Color and Fluorescent Imaging of *t*-BOC-Protected Quinizarin Methacrylate Polymers

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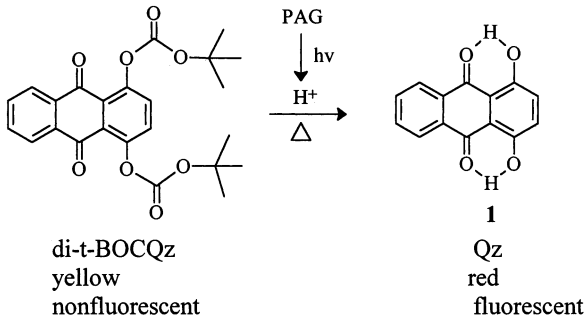
A polymerizable quinizarin (Qz) dye precursor having both methacrylate and *tert*-butoxycarbonyl (*t*-BOC) groups has been prepared and radically copolymerized to obtain mono-*t*-BOC-protected quinizarin polymers as fluorescent imaging materials. The mono-*t*-BOC-protected quinizarin methacylate **3** (*t*-BQzMA) is a unique monomer having an acid-labile *t*-BOC blocking group along with a polymerizable methacrylate group. The *t*-BOC-protected quinizarin polymers obtained by copolymerization of *t*-BQzMA with methyl methacrylate were readily modified to regenerate phenol groups by deprotection of *t*-BOC groups in the quinizarin moieties with photochemical treatment in the presence of a photoacid generator. The polymers rendered color and fluorescent imaging properties based on a photolithographic method: fluorescent images obtained without wet development and fluorescent relief patterns after wet development followed by flood exposure.

Introduction

Micrometer-sized patterning such as microcontact printing and microlithography is a topic that continues to be of interest in many aspects of materials science and practical application. Various applications of color and fluorescent materials and photofunctional polymer systems in sensors and electronic devices require patterning of these functional materials into small features with characteristic size, ideally by simple and reliable methods. Photopatterning in films of photosensitive polymers, so called photoresists in photolithography, is the most critical technology in the modern semiconductor industry where the capability for integrated circuit (IC) dimension shrinkage still defines the level of the whole IC technology. Since the pioneering discovery of the chemical amplification (CA) concept by IBM researchers, it has been a key technology for photolithographically generating patterned images in polymer films.[1] Selective removal of acid-labile protecting groups through photoinduced chemical transformation followed by chemisorption of organic dyes from solution into the patterned polymer film has given various functional images.[2−4] Our approach to developing functional images has been focused on lithographic processing utilizing polymer films in which fluorescent organic dyes are dispersed or directly attached to the polymer chains. Such fluorescent dyes include quinizarin[5−7] and pyridylbenzoxazoles.[8] The first report in the series demonstrated that the UV absorption and fluorescence of the quinizarin molecules could be readily altered and manipulated simply by blocking the intramolecular hydrogen bonds.[5] For example, the UV absorption maximum (480 nm) shifted to a shorter wavelength (335 nm) by blocking the two phenols with an acid-labile *tert*-butoxycarbonyl (*t*-BOC) group in quinizarin derivatives as shown in Scheme 1. Recently, we reported on a polymer of fluorescence imaging prepared with a norbornene monomer containing pendant *t*-BOC-protected quinizarin precursors.[6b] The *t*-BOC groups of quinizarin moieties attached directly to this polymer backbone

Scheme 1



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were effectively deprotected by photoinduced decomposition of a photoacid generator (PAG) but the polymer has shown difficulties in the synthetic and developing procedures using common solvents.

To extend the photoimaging capability of the unique quinizarin dye molecules **1** via transient protection of the intramolecular hydrogen bond, two phenol groups of quinizarin have been separately protected by the acid-labile *t*-BOC group and the polymerizable methacrylate group. Thus, a quinizarin methacrylate monomer **3**, having an acid-labile protecting group within the same molecule, has been prepared and polymerized to investigate photoimaging and fluorescent properties of the resulting polymers. As a part of our continuing efforts to study functional imaging in polymer films, we now report the synthesis and polymerization of the protected quinizarin monomer **3** and utilization of the *t*-BOC-protected quinizarin polymer for color and fluorescent imaging with or without a development step following the photolithographic processes.

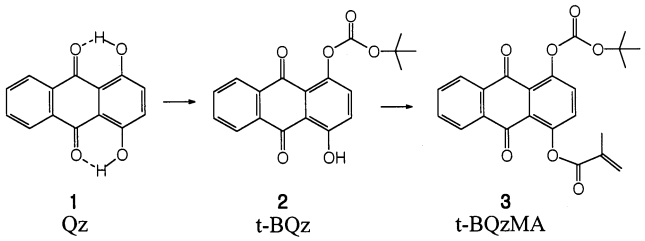
Experimental Section

Materials and Instrumentation. Most of the chemicals and solvents were purchased from Sigma-Aldrich Co. Triphenylsulfonium triflate (TPSOTf) was purchased from Kumho Co. Methyl methacrylate (MMA) was distilled before use. 2,2′-Azobis(isobutyronitrile) (AIBN) and benzoyl peroxide (BPO) as radical initiators and quinizarin were recrystallized from ethanol before use. Other reagents were used as received. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Gemini 200 spectrometer of Perkin-Elmer using $CDCl_3$. Infrared spectra were recorded on a NICOLET 800 spectrophotometer (NICOLET Instrument Co). Molecular weights were measured by gel permeation chromatography (GPC) using a GPC-717 plus auto sampler (Waters Instrument Co). UV spectra were recorded on a Shimadzu Model UV-1606 spectrophotometer. Thermal properties of polymers were analyzed by Model DSC 2010 and Model 2050 of TA Instruments (heating rate: 10 °C/min).

Mono-*t*-BOC-Protected Quinizarin (*t*-BQz) (2). To a solution of quinizarin (Qz) **2** (10.00 g, 0.042 mmol) and 10 mL of triethylamine (TEA) in 100 mL of tetrahydrofuran (THF) was added very slowly di-*tert*-butyl dicarbonate (DTBDC) (9.08 g, 0.042 mmol) in 100 mL of THF at − 5 °C. The mixture was stirred for 24 h under a nitrogen atmosphere. The reaction mixture was concentrated in vacuo and the residue was dissolved in ethyl acetate (EtOAc) and washed with aqueous $NaHCO_3$ and NaCl solution. The organic phase was separated and concentrated by evaporation. The viscous residue was subjected to silica gel column chromatography (EtOAc/hexane 1:3 by volume) to afford *t*-BQz **2** (9.10 g, 65%). *t*-BQz: mp 140 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.60 (s, 9H, CH_3), 7.29−7.49 (q, 2H, aromatic), 7.70−7.90 (m, 2H, aromatic), 8.20−8.37 (m, 2H, aromatic). IR (KBr): ν 3470, 2926, 1750, 1616, 1480, 1226 cm^{-1}. UV ($CHCl_3$, 1×10^{-4}): λ_{max} 330, 420 nm.

Mono-*t*-BOC-Protected Quinizarin Methacylate (1-Methacryloyloxy, 4-*tert*-Butyloxycarbonyloxy Anthraquinone, *t*-BQzMA) (3). *t*-BQz **2** (5.4 g, 0.0158 mmol) and TEA (4 mL) were dissolved in THF (100 mL) and reacted with methacryloyl chloride (2.00 g, 0.020 mmol) at 25 °C for 6 h. The reaction mixture was filtered, the filtrate solution concentrated in vacuo, and then the residue extracted with water and EtOAc. The viscous residue was subjected to silica gel column chromatography (10% EtOAc/hexane) to afford the desired *t*-BOC−QzMA **3** (5.20 g, 80%) as pale yellow powders. *t*-BQzMA: mp 42−43 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.60 (s, 9H, CH_3, *t*-BOC), 2.2 (s, 3H, α-CH_3), 5.90 (s, 1H, CH_2=C), 6.50 (s, 1H, CH_2=C), 7.40−7.60 (q, 2H, aromatic), 7.70−7.90 (m, 2H, aromatic), 8.20−8.37 (m, 2H, aromatic). ^{13}C NMR ($CDCl_3$): δ 18.3 (methacrylate, CH_3), 27.7 (*t*-BOC, CH_3), 84.3 (C(CH_3)$_3$ of *t*-BOC), 126.8 (*C*=CH_2 of methacrylate), 135.5 (C=

Scheme 2. Synthesis of the Mono-*t*-BOC-Protected Monomer (*t*-BQzMA) 3



CH_2 of methacrylate), 128.1, 130.6, 131.2, 133.2, 134.4, 148.2, (aromatic), 150.9 (C=O of *t*-BOC), 165.6 (C=O of methacrylate), 181.4 (C=O of Qz). IR (KBr): ν 3070, 2994, 1765, 1670, 1583, 13600, 1280 cm^{-1}.

Polymerization of 3. A solution of *t*-BQzMA **3** (0.73 g, 1.62 mmol), MMA (0.32 g, 3.24 mmol), and AIBN (0.052 g, 2 mol % to the weight of combined monomers) in dioxane (4 mL) was placed in a Pyrex glass ampule. It was subjected to repeated freeze−thaw cycles before the ampule was sealed under vacuum. The sealed ampule was heated at 65 °C for 24 h. After polymerization, the product was precipitated into methanol and dried to give a polymer P(*t*-BQMA/MMA) (1:3) as pale bright yellow powders in 0.57 g (55% yield). ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.7−1.5 (br, from methacrylate), 1.5−2.5 (br, from methacrylate), 1.5−2.5 (s, *tert*-butyl of *t*-BOC), 3.4−3.9 (br, CH_3O), 7.40−8.40 (br, aromatic). IR (KBr): ν 3010, 2950, 1760, 1675, 11625, 590, 1430, 1280 cm^{-1}. UV ($CHCl_3$, 1×10^{-4}): λ_{max} 340 nm.

Photoinduced Deprotection and Photoimaging. The polymer and 3 wt % TPSOTf as a PAG were dissolved in cyclohexanone. The solutions were filtered through a 0.2-μm membrane filter and spin-coated using a Headway Research spin coater to make 0.5−1.5-μm-thick films after soft baking at 60 °C for 1 min. Quartz plates were used for UV spectroscopy and silicon wafers for fluorescent imaging as the substrate. UV exposure was performed with a UV illuminator of Ushio Inc. (Japan) equipped with a 500-W Hg−Xe lamp and a narrow band-pass filter at 250-nm wavelength (intensity of 23 mW/cm^2). The spin-cast film of the polymer **4** with 3 wt % of TPSOTf in 0.36-μm thickness was exposed to 250-nm UV through a photomask in contact mode followed by postexposure bake (PEB) at 120 °C for 1 min to bring about acid-catalyzed deprotection. The photographs of fluorescent patterns were taken with a Zeiss Epifluor microscope under a weak UV lamp filtered to 410 nm.

Results and Discussion

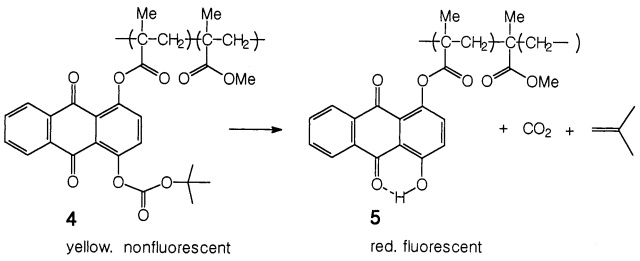
Synthesis and Polymerization of Mono-*t*-BOC-Protected Quinizarin Methacrylate (*t*-BQzMA) (3). The synthetic sequence for preparation of the mono-*t*-BOC-protected quinizarin methacrylate as a target monomer **3** is shown in Scheme 2. In the first step, the monosubstituted quinizarin having a *t*-BOC protecting group was prepared under mild reaction conditions by controlling reaction temperature and addition of a reactant, DTBDC. In the previous studies,[5−7] the reaction of quinizarin with methacryloyl chloride was unsuccessfully attempted because of an isolation problem. The reaction of quinizarin was carried out at a low temperature of about −5 °C with cautious addition of DTBDC to give the mono-*t*-BOC-substituted product **2** in high yield. The reaction of *t*-BQz (**2**) with methacryloyl chloride afforded the desired monomer **3** as pale yellow powders in 80% yield. The ^{1}H NMR spectra of monomer **3** showed a singlet peak at 1.60 ppm for *t*-BOC and two singlet peaks at 6.50 and 5.90 ppm for two olefin protons in the methacrylate group. In an IR

Table 1. Radical Copolymerizations of *t*-BQzMA (3) with Methyl Methacrylate

copolymer	feed **3**:MMA (molar ratio)	initiator (mol %)	time (h)	temp (°C)	yield (%)	composition **3**:MMA (molar ratio)	Mw[a] ($\times 10^{-3}$)	PD[b]
polymer **4**	1:2	AIBN (2)	24	55	55	1:4	18	1.6
polymer **4a**	1:1	AIBN (1)	24	55	51	1:3.5	21	2.3
polymer **4b**	1:3	AIBN (3)	24	55	60	1:8	12	2.5
polymer **4c**	1:2	BPO (1)	12	80	45	1:4	15	3.0

[a] Weight-average molecular weights of the polymer measured by GPC in THF. [b] PD = polydispersity measured by GPC.

Scheme 3



spectrum of monomer **3**, characteristic absorption bands at 1765 and 1670 cm^{-1} corresponding to the carbonyl groups of *t*-BOC and protected quinizarin were all identified.

Radical copolymerizations of the monomer **3** with MMA were carried out with various feed ratios in solution using AIBN or BPO as a radical initiator and the polymerization results are listed in Table 1. The copolymers had the number-average molecular weights (Mn) in the range of 14 000−28 000 with polydispersities of 1.6−3.0 as determined by GPC in THF. By ^1H NMR spectroscopy, the compositions of the copolymers were found to be 1:3 to 1:8 for *t*-BQzMA **3** and MMA repeating units. Here, we report photoimaging behaviors for the copolymer P(*t*-BQzMA/MMA) having a quinizarin content as high as possible (1:3.5), which will be designated as polymer **4** (Scheme 3). Note that polymer **4** displayed virtually no fluorescence and the UV/vis absorption maximum shifted to a shorter wavelength (340 nm in $CHCl_3$) compared to that of quinizarin derivatives as shown in Figure 1. These results are related to the blocking of the two phenol groups. We have previously reported that the UV absorption maximum and fluorescence of quinizarin can be readily altered and manipulated simply by blocking the intramolecular hydrogen bonds.[5] As expected, the relative fluorescent intensities are in agreement with the level of the blocking: half-blocked samples such as *t*-BQz and deprotected polymer **5** exhibit approximately half fluorescent intensity due to a quasi-aromatic structure caused by intramolecular hydrogen bonding.

Thermal and Photoinduced Deprotection of *t*-BOC Groups in Polymer Films. The advantages of the use of the protected polymer **4** are in its superior film-forming properties, easier synthesis, and its clean deprotection compared to those of our previously reported norbornene system.[6b] In the case of an amorphous polymer PMMA doped with small quinizarin derivatives, the dopants are prone to crystallize when their concentration exceeds a certain molar fraction (about 20%) as we reported previously.[5,6] All of the copolymers formed good-quality films by evaporating the solvent slowly or by spinning the solution and the films adhered well to the substrates, thereby allowing fabrication of surface-modified films. To investigate the

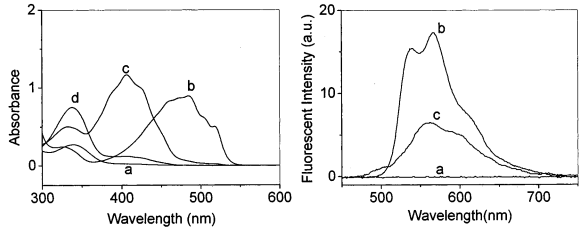


Figure 1. UV absorption spectra (left) and fluorescence emission spectra (right) in the chloroform solution: (a) the polymer **4**; (b) quinizarin; (c) *t*-BQz; (d) *t*-BQzMA (1×10^{-4} M).

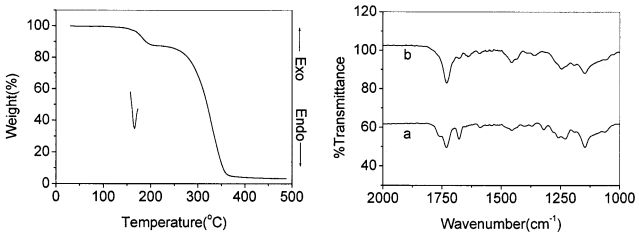


Figure 2. Thermal properties of the polymer **4** measured by DSC and TGA (left) and IR spectra (right) of 1-μm-thick films of the polymer **4** containing TPSOTf (3 wt %) on a NaCl plate: (a) before UV exposure and (b) after UV exposure for 2 min followed by PEB at 120 °C.

photoinduced deprotection of the *t*-BOC groups in the quinizarin moieties of the copolymers by chemical amplification, a solution of the polymer **4** with 3% of TPSOTf was spin-coated onto substrates to make films. The deprotection of *t*-BOC groups in the polymer films was monitored by thermal analysis and IR spectral changes (Figure 2). The complete deprotection of the *t*-BOC groups in the polymer **4** to phenolic units in the polymer **5** occurred at 170 °C with a mass loss of 13% confirmed by an endothermic event in a TGA thermogram as shown in Figure 2. The amount of the mass loss agrees well with the theoretical value of the *t*-BOC groups in the polymer **4**. In addition, the two IR absorption band intensities, the one at 1790 cm^{-1} associated with the carbonyl stretching vibration of the *t*-BOC groups and the other at 1675 cm^{-1} associated with the isolated carbonyl of quinizarin, gradually decreased with the increase in temperature and exposure time. Simultaneously, the phenolic absorption intensity at 1625 cm^{-1} related to the intramolecularly hydrogen-bonded carbonyl increased by the deprotection of *t*-BOC groups in the polymer films as compared in IR spectra. The pale yellow film on a quartz substrate was exposed to 250-nm UV for 30 s (700 mJ/cm^2) and turned to a red-colored film after PEB at 120 °C for 120 s. The regeneration of quinizarin moieties in the polymer film was also confirmed by analysis of UV spectra of the exposed film as shown in Figure 3 (left). The acid-catalyzed deprotection of *t*-BOC groups in the film was monitored by the bathochromic shift of the absorption

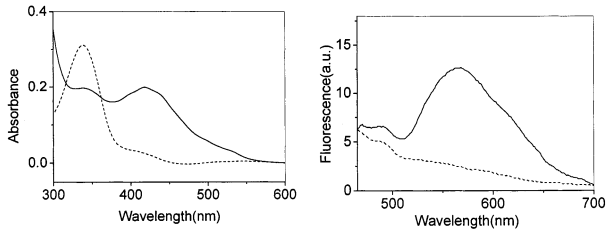


Figure 3. UV absorption (left) and fluoresence emission (right) spectra of a 0.36-μm-thick film of the polymer **4** containing TPSOTf (3 wt %) on a quartz plate before (dashed line) and after UV exposure for 2 min followed by PEB at 120 °C (solid line).

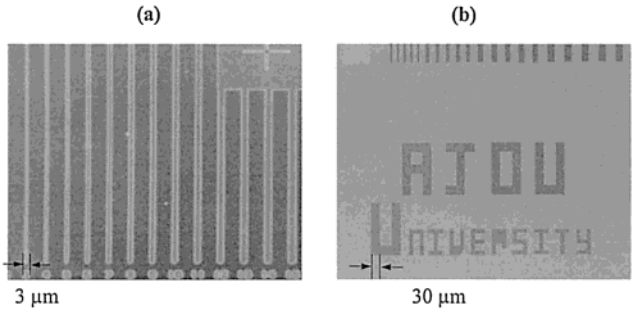


Figure 4. Fluorescent patterns on 0.36-μm-thick films of the polymer **4** with 3% PAG generated by contact exposure: (a) without wet development; (b) flood exposure and PEB after development with 4% NaOH solution. The lighter areas are corresponding to the fluorescent areas in (a) and (b).

maximum from 340 to 420 nm corresponding to the quinizarin moiety with only one phenol group. Moreover, the nonfluorescent nature of the protected polymer became fluorescent upon removal of the *t*-BOC protecting groups (Figure 3 (right)).

Color and Fluorescent Patterning. The polymer film containing TPSOTf on a silicon wafer was irradiated with 250-nm UV for 30 s through a photomask in a contact mode followed by PEB at 120 °C for 120 s. Note that the optical density of the polymer film at 254 nm was 0.2/μm. The pattern formation by photoimaging in thin films was monitored by fluorescence microscopy. As shown in Figure 4, numerous fluorescent stripes clearly came out. The fine lines in a range of 2.0to 30 μm were resolved. The high contrast fluorescent emission in the regions exposed through the photomask is sufficient to allow the formation of patterned images.

The polymer **4** offers another advantage of generating relief patterns. The protected polymer **4** is soluble in common organic solvent such as chloroform, cyclohexanone, THF, toluene, and anisole but insoluble in methanol and aqueous alkaline solutions. The deprotected polymer **5** is soluble in commercial aqueous developer, that is, 2.38 wt % tetramethylammonium hydroxide (TMAH) or 4% aqueous NaOH solution due to the phenolic groups generated by deprotection. We believe that the liphophilic polymer **4** containing only 20 mol % of a phenol-generating *t*-BOC group is hard to develop in a positive mode in aqueous base. Consequently, a strong 4% NAOH aqueous solution had to be used as a developer to obtain good quality positive-tone patterns. In Figure 4b, the letters are corresponding to the developed areas by 4% aqueous NaOH solution at room temperature for 3 min and no film remained. The polymer films remaining after development were flood-exposed to 250-nm UV, followed by PEB at 120 °C for 120 s. The resultant polymer converted to the deprotected form, exhibiting fluorescence.

The potential of the mono-*t*-BOC-protected quinizarin polymer system may be exploited fully in the production of positive fluorescent images since the phenolic group of the aromatic ring affects the fluorescence nature. In fact, the intramolecular hydrogen bond allows fluorescence to occur because the quinizarin molecules tie up the nonbonding electron pairs of the carbonyl, thereby preventing intersystem crossings of the $n-\pi^*$ state.[5] As expected, the fluorescence was effectively quenched when the fluorescent image patterns were treated with a base like TEA because the base reacted with the phenol group of quinizarin, inhibiting the intramolecular hydrogen bonding. Furthermore, it was found that this quenching process was reversible and the quenched fluorescence was completely recovered by acidic treatment. The recognition of bases (or acids) by the fluorescence emission in the polymer could be applicable as a chemosensor.

Conclusions

Even though the mono-*t*-BOC-protected quinizarin polymers provide only one intramolecular hydrogen bond in the quinizarin moieties when deprotected, they can still provide sufficient fluorescence emission and be adaptable for fluorescent imaging. This quinizarin-functionalized polymer exhibited the fluorescent properties similar to those of the quinizarin molecule or comparable to those of the polymers we have previously reported but offered greatly improved patterning potential: it could be developed by classical methods used for photoresist materials. The significantly different electronic properties between the protected and deprotected quinizarin forms in the polymers induced by intramolecular hydrogen bonding allow the *t*-BOC-protected quinizarin polymers to be useful as color or fluorescent imaging materials and a fluorescent chemosensor for detecting acid−base properties.

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