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Novel One-Component Positive-Tone Chemically Amplified I-Line Molecular Glass Photoresists

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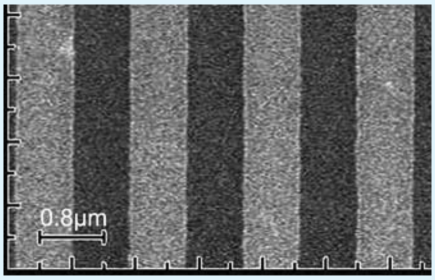

ABSTRACT: Maleopimaric acid, cycloaddition reaction product of rosin with maleic anhydride, was reacted with hydroxylamine to afford *N*-hydroxy maleopimarimide, which was then further esterified with 2-diazo-1-naphthoquinone-4-sulfonyl chloride (2,1,4-DNQ-Cl) to give *N*-hydroxy maleopimarimide sulfonate. The carboxylic acid group of the compound was then protected by the reaction of this compound with vinyl ether compounds to give the corresponding molecular glass compounds. Upon irradiation to 365 nm light, the 2,1,4-DNQ group undergo photolysis not only to be converted into indene carboxylic acid but also generate a few amount of sulfonic acid which can catalyze the deprotection of the acid labile group. So, novel one-component positive-tone chemically amplified i-line photoresists can be formed by the molecular glass compounds. The lithographic performance of the resists was evaluated using i-line exposure system with high photosensitivity and resolution.

KEYWORDS: *photoresist, molecular glass, chemically amplified, i-line, photolithography*

INTRODUCTION

In microlithography, the life of traditional near-UV lithography was extended with the improvements in exposure tools and photoresist materials. Accordingly, i-line lithography has been brought to the brink of quarter-micrometer.[1] On the photoresists side, novolac resins used as the matrix polymers are applied to DNQ-novolac based positive photoresists, which are still the workhorses of the semiconductor industry for their high contrast, good thermal stability, excellent resistance to dry-etching and absence of swelling during development.[2,3] However, the novolac based photoresist system has its performance limitations. The preparation of novolac resins from acid-catalyzed condensation of phenols and formaldehyde cannot be very well controlled to give products with constant and reproducible properties. In addition, novolac resins have different bond types, changing molecular weight and broad molecular weight distribution. These factors are unfavorable to the lithographic performance of the i-line resists and make it a difficult work to obtain DNQ-novolac based i-line resists with high performance both in laboratory preparation and industrial manufacture.[4−6]

Increasing attention has been given to amorphous low molecular weight compounds termed molecular glasses as new resist materials.[7−15] In contrast to linear polymers, molecular glasses have the characteristic properties of small molecules, such as well-defined molecular structures, definite molecular weights without any distribution and lack of chain entanglement. High-resolution patterns with lower line edge roughness (LER) can be obtained in the lithographic experiments of molecular glass resists due to their small molecular size compared to polymeric resists.[16] Therefore, molecular glass photoresists are outstanding candidates for resist materials in the next generation lithography. Some i-line molecular glass photoresist materials have also been studied with high performance.[17,18]

The performance advantages of chemically amplified (CA) photoresists, compared to DNQ-novolac chemistry, are demonstrated by their high sensitivity and resolution. In recent decade, CA resists had occupied a dominant position both in research and commercial production for KrF laser (248 nm) and ArF laser (193 nm) lithography. Reports on chemically amplified i-line resists are relatively very few and one of the reason is that most of photoacid generators (PAGs) used in CA resists usually absorb light below 300 nm.[19] However, it was reported that 2,1,4-DNQ sulfonates can also generate sulfonic acid after exposed to 365 nm UV light.[2] Making use of the speciality of 2,1,4-DNQ sulfonates we try to design new type of CA molecular glass i-line resists with the compounds as PAG.

One-component resists have received wide attention recently, including chemically amplified[20−23] and nonchemically amplified system.[24−26] The former incorporates the photoacid generating units into the matrix polymers and is expected to alleviate the problems caused by the poor compatibility between the PAGs and the polymer matrix, such as phase separation and nonuniform acid distribution, and accordingly, improve the lithographic performance. In this study, based on our previous work on nonionic photoacid generator,[27] molecular glass compounds containing 2,1,4-DNQ sulfonate group, which was expected to function as PAG, and acid labile group were designed and prepared (Scheme 1). The characterization and photoactive properties of the compounds were investigated, as well as lithographic performance of the

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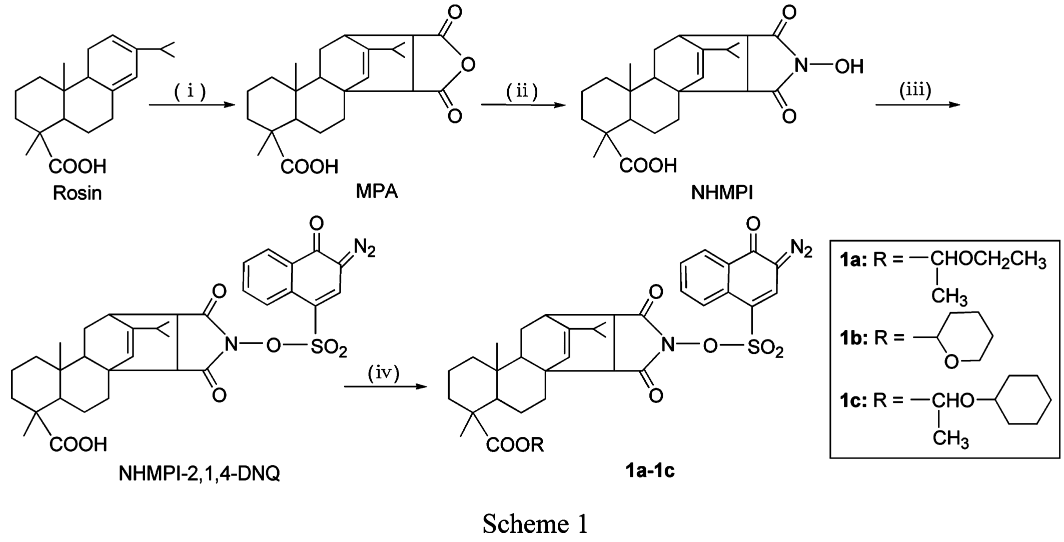
Scheme 1. Preparation of Molecular Glass Compounds 1a−1c[a]



[a] (i) maleic anhydride, N_2, 160−180 °C, 6 h; (ii) hydroxylamine, rt, 1 h and 45 °C, 2 h; (iii) 2,1,4-DNQ-Cl, triethylamine, rt, 3-4 h; (iv) vinyl ether compounds, 50−60 °C, 3-4 h.

one-component i-line resists formulated with the molecular glass compounds.

■ RESULTS AND DISCUSSION

Preparation. The preparation of compounds **1a−1c** is shown in Scheme 1. MPA was prepared by the Diels-Alder reaction of rosin with maleic anhydride according to the literature.[28] The preparation of NHMPI was not reported other than our previous work.[27] The *N*-hydroxyl group of NHMPI was easily esterified with 2,1,4-DNQ-Cl to give NHMPI-2,1,4-DNQ employing triethylamine as a base. The reaction is similar to the esterification reaction of phenolic compounds since the *N*-hydroxyl group of NHMPI shows weak acidity. Compounds **1a−1c** were prepared by the electrophilic addition reaction of the carboxylic group of NHMPI-2,1,4-DNQ with vinyl ether compounds. Usually, the reactions of the carboxylic group with vinyl ether compounds were carried out in the presence of organic strong acids as catalyst, such as *P*-toluenesulfonic acid (PTSA). However, these reactions are too sensitive to the amount of strong acid catalysts to be well controlled, because strong acids can lead to the decomposition of the protected group, resulting in the incompleteness of the reaction. Herein, the protection reaction of the carboxylic group was conducted by heating in the presence of excess of vinyl ether compounds without strong acid catalyst. The reaction can be investigated by TLC and the FTIR spectra of reactants and products. As an example, the FTIR spectra of NHMPI-2,1,4-DNQ and **1c** are shown in Figure 1. The characteristic absorption bands of carboxylic group of NHMPI-2,1,4-DNQ at 3400−3000 cm^{-1} and 1694 cm^{-1} gradually decreased and finally disappeared as the reaction proceeded, whereas a new absorption peak formed at 1715 cm^{-1}, indicating the presence of carbonyl group of ester. The results indicate that the carboxylic group of NHMPI-2,1,4-DNQ was converted into the ester acetal group, affording the corresponding protected compound. The reactions are very slow and even need a few days to finish at room temperature. Higher temperature can accelerate the reaction. All the reactions can be finished in a few hours when the reaction temperatures were raised to 50−60 °C. The experimental results show that the reactivity of the vinyl ether compounds varies according to VEE > CVE > DHP. The difference in the reactivity of vinyl ether compounds can be correlated to the electron-donating ability of their corresponding alkyl group and the effect of spatial hindrance.

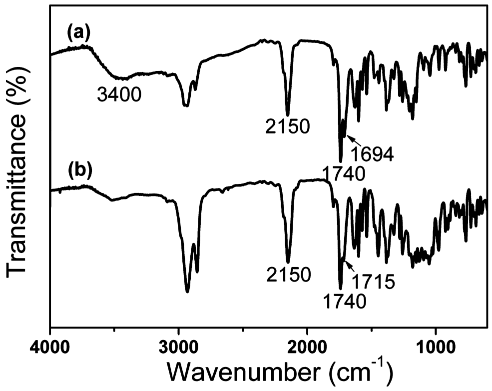


Figure 1. FTIR spectra of (a) NHMPI-2,1,4-DNQ and (b) **1c** films cast on a NaCl plate from acetone.

Characterization of Molecular Glass Compounds. Solubility is one of the important requirements for resist materials. The compounds **1a−1c** showed good solubility in common organic solvents such as acetone, ethyl lactate, N, N-dimethylformamide (DMF), tetrahydrofuran (THF), ethylene glycol monoethyl ether, PGMEA and cyclohexanone. The solubility of the compounds in high polar protic solvents, such as methanol, ethanol, and water, is quite low.

The thermal behavior of the compounds **1a−1c** was investigated by TGA and DSC. The TGA of all compounds showed a one-stage decomposition process. The compounds began to decompose around 125 °C. To explore the thermal decomposition behavior, we measured the TGA of the product (NHMPI-CVE) of the reaction of compound NHMPI with CVE, in which the *N*-hydroxyl group and the carboxylic group were both reacted with CVE, and show it in Figure 2. It can be seen that the compound began to decompose around 160 °C, suggesting that the protected carboxylic group will not break up

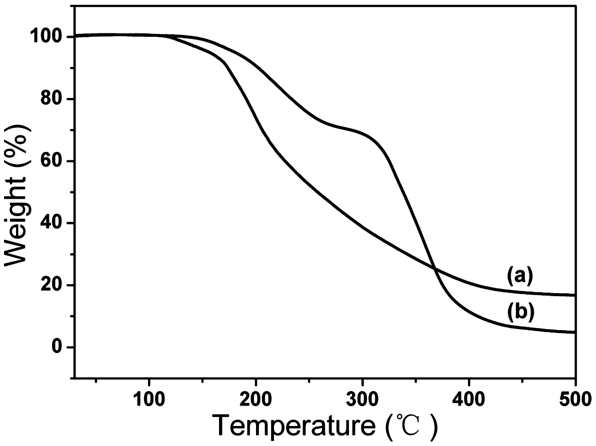


Figure 2. TGA curves of (a) **1c** and (b) NHMPI-CVE.

below this temperature. As an example, the TGA curve of **1c** showed that the compound began to decompose around 125 °C, which corresponds to the decomposition of the diazo group, and the weight decreased slightly until it reached around 160 °C, which corresponds to the decomposition of the protecting group, and then the weight decreased drastically. The TGA of the compounds exhibited a one-stage decomposition process due to the decomposition of the protecting group occurred as the decomposition of the diazo group proceeded. DSC measurements were done for the compounds **1a**−**1c** and showed no apparent T_g before the onset of decomposition. The bulky DNQ group and the hydrophenanthrene skeleton of rosin probably restrict molecular motion. This is similar to that reported previously for molecular glass compounds.[29]

Low molecular weight organic compounds are more likely to crystallize than polymers.[7] Thus, a major challenge in developing molecular glass resists is that the low molecular weight organic compounds can form stable amorphous phase above room temperature. The amorphous character of the compounds **1a**−**1c** was characterized using PXRD. The traces from the compounds show one broad amorphous peaks with maxima around 15° (Figure 3), indicating that the compounds are fully amorphous. This is because of the bulky asymmetric structure of compounds. Therefore, the compounds are suitable for spin-coating to form stable, uniform, and amorphous thin films from the organic solution, displaying good film formability.

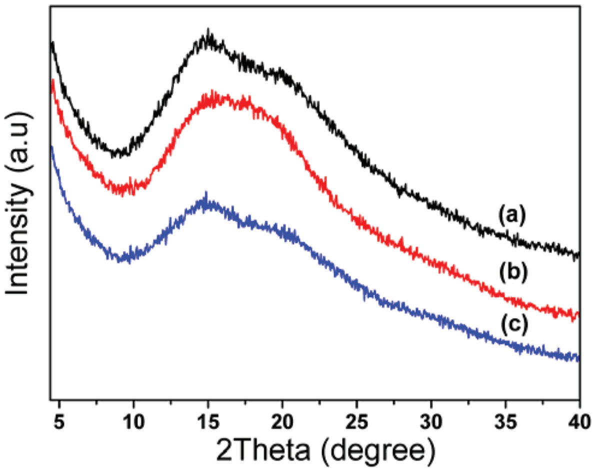


Figure 3. PXRD traces of (a) **1a**, (b) **1b**, and (c) **1c**.

Photoactive Properties and Deprotection of Molecular Glass Compounds. The photoactive properties of DNQ sulfonates to UV light are well known. Figure 4 shows the UV spectra change of **1a** film before and after exposure to 365 nm light with different doses. With the increase of the exposure dose, the absorbance at 365 nm decreased dramatically. It shows high photospeed and excellent photobleaching effect, which benefit the performance of resist materials. The photobleaching effect also benefits from the transparency of the parent compound.

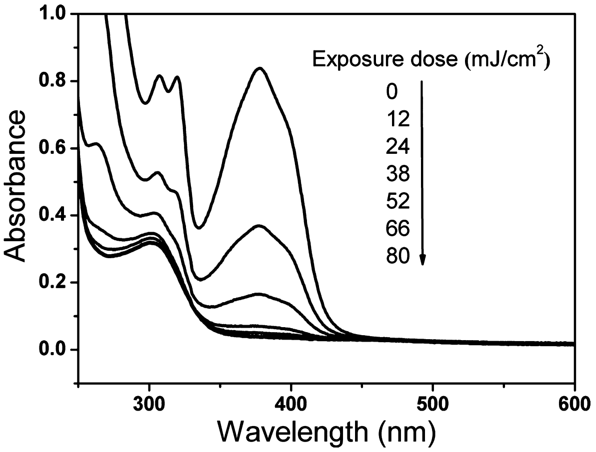


Figure 4. UV spectra change of **1a** film before and after exposure to 365 nm light with different doses.

It was reported that the photolysis of 2,1,4-DNQ sulfonates can generate sulfonic acid, which does not occur in 2,1,5-DNQ sulfonates.[30] Aromatic sulfonic acids are strong acid and can catalyze usual deprotection reactions in chemically amplified resist system. The photochemical reaction of compounds **1a**−**1c** was studied by measuring their FTIR spectra before and after exposure to 365 nm UV light. As an example, Figure 5 shows the FTIR spectra change of **1b** film cast on a NaCl plate before and after exposure to light. It can be seen that the intensity of the absorption peak at 2150 cm^{-1}, which was assigned to the diazo group, decreased remarkably after

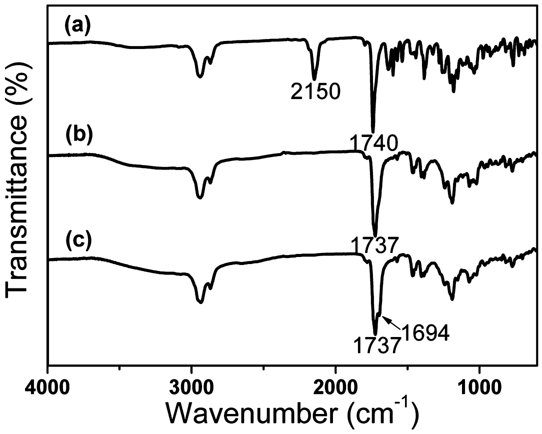
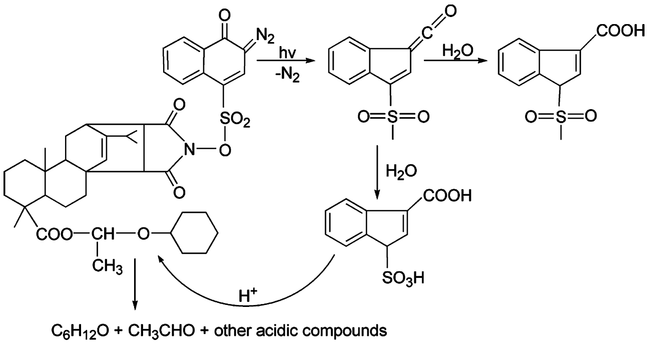


Figure 5. FTIR spectra change of **1b** film (a) before exposure, (b) after exposure (dose = 120 mJ/cm^2) without post-exposure bake, and (c) after exposure and baked at 100 °C for 60 s.

irradiated because of the photodecomposition of diazo group. On the other hand, the absorption peak at 1694 cm^{-1} appeared after exposure and baked at 100 °C for 60 s. This suggests that the deprotection reaction occurred during post exposure bake to give the corresponding carboxylic group. The results also demonstrate that the amount of the sulfonic acid generated in the photolysis process of the 2,1,4-DNQ sulfonates is small, because a large amount of sulfonic acid will result in a fully deprotection reaction under the above experimental condition.

The chemistry of the exposed area can be drawn in Scheme 2 using **1c** as an example. Upon irradiation, the DNQ group underwent Wolff rearrangement, followed by hydrolysis to the indene carboxylic acid. Furthermore, the 2,1,4-DNQ sulfonate also yield a small amount of sulfonic acid,[2,31] which catalyzed the deprotection of the acid-labile ester acetal group to give cyclohexanol, aldehyde and other acidic compounds,[32,33] providing base-soluble products. Therefore, the significant polarity change can generate a large solubility difference between the exposed area and the unexposed area in aqueous base developer, affording a working positive-tone chemically amplified photoresist system.

Scheme 2. Chemistry of the Exposed Area of the Film Formed by 1c



Lithographic Evaluation. For molecular glass resists, a problem frequently encountered is low T_g which will affect the strength of the resist patterns. Although the T_g values of compounds **1a**−**1c** were not determined, the softening temperatures of the films formed by the compounds are quite different. Among these compounds, the film of **1a** cast on glass plate was found deformed at 100 °C under a constant external force with a micro melting point apparatus and so that **1a** was not further evaluated for lithographic experiments. Lithographic evaluation was performed on **1b** and **1c**. In the lithographic experiments for the one-component resist formulated with **1b**, as shown in Figure 6a, a fine positive-tone pattern with 0.75 μm line width was obtained with an exposure dose of 55 mJ/cm^2. No obvious deformation was observed for the pattern with post exposure bake (PEB) at 100 °C for 60 s. The cross-section SEM of the i-line lithographic patterns is also presented (Figure 6b) in which T-topping is apparent. This is the characteristic property of chemically amplified system. As for the line, the widening of the top resulted from that the environmental base matter in the exposure room, such as high amine content, cause the loss of acid at the top of exposed resist; meanwhile, the narrowing of the bottom resulted from the acid diffusion from the exposed area to the unexposed area. Experiments for **1c** can also provide a 0.75 μm line width pattern with an exposure dose of 58 mJ/cm^2, but there is a slight deformation for the pattern. This probably because that **1b** containing tetrahydropyrane group is more rigid than other two compounds and have higher softening temperature.

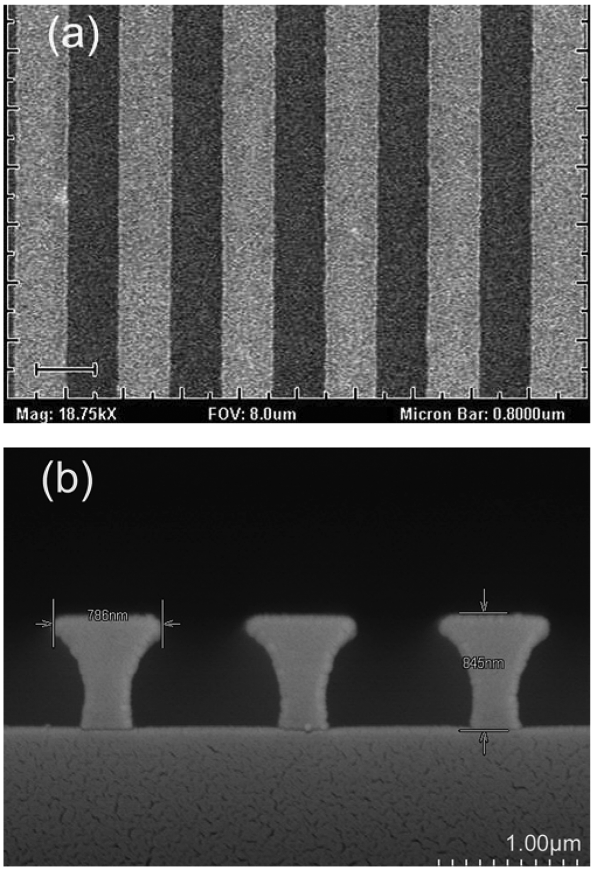


Figure 6. SEM images of positive-tone pattern with 0.75 μm line width obtained using compound **1b**, (a) top-view, and (b) cross-section.

The one-component i-line molecular glass resists exhibited higher sensitivity than conventional DNQ-novolac i-line resists system for their chemical amplification mechanism. In addition, the reduction of thickness of the resist films before and after development is less than 1 %. This is because that the unexposed film is completely insoluble in aqueous-alkaline developer during development. This is another advantage over conventional DNQ-novolac system.

■ CONCLUSIONS

In this paper, new molecular glass compounds containing acid labile group and 2,1,4-DNQ sulfonate group were designed and prepared in good yield. The molecular glass compounds have well-defined molecular structures and definite molecular weights. The compounds exhibited excellent solubility in common organic solvents, fully amorphous character and good film formability. Upon irradiation to 365 nm light, the 2,1,4-DNQ group readily underwent photolysis. The small amount of sulfonic acid generated in the photolysis process can further catalyze the deprotection of the compound. One-component i-line photoresists can be formulated with the compounds, respectively. Fine positive-tone patterns with 0.75 μm line width were obtained under exposure doses of 50-60 mJ/cm^2 in the photolithography experiments. The high photosensitivity can be accredited to the combinational effect of the photolysis of DNQ group and the chemical amplification.

The novel one-component molecular glass resists has potentiality to become high-performance i-line photoresists.

■ EXPERIMENTAL SECTION

Materials. Rosin, industrial product, used as received. 2-Diazo-1-naphthoquinone-4-sulfonyl chloride, industrial product, purified by dissolved in 1,4-dioxane and then precipitated in ethanol. Vinyl ethyl ether (VEE), dihydropyran (DHP), and cyclohexyl vinyl ether (CVE) were purchased from Acros and used as received. Propylene glycol monomethyl ether acetate (PGMEA) was obtained from Aladdin Reagents Company (Shanghai, China) and used as received. Maleic anhydride, triethylamine, glacial acetic acid, and other organic solvents were obtained from Beijing Chemical Reagents Company (Beijing, China) and used as received.

Characterization. ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded on a BRUKER AVANCE III 400 MHz spectrometer using tetramethylsilane (TMS) as an internal standard in chloroform-*d* ($CDCl_3$) or acetone-d_6. FTIR spectra were obtained with a Nicolet AVATAR 360 spectrometer. Elemental analyses were performed on a Vario EI elemental analyzer. Ultraviolet-visible (UV-vis) spectra were recorded on a GBC Cintra 10e spectrophotometer by forming films on quartz plates. Thermogravimetric analyses (TGA) were performed on a METTLER STAR^e system instrument at a heating rate of 10 °C/min under a nitrogen flow of 20 mL/min. The glass transition temperatures (T_g) of the molecular glass compounds were determined by using differential scanning calorimeter (DSC) measurements performed on a METTLER STAR^e system instrument at a heating rate of 10 °C/min under nitrogen. Powder X-ray diffraction (PXRD) traces were recorded using a PANalytical X' Pert PRO MPD diffractometer. For photoactive properties characterization, a 365 nm UV lamp (GY-13, Tianjin, China) was used. Exposures were carried out on a i-line exposure system (Nikon Corporation, model NSR2005I9C). Resist film thickness was measured using a Nanometrics Nano SPEC210 profilometer. Cross-section scanning electron micrograph was taken on a Hitachi S4800 field emission scanning electron microscope (SEM). Top-view SEM micrographs were obtained with a KLA-Tencor 8250 CD-SEM system.

Preparation of Maleopimaric Acid (MPA). Rosin (70 g, 231.8 mmol) and maleic anhydride (19.6 g, 200 mmol) were placed in a three-necked flask equipped with a mechanical stirrer, a nitrogen inlet and a condenser. The mixture was stirred at 160−180 °C for 6 h under a nitrogen atmosphere, and then poured out and cooled to room temperature to give yellow crude product. The crude product was recrystallized twice from glacial acetic acid to afford white crystals. Yield: 40 %. IR (KBr, cm^{-1}): 3400 (−OH of −COOH), 2958, 2870 ($-CH_3$ and $-CH_2$), 1844, 1775 (−C=O of anhydride), 1693 (−C=O of −COOH). ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) 5.5 (s, 1H, unsaturated proton), 3.2−0.5 (alicyclic and aliphatic protons). ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) 16.9−53.3 (alicyclic and aliphatic carbon), 125.2, 148.1 (−CH=C−), 171.0, 172.7 (−C=O of anhydride), 185.3 (−C=O of −COOH). Anal. Calcd for $C_{24}H_{32}O_5$: C, 71.97; H, 8.05. Found: C, 71.77; H, 6.57.

Preparation of N-Hydroxy Maleopimarimide (NHMPI). MPA (10 g, 25 mmol) was dissolved in ethyl acetate (30 mL). Anhydrous alcohol solution of hydroxylamine (0.91 g, 27.5 mmol) was added dropwise to the above solution with stirring at room temperature. Upon complete addition, the mixture was stirred at room temperature for 1 h and at 45 °C for 2 h, and then concentrated under reduced pressure to give white precipitate. The precipitate was filtrated and washed with ethyl acetate and distilled water, then dried under vacuum to give a fine white powder. Yield: 70 %. IR (KBr, cm^{-1}): 3400 (−OH of −COOH and −N−OH), 2958, 2870 ($-CH_3$ and $-CH_2$), 1766, 1709 (the imide carbonyl), 1693 (−C=O of −COOH). ^{1}H-NMR (400 MHz, acetone-d_6): δ (ppm) 5.5 (s, 1H, unsaturated proton), 3.0−0.5 (alicyclic and aliphatic protons). ^{13}C-NMR (100 MHz, acetone-d_6): δ (ppm) 16.0−54.8 (alicyclic and aliphatic carbon), 125.4, 147.8 (−CH=C−), 172.4, 173.2 (−C=O of anhydride), 180.0 (−C=O of −COOH). Anal. Calcd for $C_{24}H_{33}NO_5$: C, 69.37; H, 8.00; N, 3.37. Found: C, 69.14; H, 7.91; N, 3.21.

Preparation of 2,1,4-DNQ Sulfonate (NHMPI-2,1,4-DNQ). NHMPI (5.0 g, 12 mmol) and 2,1,4-DNQ-Cl (3.22 g, 12 mmol) were dissolved in acetone (40 mL). Triethylamine (1.75 mL, 12.6 mmol) was added dropwise to the above solution with stirring. The mixture was stirred at room temperature for 3-4 h. Thin layer chromatography (TLC) indicated that the reaction completed, then the obtained mixture was poured into a large amount of distilled water to give yellow precipitate. The precipitate was filtrated and washed thoroughly with distilled water, and then dried overnight at 40 °C under vacuum to afford a fine yellow powder. Yield: 94 %. IR (KBr, cm^{-1}): 3450 (−OH of −COOH), 2958, 2870 ($-CH_3$ and $-CH_2$), 1796, 1740 (the imide carbonyl), 2150 ($-C{=}N_2$), 1600, 1571 (benzene skeleton), 1384, 1180 (−S=O), 1693 (−C=O of −COOH). ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) 5.5 (s, 1H, unsaturated proton), 3.0−0.5 (alicyclic and aliphatic protons), 8.4−7.5 (protons of naphthoquinone). ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) 15.0−54.0 (alicyclic and aliphatic carbon), 124.5, 147.4 (−CH=C− of rosin moiety), 170.0, 168.9 (−C=O of anhydride), 176.6 (−C=O of −COOH), 184.4 (−C=O of naphthoquinone), 118.2, 126.2, 126.4, 128.6, 129.5, 130.1, 131.0, 133.8 (carbon of naphthoquinone). Anal. Calcd for $C_{34}H_{37}N_3O_8S$: C, 63.04; H, 5.76; N, 6.49. Found: C, 62.64; H, 5.04; N, 6.39.

Preparation of 1a. NHMPI-2,1,4-DNQ (1.0 g, 1.5 mmol) was dissolved in ethyl acetate (10 mL). Vinyl ethyl ether (0.33 g, 4.5 mmol) was added to the above solution with stirring. The mixture was stirred at 50−60 °C for 3-4 h, and then poured into a 10-fold excess of petroleum ether to give yellow precipitate. The precipitate was collected by filtration and washed with petroleum ether, then dried overnight at 40 °C under vacuum to afford a fine yellow powder. Yield: 90 %. IR (KBr, cm^{-1}): 2958, 2870 ($-CH_3$ and $-CH_2$), 1796, 1740 (the imide carbonyl), 2150 ($-C{=}N_2$), 1600, 1571 (benzene skeleton), 1384, 1180 (−S=O), 1715 (−C=O of −COO−R). ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) 5.5 (s, 1H, unsaturated proton), 3.2−0.5 (alicyclic and aliphatic protons), 8.4−7.5 (protons of naphthoquinone). ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) 14.0−54.0 (alicyclic and aliphatic carbon), 82.5, 62.3 (carbon connected with oxygen atom of ester acetal moiety), 148.1, 125.5 (−CH=C− of rosin moiety), 170.6, 169.6 (−C=O of anhydride), 176.7 (−C=O of −COOR), 181.0 (−C=O of naphthoquinone), 117.6, 126.5, 127.0, 129.0, 130.5, 132.3, 133.2, 134.0 (carbon of naphthoquinone). Anal. Calcd for $C_{38}H_{45}N_3O_9S$: C, 63.40; H, 6.30; N, 5.84. Found: C, 62.71; H, 5.24; N, 5.84.

1b and **1c** were prepared with similar procedure.

1b. Yield: 85 %. IR (KBr, cm^{-1}): 2958, 2870 ($-CH_3$ and $-CH_2$), 1796, 1740 (the imide carbonyl), 2150 ($-C{=}N_2$), 1600, 1571 (benzene skeleton), 1384, 1180 (−S=O), 1715 (−C=O of −COO−R). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 5.5 (s, 1H, unsaturated proton), 3.6−0.6 (alicyclic and aliphatic protons), 8.4−7.5 (protons of naphthoquinone). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 15.0−54.0 (alicyclic and aliphatic carbon), 92.9, 63.1 (carbon connected with oxygen atom of ester acetal moiety), 147.3, 124.5 (−CH=C− of rosin moiety), 170.5, 169.9 (−C=O of anhydride), 176.9 (−C=O of −COOR), 183.8 (−C=O of naphthoquinone), 118.2, 126.1, 126.3, 128.5, 129.5, 130.0, 130.9, 133.7 (carbon of naphthoquinone). Anal. Calcd for $C_{39}H_{45}N_3O_9S$: C, 64.00; H, 6.20; N, 5.74. Found: C, 63.34; H, 5.65; N, 5.33.

1c. Yield: 86 %. IR (KBr, cm^{-1}): 2958, 2870 ($-CH_3$ and $-CH_2$), 1796, 1740 (the imide carbonyl), 2150 ($-C{=}N_2$), 1600, 1571 (benzene skeleton), 1384, 1180 (−S=O), 1715 (−C=O of −COO−R). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 5.5 (s, 1H, unsaturated proton), 3.6−0.6 (alicyclic and aliphatic protons), 8.4−7.5 (protons of naphthoquinone). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 15.0−54.0 (alicyclic and aliphatic carbon), 95.1, 70.3 (carbon connected with oxygen atom of ester acetal moiety), 147.3, 124.5 (−CH=C− of rosin moiety), 169.9, 168.8 (−C=O of anhydride), 176.5 (−C=O of −COOR), 184.3 (−C=O of naphthoquinone), 118.2, 126.1, 126.3, 128.5, 129.5, 130.1, 130.9, 133.7 (carbon of naphthoquinone). Anal. Calcd for $C_{42}H_{52}N_3O_9S$: C, 65.10; H, 6.76; N, 5.42. Found: C, 64.34; H, 6.28; N, 5.67.

Photoactive Properties of Molecular Glass Compounds. A film of **1a** was formed by coating a dilute solution of the compound in PGMEA on a quartz plate and then baking at 100 °C for 120 s to remove the solvent. The film was exposed to a UV lamp (365 nm). The UV absorbance of the film was recorded before and after exposure with different doses.

A film of **1b** was formed on a NaCl plate with above procedure. The film was exposed to a UV lamp (365 nm) and the FTIR spectra of the film were recorded before exposure, after exposure (dose = 120 mJ/cm^2) without post-exposure bake and after exposure with post-exposure bake.

Lithographic Evaluation. A typical procedure is described in the following section using compound **1b** as an example. The resist was formulated by dissolving **1b** in PGMEA to make a 20 wt % solution. After being filtered through a 0.2 μm polytetrafluoroethylene membrane filter, the solution was spin-coated at 1000 rpm for 25 s onto a 6 inch silicon wafer vapor primed with hexamethyldisilazane (HMDS) to yield a film approximately 0.8 μm thick. The film was prebaked at 90 °C for 60 s. Exposure was then performed on a Nikon NSR2005I9C stepper (NA = 0.54, mask line/space = 1/1) with a high-pressure mercury lamp. The exposed wafer was baked at 100 °C for 60 s and then developed in a 2.38 wt % tetramethylammonium hydroxide (TMAH) aqueous solution for 60 s at room temperature, followed by rinsing with de-ionized water.

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) Dammel, R. R. *J. Photopolym. Sci. Technol.* **1998**, *11*, 687−704.

(2) Dammel, R. *Diazonaphthoquinone-Based Resists*; SPIE Optical Engineering Press: Bellingham, WA, 1993.

(3) Thompson, L. F.; Willson, C. G.; Bowden, M. J. *Introduction to Microlithography*; ACS Symposium Series; American Chemical Society: Washington, D.C., 1983; Vol. *219*.

(4) Hanabata, M.; Oi, F.; Furuta, A. *Polym. Eng. Sci.* **1992**, *32*, 1494−1499.

(5) Hanabata, M. *Adv. Mater. Opt. Electron.* **1994**, *4*, 75−82.

(6) Khanna, D. N.; Durham, D. L.; Seyedi, F.; Lu, P. H.; Perera, T. *Polym. Eng. Sci.* **1992**, *32*, 1500−1508.

(7) Shirota, Y. *J. Mater. Chem.* **2000**, *10*, 1−25.

(8) Shirota, Y. *J. Mater. Chem.* **2005**, *15*, 75−93.

(9) Strohriegl, P.; Grazulevicius, J. V. *Adv. Mater.* **2002**, *14*, 1439−1452.

(10) Yang, D.; Chang, S. W.; Ober, C. K. *J. Mater. Chem.* **2006**, *16*, 1693−1696.

(11) Silva, A. D.; Felix, N.M.; Ober, C. K. *Adv. Mater.* **2008**, *20*, 3355−3361.

(12) Dai, J. Y.; Chang, S. W.; Hamad, A.; Yang, D.; Felix, N.; Ober, C. K. *Chem. Mater.* **2006**, *18*, 3404−3411.

(13) Chang, S.W.; Ayothi, R.; Bratton, D.; Yang, D.; Felix, N.; Cao, H. B.; Deng, H.; Ober, C. K. *J. Mater. Chem.* **2006**, *16*, 1470−1474.

(14) Oizumi, H.; Kumasaka, F.; Tanaka, Y.; Hirayama, T.; Shiono, D.; Hada, H.; Onodera, J.; Yamaguchi., A.; Nishiyama, I. *Microelectron. Eng.* **2006**, *83*, 1107−1110.

(15) Hirayama, T.; Shiono, D.; Hada, H.; Onodera, J.; Ueda, M. *J. Photopolym. Sci. Technol.* **2004**, *17*, 435−440.

(16) Kadota, T.; Kageyama, H.; Wakaya, F.; Gamo, K.; Shirota, Y. *Mater Sci. Eng., C* **2001**, *16*, 91−94.

(17) Young-Gil, K.; Kim, J. B.; Fujigaya, T.; Shibasaki, Y.; Ueda, M. *J. Mater. Chem.* **2001**, *12*, 53−57.

(18) Nakayama, T.; Ueda, M. *J. Mater. Chem.* **1999**, *9*, 697−702.

(19) Iwashima, C.; Imai, G.; Okamura, H.; Tsunooka, M.; Shirai, M. *J. Photopolym. Sci. Techchnol.* **2003**, *16*, 91−96.

(20) Wang, M. X.; Yueh, W.; Gonsalves, K. E. *Macromolecules* **2007**, *40*, 8220−8224.

(21) Wu, H. P.; Gonsalves, K. E. *Adv. Funct. Mater.* **2001**, *11*, 271−276.

(22) Watanabe, T.; Fukushima, Y.; Shiotani, H.; Hayakawa, M.; Ogi, S.; Endo, Y.; Yamanaka, T.; Yusa, S.; Kinoshita, H. *J. Photopolym. Sci. Technol.* **2006**, *19*, 521−524.

(23) Gonsalves, K. E.; Wang, M. X.; Lee, C.-T.; Yueh, W.; T-T, M.; Batina, N.; Henderson, C. L. *J. Mater. Chem.* **2009**, *19*, 2797−2802.

(24) Kim, J.-B.; Kim, K.-S. *Macromol. Rapid Commun.* **2005**, *26*, 1412−1417.

(25) Park, J. Y.; Yun, J. M.; Kim, J.-B. *J. Polym. Sci., Part A: Polym. Chem* **2008**, *46*, 7534−7542.

(26) Ganesan, R.; Youn, S.-K.; Kim, J.-B. *Macromol. Rapid Commun.* **2008**, *29*, 437−441.

(27) Wang, L. Y.; Wang, W. J.; Guo, X. *Proc. SPIE.* **2004**, *5376*, 608−615.

(28) Lee, J. S.; Hong, S. I. *Eur. Polym. J.* **2002**, *38*, 387−392.

(29) Bratton, D.; Ayothi, R.; Deng, H.; Cao, H. B.; Ober, C. K. *Chem. Mater.* **2007**, *19*, 3780−3786.

(30) Buhr, G.; Lenz, H.; Scheler, S. *J. Photopolym. Sci. Techchnol.* **1989**, *2*, 417−428.

(31) Baumbach, B.; Bendig, D. J.; Nagel, T.; Lubsky, B. *J. Prakt. Chem.* **1991**, *333*, 625−635.

(32) Moon, S.; Kamenosono, K.; Kondo, S.; Umehara, A.; Yamaoka, T. *Chem. Mater.* **1994**, *6*, 1854−1860.

(33) Moon, S.; Naitoh, K.; Yamaoka, T. *Chem. Mater.* **1993**, *5*, 1315−1320.