Gaussian deconvolution. We ascribe the peaks at 531.5 and 533.7 eV to the C=O and



Figure 10. ¹H-NMR spectra of the (a) unexposed and (b) exposed MMA/ PQ/DMNA photopolymer.



Figure 11. XPS spectra of the exposed PMMA/PQ/DMNA photopolymer: (a) N 1s and (b) O 1s energy levels.

C-O-C moieties of photoproduct IV and that at 533.1 eV to the C-OH units of photoproduct III. The single peak of PMMA appears at 532.3 eV.38,39 These signals suggest that DMNA did not react with either MMA or PQ to form new photoproducts when exposed to light, consistent with the results we obtained from FTIR and ¹H NMR spectroscopic analysis. According to our experimental data, the photoreactions of PMMA/PQ/DMNA proceeded through PQ reacting with residual MMA monomer without any involvement of DMNA. The dynamic range of the photopolymer increased because the nitroaniline molecules increased its birefringence. In the PMMA/PQ/nitroaniline systems, DMNA increased the birefringence of the photopolymer to a greater extent that did either pNA or MNA. Through this demonstration of the holographic data storage characteristics, we confirm that the properties of the PMMA/PQ photopolymer were further enhanced in the presence of DMNA.

CONCLUSIONS

The holographic data storage characteristics of PMMA/PQ photopolymers are enhanced significantly after incorporating nitroaniline compounds. From single-hologram recording experiments, we found that the diffraction efficiency of the PMMA/ PQ/DMNA photopolymer was highest among our studied photopolymer systems. Furthermore, from multiple-hologram recording tests, the PMMA/PQ/DMNA photopolymer also exhibited the largest values of M# and sensitivity. The values of η_{max} and M# improved by 1.89 and 2.70 times, respectively, after codoping DMNA into the PMMA/PQ photopolymer. FTIR, ¹H-NMR and XPS spectra of the corresponding photoproduct indicated that the DMNA units did not bond to either PQ or the MMA monomer during the synthesis of the PMMA/PQ/DMNA photopolymer. Taken together, our results indicate that increasing the birefringence of the PMMA/PQ photopolymer, through co-doping with nitroaniline compounds, can enhance the holographic recording characteristics without interrupting the original PMMA/PQ photoreaction.

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