Design, Synthesis, and Imaging Study of a Photoactive Polymer Containing Aryl Substituted Diazoketo Groups

Lu Liu, Yingquan Zou

College of Chemistry, Beijing Normal University, Beijing 100875, China

ABSTRACT: A photoactive polymer containing aryl substituted diazoketo groups was prepared by radical polymerization of methyl methacrylate, 2-hydroxyethyl methacrylate and photoactive 2-(2-diazo-3-oxo-3-(4-dimethylaminophenyl)-propionyloxy)-ethyl methacrylate. Upon UV irradiation at 365 nm, the diazoketo groups of the copolymer underwent the Wolff rearrangement and afforded ketenes that reacted with water to provide carboxylic moieties that could be removed by basic developer. It was demonstrated that this photoactive polymer could be used as a novel single component positive photoresist. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 123: 554–561, 2012

Key words: photoresists; photoactive polymers; monomers; synthesis; imaging

INTRODUCTION

Photoresists are indispensable substances in semiconductor device, microelectronic device and printed circuit board fabrication. The major required characteristic of the photoresists is that it can provide solubility difference between its exposed part and the unexposed part. The commonly used negative photoresists were rubber/bisazide-based negative photoresists. Largely due to their poor contrast, they were replaced by diazonaphthoquinone (DNQ)/ novolac based positive photoresists which exhibited high contrast, good thermal stability, good antidry etching ability and were easy to be developed.[1–3] With the switch from organic solvent developable negative photoresists to the alkaline solution soluble DNQ/novolac based positive photoresists, the growth of the photoresist market has skyrocketed. However, the DNQ/novolac based photoresists still have some drawbacks. First, the thermodynamic stability of the DNQ/novolac based photoresists in an aqueous-alkaline developer corresponds to a completely dissolved layer and their image discrimination is based on "dissolution inhibition" effect.[4] Second, novolac resin made from condensation of phenol and formaldehyde has certain polydispersity. So, at the cross sections of the unexposed and the exposed regions,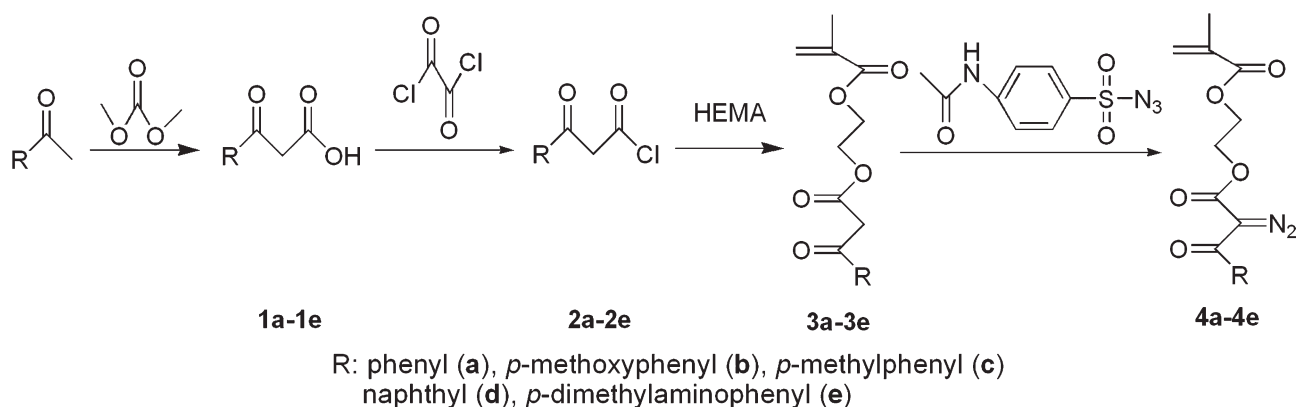 the low-molecular-weight component of the novolac resin of the unexposed regions dissolves more quickly than the high-molecular-weight component in the developer. The rate difference of dissolution is believed to be the main reason of the observed line edge roughness for novolac resin based potoresists. Moreover, properties of novolac resin are very sensitive to the conditions of its preparation process, so it is very difficult to obtain novolac resin with highly consistent properties for photoresist application, which is problematic for repeatable and precise pattern fabrications.

To solve these problems, it is desirable to develop a new photoresist which does not have to be used with novolac resin. Jin-Baek Kim has reported a diazoketo-based photoactive polymer which could be used as a single component photoresist.[5] Our goal in this investigation is to synthesize diazoketo polymer with aryl substitute groups which can be used in UV I-line (365 nm) photolithography.[6,7] Furthermore, the novel photoresist should not be dissolved in alkaline developer before UV exposure, and after exposure the diazoketo groups of the polymer underwent the Wolff rearrangement and afforded ketenes that reacted with water to become base-soluble. So the dissolving rate difference of the polymer before and after exposure will lead to excellent development latitude.

The photoactive polymer was obtained by radical copolymerization of photoactive monomer, methyl methacrylate, and 2-hydroxyethyl methacrylate. The photoactive monomer contained aryl substituted diazoketo groups and had a maximum absorption at 356 nm. In this article, the photobleaching effect, scratch resistance, and lithographic performance of the photoactive polymers were discussed.

R: phenyl (**a**), *p*-methoxyphenyl (**b**), *p*-methylphenyl (**c**)
naphthyl (**d**), *p*-dimethylaminophenyl (**e**)

Scheme 1 The synthetic scheme of the monomers 4a-4e.

EXPERIMENTAL

Material

Sodium hydride (57–63% dispersed in oil), dimethyl carbonate, acetophenone, 4′-methoxyacetophenone, 4′-methylacetophenone, 1-acetylnaphthalene, oxalyl chloride, methyl methacrylate (MMA), 2-hydroxyethyl methacrylate (HEMA), and *p*-acetamidobenzenesulfonyl azide were purchased from Alfa Aesar. 4′-dimethylaminoacetophenone was purchased from TCI (Shanghai) Development Co., Ltd. 2-diazo-1-naphthoquinone-5-sulfonyl chloride (**215** for short), 2-diazo-1-naphthoquinone-4-sulfonyl chloride (**214** for short) and BX-17 resin (**17** for short, $\overline{M} \approx 1500$) were obtained from Taixing city East Industrial Corp. (Taixing, China). DNQ/novolac plate were provided by Jiangsu Jin Ma Co., Ltd. 2,2′-azoisobutyronitrile (AIBN) was purified by recrystallization in methanol, tetrahydrofuran (THF, dried by Na), dichloromethane (dried by CaH$_2$) and acetonitrile (dried by P$_2$O$_5$) were obtained from Beijing Chemical Reagents Company (Beijing, China). All chemicals were used as received unless noted otherwise.

Measurement

The ^{1}H NMR and ^{13}C NMR spectra of the synthesized compounds were recorded on a Bruker Avame PRX400 spectrometer in CDCl$_3$. Elemental analysis was performed on a Vario El. Mass spectra were performed on a Quattro microtriple quadrupole mass spectrometer (Micromass, Manchester, UK). RTIR (Real-time infrared spectroscopy) was recorded on a Nicolet 5700 spectrometer (Nicolet Instrument, Thermo Company, USA). The irradiation was performed with the UV spot light source (Rolence-100 UV, Taiwan, China) and the light intensity at 365 nm was detected by radiometry (UV-A, Beijing Normal University, China). UV spectra were recorded with a Cintra10e spectrophotometer. Film

scratch resistance tester (QHZ) was used to measure the scratch resistance of the photoresist film. A SC-1B photoresist spinner was employed for applying the photoresist solutions onto polished silicon wafers. Exposures were carried out on a BGJ-3 exposure system in contact printing mode. Scanning electron micrograph images were obtained with a scanning electron microscope (Hitachi, *S*-4800).

Synthesis of the photoactive monomers

Five photoactive monomers (**4a-4e**) that contain aryl substituted diazoketo groups have been synthesized in this paper as shown in Scheme 1.

General procedures

Sodium hydride 10.5 g (0.25 mol) and dimethyl carbonate 16.2 g (0.18 mol) were dissolved in anhydrous THF (50 mL) and heated to 65°C. Then, aryl acetone (0.10 mol) was added to the reaction mixture dropwise and stirred at 65°C for 2 h. The solvent was removed under reduced pressure. The product obtained was hydrolyzed with aqueous solution of NaOH (0.5 mol/L, 320 mL). Then aqueous solution of HCl (6 mol/L) was added to the mixture. The precipitated acid was collected by filtration and dried under vacuum for 24 h.[8] If there is no precipitation, the mixture was extracted with dichloromethane (50 mL × 2). Organic layers were combined and washed with brine, dried over anhydrous MgSO$_4$, and solvent was removed under reduced pressure to afford corresponding acid. The acid (**1a-1e**) was used in the next step without further purification. Three drops of *N,N*-dimethyl formamide (DMF) as catalyst was added to a solution of the acid (**1a-1e**) (0.010 mol) in anhydrous dichloromethane, and oxalyl chloride 1.5 g (0.012 mol) was added to the reaction mixture at 30°C and stirred for 4 h to give acid chloride (**2a-2e**). A solution of
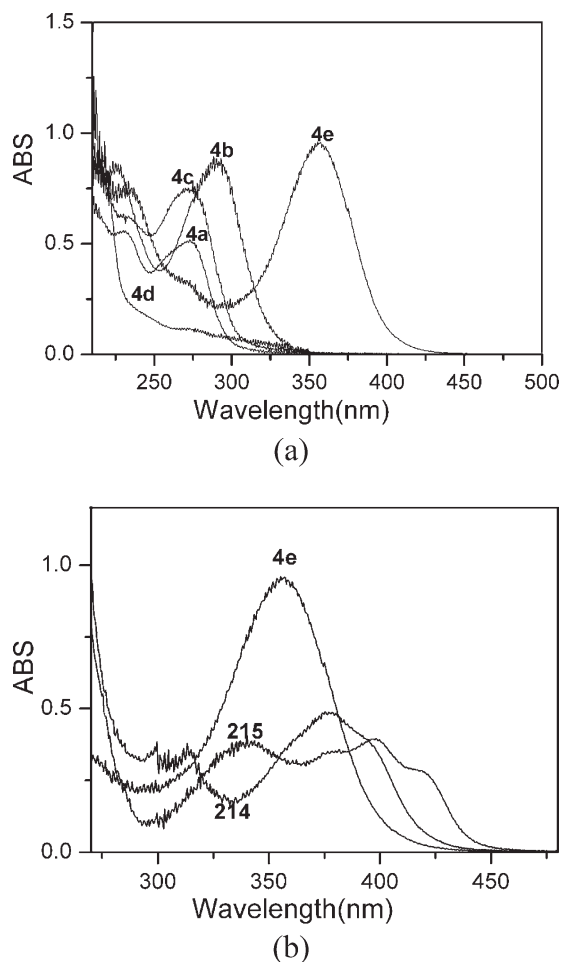
Figure 1 (a) The UV spectra of the monomers 4a-4e. (b) The UV spectra of monomer 4e, 214, and 215.

carried out with the mixture of ethyl acetate and petroleum ether (1/6, v/v) as eluent to afford 3a-3e.[9,10] A solution of *p*-acetamidobenzenesulfonyl azide 2.4 g (0.010 mol) in anhydrous acetonitrile was added to a solution of 3a-3e (0.010 mol) and triethylamine 1.5 g (0.015 mol) in acetonitrile at 0°C. The reaction mixture was stirred in nitrogen atmosphere at 0°C for 30 min and was then heated to 30°C with stirring for 3 h. Then the reaction mixture was concentrated under reduced pressure and directly applied to the top of a silica gel column. Column chromatography was carried out with the mixture of ethyl acetate and petroleum ether (1/6, v/v) as eluent to afford 4a-4e.[11–16]

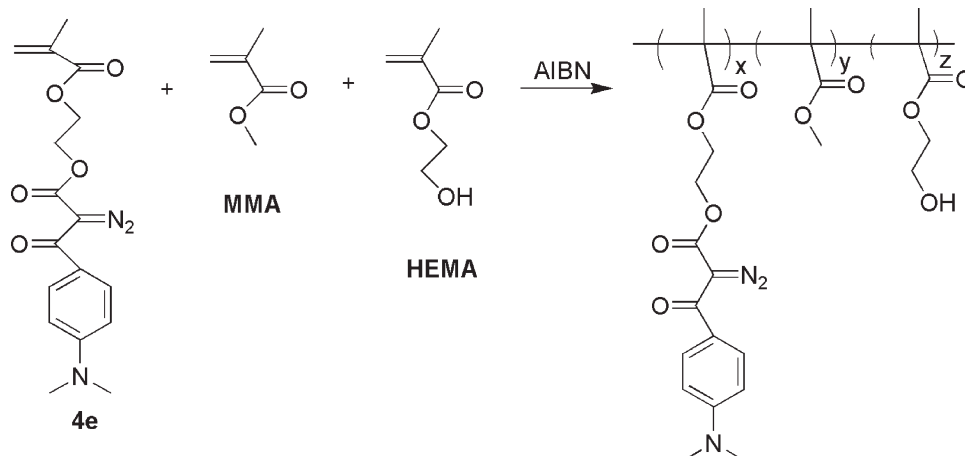The ^{1}H NMR and ^{13}C NMR spectra data of the synthesized monomers 4a-4e were summarized as follow. The carbon peaks of the diazo groups appear at 74.70–77.07 ppm in ^{13}C NMR spectra.

4a: 2-(2-diazo-3-oxo-3-phenylpropionyloxy)-ethyl methacrylate (85% yield for the last step, yellow oil)

UV (ethanol): λ_{max} (ε) = 273 nm (1.0 × 10^4 L mol^{-1} cm^{-1}). IR (KBr): 2143 cm^{-1} (s, C=N=N), 1720 cm^{-1} (s, C=O), 1631 cm^{-1} (s, C=O). ^{1}H NMR (CDCl$_3$): δ = 7.56-7.33 (m, 5H) (phenyl), 6.05 (s, 1H) and 5.55-5.54 (t, 1H) (H$_2$C =), 4.38-4.36 (m, 2H) and 4.27-4.25 (m, 2H) (O—CH$_2$CH$_2$—O), 1.88 (s, 3H) (—CH$_3$). ^{13}C NMR (CDCl$_3$): δ = 185.56 (C=O), 165.96 (C=O), 159.73 (C=O), 136.00, 134.82, 131.35, 127.33, 126.88, and 125.18 (phenyl and C=C), 75.28 (C=N$_2$), 62.05 and 61.04 (O—CH$_2$CH$_2$—O), 17.21 (—CH$_3$).

4b: 2-(2-diazo-3-oxo-3-(4-methoxyphenyl)-propionyloxy)-ethyl methacrylate (80% yield for the last step, yellow solid)

UV (ethanol): λ_{max} (ε) = 291 nm (1.8 × 10^4 L mol^{-1} cm^{-1}). IR (KBr): 2143 cm^{-1} (s, C=N=N), 1716 cm^{-1} (s, C=O), 1631 cm^{-1} (s, C=O). ^{1}H NMR (CDCl$_3$):

2-hydroxyethyl methacrylate 3.2 g (0.025 mol) and triethylamine was added to the reaction mixture at room temperature and stirred for another 4 h. Then the reaction mixture was concentrated under reduced pressure and directly applied to the top of a silica gel column. Column chromatography was

Scheme 2 The synthetic scheme of the polymers.

TABLE I
Radical Polymerization of Monomer 4e, MMA, and HEMA[a]

Polymer	Molar feed ratio (monomer 4e/MMA/HEMA)	Copolymer composition[b] (monomer 4e/MMA/HEMA)	Yield (%)
A	100 : 0 : 0	100 : 0 : 0	79.5
B	50 : 50 : 0	51 : 49 : 0	80.1
C	50 : 30 : 20	52 : 30 : 18	82.5

[a] Polymerizations were carried out at 65°C for 24 h in THF; number-average molecular weight was designed to be 2000; The amount of AIBN was determined by the designed number-average molecular weight; M/S (the ratio of the weight of monomer relative to the weight of solvent) is five in all cases.
[b] Determined by integration of the corresponding peaks in the ^{1}H NMR spectra.

δ = 7.68-7.66 (d, 2H) and 6.92-6.90 (d, 2H) (phenyl), 6.13 (s, 1H) and 5.63 (s, 1H) (H$_2$C =), 4.47-4.45 (t, 2H) and 4.37-4.36 (t, 2H) (O—CH$_2$CH$_2$—O), 3.87 (s, 3H) (O—CH$_3$), 1.96 (s, 3H) (—CH$_3$). ^{13}C NMR (CDCl$_3$): δ = 185.08 (C=O), 167.02 (C=O), 163.22 (C=O), 161.07, 135.77, 131.07, 129.19, 126.31, and 113.15 (phenyl and C=C), 75.77 (C=N$_2$), 62.79 and 62.11 (O—CH$_2$CH$_2$—O), 55.44 (O—CH$_3$), 18.29 (—CH$_3$).

4c: 2-(2-diazo-3-oxo-3-(4-methylphenyl)-propionyloxy)-ethyl methacrylate (81% yield for the last step, yellow solid)

UV (ethanol): λ_{max} (ε) = 272 nm (1.5 × 10^4 L mol^{-1} cm^{-1}). IR (KBr): 2111 cm^{-1} (s, C=N=N), 1722 cm^{-1} (s, C=O), 1642 cm^{-1} (s, C=O). ^{1}H NMR (CDCl$_3$): δ = 7.48-7.47 (d, 2H) and 7.16-7.14 (d, 2H) (phenyl), 6.05 (s, 1H) and 5.55 (s, 1H) (H$_2$C =), 4.39-4.36 (t, 2H) and 4.29-4.27 (t, 2H) (O—CH$_2$CH$_2$—O), 2.33 (s, 3H) (ph-CH$_3$), 1.88 (s, 3H) (—CH$_3$). ^{13}C NMR (CDCl$_3$): δ = 185.30 (C=O), 165.97 (C=O), 159.84 (C=O), 142.27, 134.73, 133.09, 127.57, 127.56, and 125.29 (phenyl and C=C), 74.95 (C=N$_2$), 61.96 and 61.07 (O—CH$_2$CH$_2$—O), 20.68 (ph-CH$_3$), 17.26 (—CH$_3$).

4d: 2-(2-diazo-3-oxo-3-naphthylpropionyloxy)-ethyl methacrylate (75% yield for the last step, yellow oil)

UV (ethanol): λ_{max} (ε) = 215 nm (3.6 × 10^4 L mol^{-1} cm^{-1}). IR (KBr): 2143 cm^{-1} (s, C=N=N), 1721 cm^{-1} (s, C=O), 1633 cm^{-1} (s, C=O). ^{1}H NMR (CDCl$_3$): δ = 7.89-7.38 (m, 7H) (naphthyl), 5.95 (s, 1H) and 5.49 (s, 1H) (H$_2$C =), 4.22-4.20 (t, 2H) and 4.03-4.00 (t, 2H) (O—CH$_2$CH$_2$—O), 1.81 (s, 3H) (—CH$_3$). ^{13}C NMR (CDCl$_3$): δ = 186.72 (C=O), 165.84 (C=O), 159.30 (C=O), 134.63, 134.21, 132.33, 130.23, 128.75, 127.52, 126.28, 125.36, 125.23, 124.58, 123.41, and 123.30 (naphthyl and C=C), 77.07 (C=N$_2$), 61.94 and 60.86 (O—CH$_2$CH$_2$—O), 17.21 (—CH$_3$).

4e: 2-(2-diazo-3-oxo-3-(4-dimethylaminophenyl)-propionyloxy)-ethyl methacrylate (70% yield for the last step, yellow solid)

UV (ethanol): λ_{max} (ε) = 356 nm (1.9 × 10^4 L mol^{-1} cm^{-1}). IR (KBr): 2110 cm^{-1} (s, C=N=N), 1723 cm^{-1}
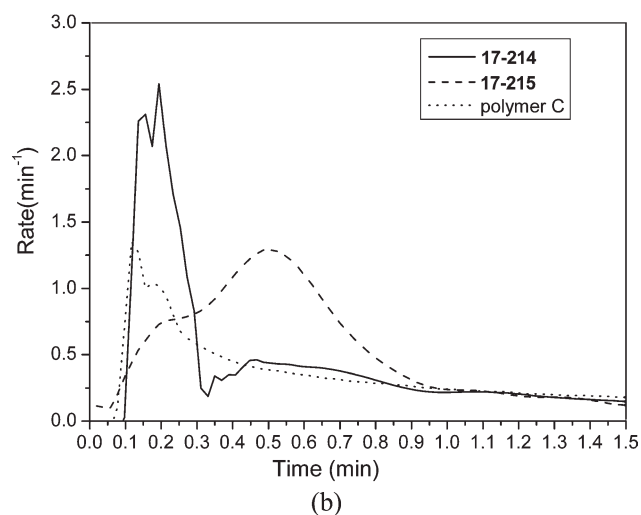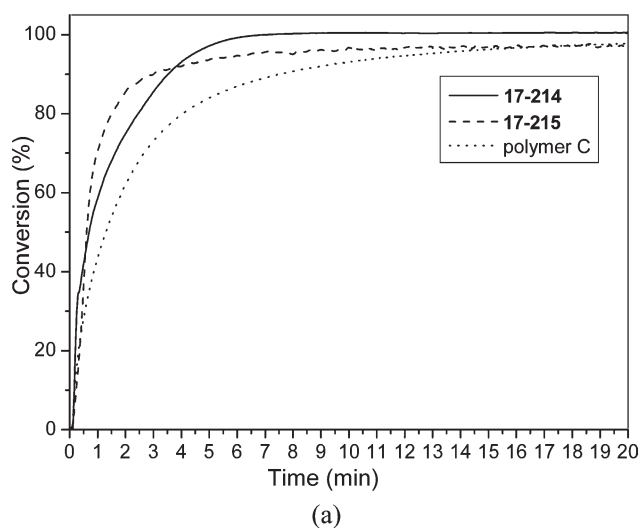

Figure 2 (a) The conversion of the diazo group of the photoactive compounds. (b) The conversion rate of the diazo group of the photoactive compounds.

(s, C=O); 1627 cm^{-1} (s, C=O). ^{1}H NMR (CDCl$_3$): δ = 7.60-7.58 (d, 2H) and 6.66-6.63 (d, 2H) (phenyl), 6.06 (s, 1H) and 5.54 (s, 1H) (H$_2$C =), 4.40-4.38 (t, 2H) and 4.31-4.29 (t, 2H) (O—CH$_2$CH$_2$—O), 2.99 (s, 6H) (—N(CH$_3$)$_2$), 1.88 (s, 3H) (—CH$_3$). ^{13}C NMR (CDCl$_3$): δ = 183.80 (C=O), 167.00 (C=O), 161.54 (C=O), 153.06, 135.85, 131.29, 126.20, 126.14, and 110.69 (phenyl and C=C), 74.70 (C=N$_2$), 62.79 and 62.19 (O—CH$_2$CH$_2$—O), 40.33 (—N(CH$_3$)$_2$), 18.21 (—CH$_3$). C$_{17}$H$_{19}$O$_5$N$_3$ (345.36): Calcd. N 12.17, C 59.12, H 5.545; Found. N 11.97, C 58.97, H 5.012. MS (ESI): m/z: Calcd. for C$_{17}$H$_{19}$O$_5$N$_3$ (M + H$^+$) 346.3; Found 346.3.

Polymerization

The polymers were synthesized by free radical polymerization in the nitrogen atmosphere. Monomers and AIBN were dissolved in THF, and the resulting mixture was heated at 65°C for 24 h. After the polymerization, the solutions were precipitated in petroleum ether. The precipitated polymers were collected by filtration and dried under vacuum for 24 h.[17]

The comparison of the sensitivity of polymer C, 17-214, and 17-215

Ester **17-214** was obtained via condensation reaction of **17** novolac resin and **214**. **17-215** was obtained in the similar manners. They are commonly used as photoactive compounds in the DNQ/novolac based photoresists. **17-214**, **17-215** and polymer C were dissolved in THF with the same concentration of the diazo groups. A drop of the resulting solution was applied on NaCl crystal and exposed to UV radiation using a spot light source at room temperature. The intensity of UV radiation on the surface of the samples was 30 mW cm^{-2}. A series of RTIR measurements were carried out to determine the conversion rate of the diazo groups. The degree of the conversion of the diazo groups could be calculated by measuring the peak area at each time of the reaction and determined by using the following equation:

$$\text{Conversion}\% = [1 - (A_t/A_0)] \times 100\%$$

Where conversion is the diazo group's conversion at time t. A_0 and A_t are the peak areas of the functional group before and after irradiation at time t. The conversion rate could be determined from the differential of the curve of conversion versus irradiation time.[18]

The UV spectra of the polymers exposed after definite time intervals

The polymers were dissolved in THF and coated on the inside of the quartz cuvette. A film of the
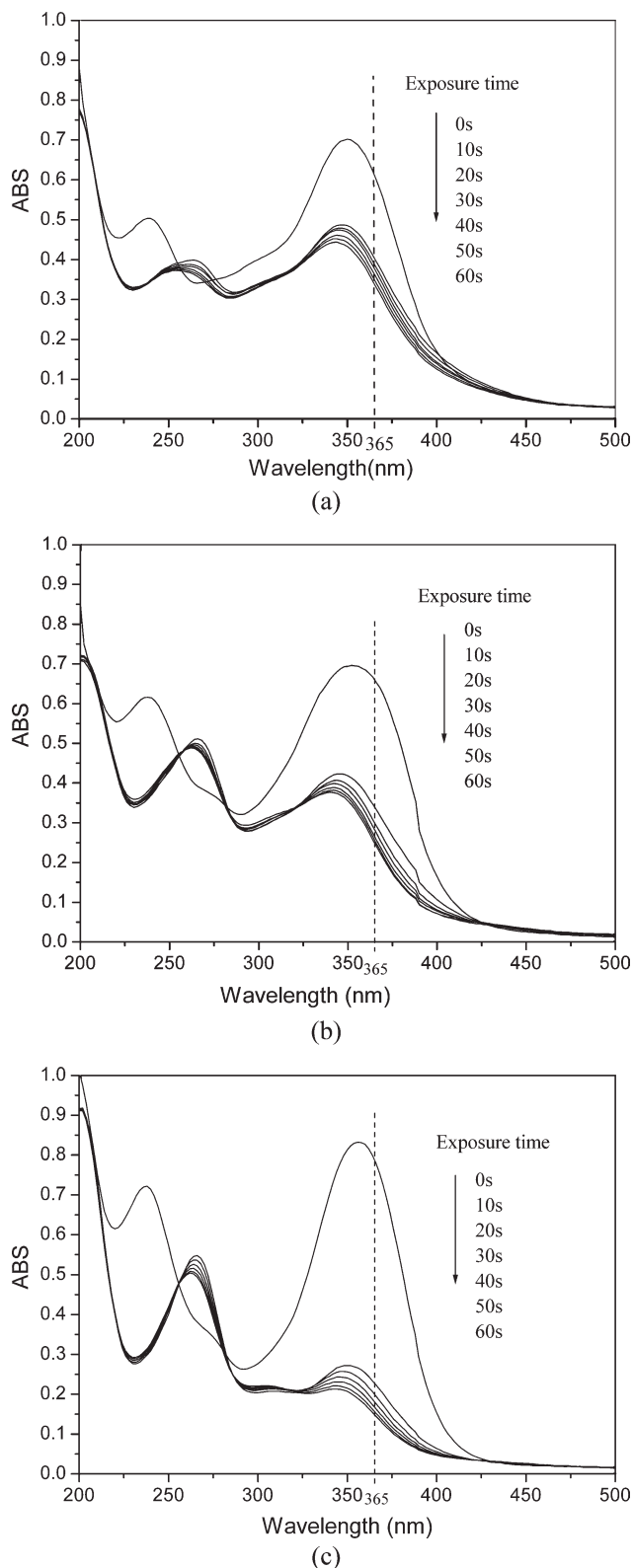

(a)

(b)

(c)

Figure 3 (a) The UV spectra of polymer A exposed after definite time intervals. (b) The UV spectra of polymer B exposed after definite time intervals. (c) The UV spectra of polymer C exposed after definite time intervals.
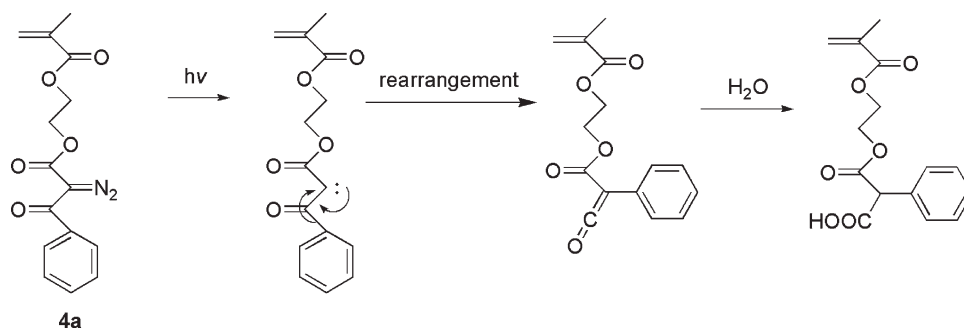
Figure 4 The mechanism of the photoreaction of monomer 4a.

polymer under test was formed after the solvent was evaporated. The UV absorbance of the film was measured after every 10 s of exposure to UV irradiation. The light intensity at 365 nm is 30 mW cm^{-2}. From the film's absorbance values before and after exposure at 365 nm, the sample's degrees of photobleaching were calculated.

Photoreaction and its mechanism

A solution was prepared by dissolving 0.05 g monomer **4a** in 10 mL CDCl$_3$. The sample was exposed to UV irradiation at 254 nm in a photoreactor for 120 min. The ^{1}H NMR spectra before and after exposure were recorded. For FT-IR studies, monomer **4a** was coated on a NaCl cell and FT-IR spectra were recorded.

Scratch resistance and lithographic evaluation

A solution was prepared by dissolving 0.2 g polymer in 2.0 g cyclohexanone. The polymer solution was filtered through 0.2 μm membrane before spincoated onto an aluminum plate. The scratch strength was enhanced by adding the poises to the tester. Until the strength was big enough to scratch up the

film with the indicator, the weight of the poises showed the scratch resistance of the film. For the investigation of lithographic evaluation, the polymer film was prepared by spin-coating of the polymer solution onto a silicon wafer and prebaked at 100°C for 90 s. UV exposure was carried out in contact printing mode. After exposure, the wafer was developed by dipping in a 2.38 wt % tetramethylammonium hydroxide aqueous solution. The pattern profile was obtained with a Hitachi-SEM.

RESULTES AND DISCUSSION

Synthesis of the photoactive monomers

The photoactive monomers with aryl substitute group (phenyl, *p*-methoxyphenyl, *p*-methylphenyl, naphthyl, *p*-dimethylaminophenyl) have been designed, synthesized and fully characterized.

The UV spectra of the monomers **4a-4e** are shown in Figure 1(a). The introduction of aryl groups lead to the red shift of the maximum-absorption. It is shown that the order of the ability of the five substitute groups from weak to strong is naphthyl, *p*-methylphenyl, phenyl, *p*-methoxyphenyl, *p*-dimethylaminophenyl. Specially, the maximum-absorption wavelength of
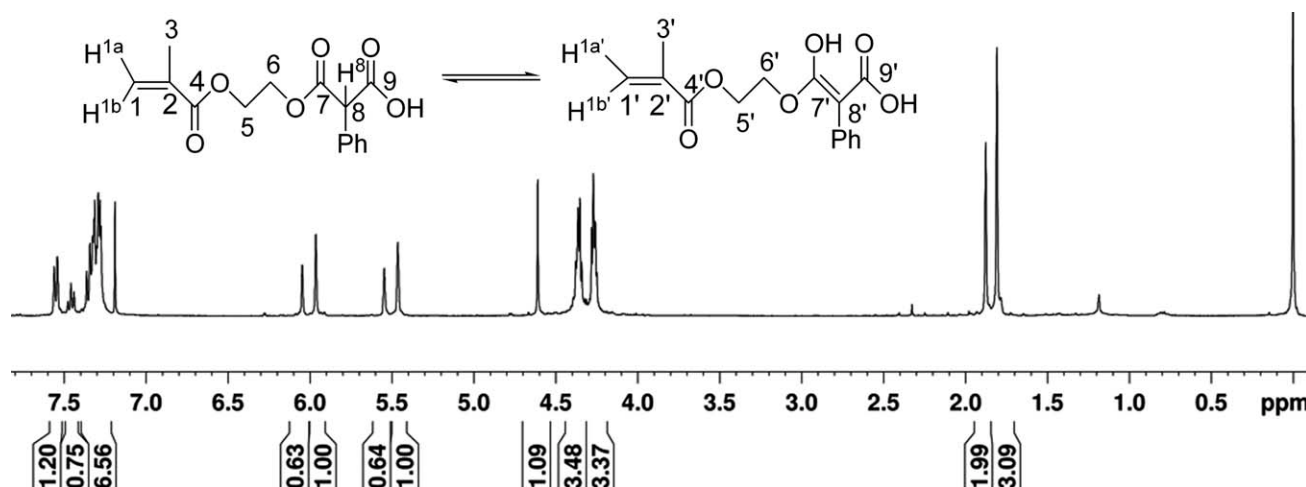

Figure 5 The ^{1}H NMR spectrum of the product of the photoreaction of monomer 4a.
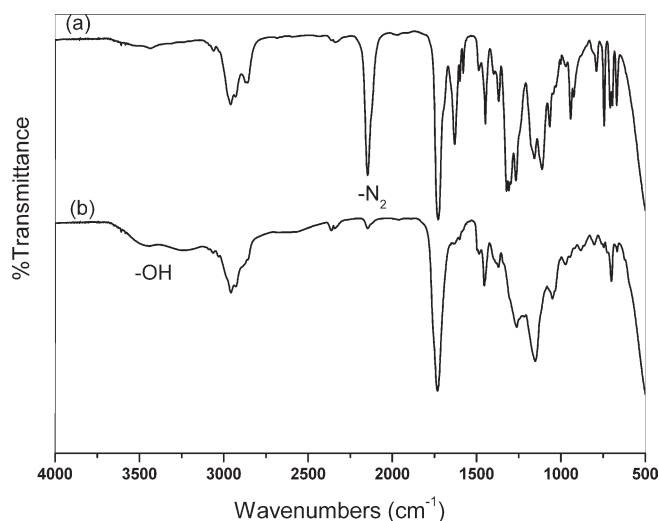
Figure 6 The FT-IR spectra of monomer 4a before and after irradiation.

monomer **4e** has been moved to 356 nm, and it still has a relatively strong absorption at 365 nm which suggested that it could be used as the photoactive component in the development of a new I-line photoresist. Figure 1(b) is the UV spectra of monomer **4e**, **214**, and **215** with the same molar concentration. It proves that monomer **4e** has stronger absorption than **214** and **215** which are used as the photoactive components in traditional I-line photoresists at 365 nm.

Polymerization

The synthetic method of the photoactive polymers is shown in Scheme 2. Copolymers of monomer **4e**, MMA and HEMA with various compositions were prepared by AIBN initiated free radical polymerization. The monomers MMA and HEMA are used to enhance the adhesion properties of the resulting polymers.

Polymer A: IR (KBr): 2141 cm^{-1} (s, C=N=N), 1726 cm^{-1} (s, C=O), 1595 cm^{-1} (s, C=O). Polymer B: IR (KBr): 2141 cm^{-1} (s, C=N=N), 1728 cm^{-1} (s, C=O), 1596 cm^{-1} (s, C=O). Polymer C: IR (KBr): 3435 cm^{-1} (s, —OH), 2141 cm^{-1} (s, C=N=N), 1726 cm^{-1} (s, C=O), 1595 cm^{-1} (s, C=O). The composition results are summarized in Table I. The polymerization yields were 79.5–82.5%.

The comparison of the sensitivity of polymer C, 17-214, and 17-215

RTIR spectroscopy has become an important method for obtaining kinetics data of photo-transformations. The photoreaction rate of the compound was monitored by the change of the absorption area of the diazo group peaks around 2140 cm^{-1} with OMINIC 7.0 software. Upon irradiation, the decrease rate of

the absorption peak area of the diazo group reflected the photoreaction rate of the compound.[18]

Upon UV irradiation, the conversion of **17-214**, **17-215** and polymer C are 68, 80, and 54% respectively, at 90 s. After 4 min, the conversions of the three photoactive compounds all achieved 80% [Fig. 2(a)]. Polymer C used the least time to reach its highest conversion rate and its highest conversion rate was lower than that of **17-214** but slightly higher than that of **17-215** [Fig. 2(b)]. Conversion data suggested that though polymer C's sensitivity is lower than the traditional photoactive compound **17-214** and **17-215**, it still could reach the conversion of 54% at 90 s, which means that polymer C's sensitivity is high enough to be used as I-line photoresists.

The UV spectra of the polymers exposed after definite time intervals

Figure 3(a) shows the UV spectra of polymer A which was exposed for 0, 10, 20, 30, 40, 50, and 60 s, respectively. The absorbance of the polymer at 365 nm gradually decreased with the increase of the exposure time. At the first 10 s, polymer A's photoreaction rate is the fastest. And the condition is the same for polymer B [Fig. 3(b)] and polymer C [Fig. 3(c)]. The result is consistent with the decomposition rate of the diazo groups which was detected by the RTIR. Upon irradiation for 60 s, the absorbances of the polymers were decreased by 46–84% at 365 nm. The polymers showed excellent bleaching effect.

Photoreaction and its mechanism

The mechanism of the photoreaction of the monomer, take monomer **4a** as an example, is shown in Figure 4. Upon irradiation, the diazoketo groups
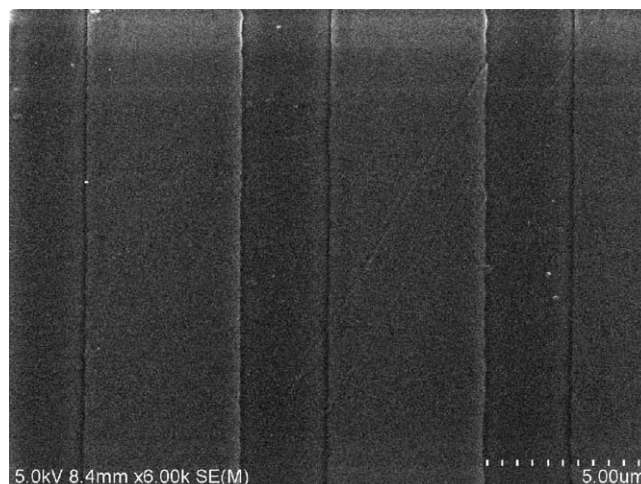

Figure 7 The scanning electron micrograph of 3 μm line and space patterns printed with polymer C.

underwent the Wolff rearrangement and afforded ketenes that reacted with water to provide base-soluble products. So the exposed part dissolved more quickly than the unexposed part and a positive image was obtained after development.

The mechanism of the photoreaction was studied with ^{1}H NMR spectroscopy. The product of the photoreaction of monomer **4a** undergoes ketone-enol tautomerism (Fig. 5). As is shown in Figure 5, $\delta = 5.96$ (s, 1H) and 5.46 (d, 1H) (H^{1a} and H^{1b}), 4.61 (s, 1H) (H^8), 1.81 (s, 3H) ($-C^3H_3$) are the peaks of the ketone form. $\delta = 6.05$ (s, 0.63H) and 5.54 (d, 0.64H) ($H^{1a'}$ and $H^{1b'}$), 1.87 (s, 1.99H) ($-C^{3'}H_3$) are the peaks of the enol form. Among which, $\delta = 4.61$ (s, 1H) integral peak is formed by H^8 in the ketone form. In contrast, it doesn't appear in the enol form since the absence of $H^{8'}$ in the enol form. The ratio of the abundance of the enol form relative to the abundance of the ketone form is 0.64. Since the chemical shift values of the enol form of phenyl are close to that of the ketone form, the integral peaks of the two forms overlapped and the integral area of the phenyl at $\delta = 7.56$-7.28 (m, 8.51H) is the summation of the two forms. And so do the integral peaks of the two methylenes, $\delta = 4.36$-4.35 (m, 3.48H) (C^5H_2 and $C^{5'}H_2$) and $\delta = 4.28$-4.26 (m, 3.37H) (C^6H_2 and $C^{6'}H_2$). This mechanism is further proved by the FT-IR spectrum of monomer **4a**. After irradiation, the intensity of the absorption at 2143 cm^{-1}, which arises from the diazo group, decreased sharply. In contrast, at 3100–3600 cm^{-1} appeared the absorption which arose from the hydroxyl of the carboxylic acid unit (Fig. 6).

Scratch resistance and lithographic evaluation

The scratch resistance of the single component photoresist film was 700–750 g, in contrast the scratch resistance of the traditional DNQ/novolac film was 650–700 g. As is shown in Figure 7, 3 μm line and space patterns were obtained with polymer C.

CONCLUSIONS

We designed and synthesized a new type of photoactive polymer with aryl substituted diazoketo groups. By changing the monomer's substitute group, the maximum-absorption wavelength of the photoactive monomer **4e** has been moved to 356 nm. It also has larger absorption at 365 nm than **214** and **215**, photoactive components of the traditional I-line photoresists. Upon irradiation, diazoketo groups undergo a series of reactions that complete in the formation of a carboxylic acid. The polymer in the exposed region becomes more soluble in the aqueous base developer. The photoresists formulated with poly (monomer **4e**-co-MMA-co-HEMA) could be used as I-line single component photoresists. Since our photoactive polymer does not have to be used with novolac resin together, it will not suffer the problems (low development latitude, large line edge roughness) arisen from using novolac resin as binder. The polymer film showed good bleaching effect and strong scratch resistance. After exposure, 3 μm line and space patterns were obtained. This kind of photoactive polymer should have great potential as a new positive photoresist in TFT-LCD and IC discrete devices fabrication processes.

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