

Transient Protection of Intramolecular Hydrogen Bonding: A Simple but Elegant Approach for Functional Imaging

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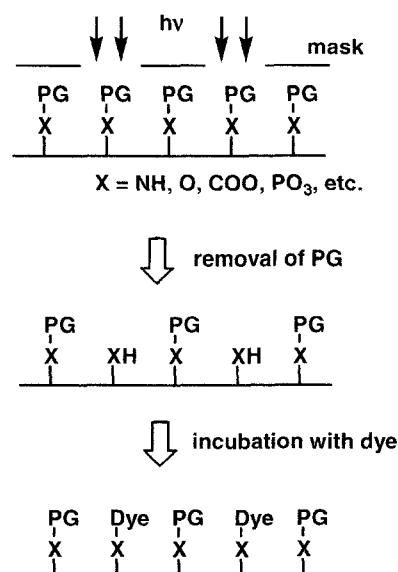
Abstract: We have developed a novel method for patterning functional images in thin polymer films. The key materials we utilized for the imaging were dihydroxyanthraquinones protected with acid-labile *tert*-butoxycarbonyl (*t*-Boc) blocking groups. Among the tested compounds, 1,4-dihydroxyanthraquinone (quinizarin; **1**) underwent the most drastic change in terms of its color and fluorescence upon protection. We prepared the *t*-Boc-protected quinizarin and polymers bearing the protected quinizarins as pendent groups. To investigate the possibility of a single-component imaging system, we synthesized a styrenic monomer **14** incorporating protected quinizarin and a maleimide derivative **15** bearing a photoacid generating group and subjected them to polymerization. Selective removal of the protecting groups of the quinizarin moieties in the exposed area using photolithographic techniques allowed regeneration of quinizarin and patterned fluorescence images in the polymer films.

Keywords: intramolecular hydrogen bonding, fluorescence, patterned images, polymer film, chemical amplification.

Introduction

The generation of patterned images in polymer films has been extensively studied and used in fundamental and applied research areas. The development of patterned color or fluorescent images, especially, is of great technological importance in the electronics and display industry. Recently, generation of functional images by selective immobilization of organic dyes in the polymer film has been reported.¹⁻⁴ As outlined in Scheme I, the two-step procedures which take advantage of photolithographic technique are commonly used for patterned functional images in polymer film. The first step involves generation of reactive species through photoinduced deprotection of the protecting groups (PGs). For this purpose, a photolithographic method called chemical amplification (CA) process has been widely used.⁵⁻⁹ In the CA process, a catalytic amount of acid produced by a photochemical reaction of a photoacid generator (PAG) induces a cascade of subsequent chemical transformation through acid-catalyzed deprotection of acid-labile protecting groups, typically *tert*-butoxycarbonyl (*t*-Boc) or *tert*-butyl (*t*-Bu) groups. In the second step, the reactive groups generated by photoinduced chemical transformation in the

exposed area of the polymer film interact with functional dyes absorbed from the solution. The functional dyes can interact with the reactive moieties by covalent modification, ionic or hydrogen bonding.



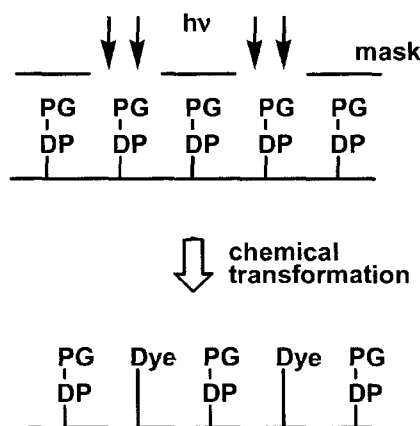
Scheme I. A general method for patterned functional images in polymer film.

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The two-step procedures represented in Scheme I, however, have potential problems such as difficulty of dye penetration into polymer matrices and long-term stability of the patterned images when dye molecules are incorporated into the polymer matrices by ionic or hydrogen bonding. In order for the functional dyes to penetrate into the polymer matrix, the polymer should have good swelling properties in the developing solvent. If hydrophobic organic dyes are to be used, the developing process with the functional dyes should be carried out in hydrophobic solvents in which the polymer can have better swelling behaviors. Then, the matrix polymer may partially soluble during the wet-developing stage which may lead to poor resolution of the patterned images. On the contrary, if water-soluble dyes are used, the polymer matrices have poor swellability in water-based developing solvents. For these reasons, wet-developing processes are, in general, performed in a mixture of water and organic solvents. Under these conditions, functional dyes may have difficulties to reach to the bottom of the polymer film.

In order to avoid the intrinsic problems associated with the two-step procedures described above, we¹⁰⁻¹³ and other groups¹⁴⁻¹⁸ have developed direct methods of generating color or fluorescence images in the polymer film without the wet-developing processes. We, especially, focused on the generation of functional images using the 'precursor approach'. As outlined in Scheme II, the dye precursors (DPs) are temporary protected with protecting groups. The dye precursors reveal original properties of dye molecules upon removal of the protecting groups by chemical transformation. In recent preliminary studies, we reported on the generation of color/fluorescent images with *t*-Boc-protected quinizarin dye precursors using above strategies.^{10,12,13} Here we present comprehensive characterization of the precursor approaches based on transient protection of intramolecular hydrogen bonding for the functional images in the polymer film.



Scheme II. Precursor method for patterned functional images in polymer film.

Experimental

General. Quinizarin (**1**), anthrarufin (**2**) and 1,8-dihydroxyanthraquinone (**3**), leucoquinizarin (**7**), 5-norbornene-2-carboxaldehyde (**8**), 4-vinylbenzaldehyde (**12**), allylpalladium chloride dimer, di-*t*-butyl dicarbonate and methyl methacrylate were purchased from Aldrich Chemical Co. ¹H NMR and ¹³C NMR spectra were recorded on CDCl₃ solutions by using a Varian Gemini 200 spectrometer. Chemical shifts are reported in ppm relative to tetramethylsilane (TMS) which was used as an internal standard. IR spectra were recorded on a Polaris FT-IR spectrometer of Mattson Instrument Co. UV spectra were recorded on a JASCO Model V530 UV-Vis spectrometer. Melting points were recorded by using a Griffin Mel-Temp capillary melting point apparatus and are reported uncorrected. Synthesis and spectroscopic data of **4** were previously reported.¹²

5: To a solution containing 5.0 g (21 mmol) of 1,5-dihydroxyanthraquinone (**2**) in 100 mL of pyridine was added 11.3 g (52 mmol) of di-*t*-butyl dicarbonate. The resulting solution was stirred at room temperature for 7 h and poured into cold water. The precipitates were collected and recrystallized from MeOH to give 5.6 g (61%) of the *t*-Boc-protected quinone **5**. m.p. 188 °C; ¹H NMR δ = 1.63 (s, 18H), 7.50 (m, 2H), 7.78 (m, 2H), 8.22 (m, 2H); ¹³C NMR δ = 27.8, 84.6, 124.7, 126.0, 129.5, 135.3, 136.1, 150.3, 151.3, 181.5

6: The *t*-Boc-protected 1,8-dihydroxyanthraquinone **6** was prepared in 64% yield by using similar procedures employed for the preparation of **5**. m.p. 167 °C; ¹H NMR δ = 1.59 (s, 18H), 7.43 (m, 2H), 7.75 (m, 2H), 8.20 (m, 2H); ¹³C NMR δ = 27.8, 84.1, 125.5, 126.2, 130.0, 134.4, 134.7, 150.3, 151.3, 181.0, 182.1.

9: A solution containing leucoquinizarin (**7**) (30.0 g, 0.124 mol), 5-norbornene-2-carboxaldehyde (**8**) (18 mL, 0.147 mol) and a catalytic amount of piperidinium acetate in 2-propanol (200 mL) was stirred under reflux for 6 h. The bulk of 2-propanol was removed *in vacuo* and the residue was subjected to silica gel column chromatography (10% EtOAc-hexane) to give 37.0 g (88%) of the intermediate **9** as red crystals, m.p. 141.8 °C (DSC). ¹H NMR (CDCl₃): δ = 0.67 (1H, m), 1.24 (2H, m), 1.41-1.52 (3H, m), 1.91 (1H, m), 2.50-2.58 (2H, m), 2.80-2.84 (2H, m), 6.06 (1H, m), 6.23 (1H, m), 7.13 (1H, s), 7.81 (2H, m), 8.33 (2H, m). ¹³C NMR (CDCl₃): δ = 32.2, 35.1, 37.8, 42.7, 45.2, 49.6, 111.0, 112.1, 127.0, 128.5, 132.4, 133.7, 134.3, 136.5, 136.8, 137.7, 144.6, 144.9, 157.3, 157.8, 186.3, 187.2.

10: To a solution containing **9** (10.0 g, 0.029 mol) in THF (100 mL) was added di-*tert*-butyl dicarbonate (13.0 g, 0.064 mol) and dimethylaminopyridine (0.5 g). The resulting mixture was stirred at room temperature for 4 h, concentrated *in vacuo*, and the residue was subjected to silica gel column chromatography (10% EtOAc-hexane) to yield the monomer *t*-BQN **10** (15.0 g, 93%). ¹H NMR (CDCl₃): δ = 0.62 (1H, m), 1.22 (1H, m), 1.42 (1H, m), 1.61 (18H, s), 1.90

(1H, m), 2.40 (1H, m), 2.47-2.50 (2H, m), 2.71-2.77 (2H, m), 6.02-6.22 (2H, m), 7.36(1H, s), 7.70-7.72(2H, m), 8.13-8.17 (2H, m); ^{13}C NMR (CDCl_3): δ = 22.7, 32.2, 35.1, 38.3, 42.6, 45.4, 49.6, 84.1, 84.3, 124.4, 126.3, 126.7, 126.9, 131.1, 132.2, 133.4, 133.5, 133.9, 136.7, 137.9, 144.9, 146.5, 147.7, 150.7, 151.0, 181.7, 182.1.

P(*t*-BQN) 11: A mixture containing $[(\eta^3\text{-allyl})\text{PdCl}]_2$ (22.0 mg, 0.06 mmol) and AgSbF_6 (50.0 mg, 0.15 mmol) in 1.3 mL of CH_2Cl_2 was stirred at 20°C for 30 min and filtered. To the clear yellow solution was added *t*-BQN 10 (3.3 g, 6.00 mmol). The reaction mixture was stirred at 20°C for 48 h. The polymer was isolated by precipitation into methanol to give 1.5 g (45%) of the polymer P(*t*-BQN) 11.

13: A mixture of 0.9 g (6.8 mmol) of 4-vinyl benzaldehyde, 0.65 g (2.7 mmol) of leucoquinizarin and 0.16 g of piperidinium acetate in 30 mL of toluene was stirred under reflux for 10 h. The precipitates were collected and subjected to silica gel column chromatography (hexane : ethyl acetate = 7 : 3 by vol.) to give 0.32 g (32%) of 13 as a red crystalline solid. m.p. 157°C; ^1H NMR δ 4.1 (s, 2H), 5.2-5.80 (d, J = Hz, 1H), 6.70 (q, 1H in vinyl), 7.05 (s, 1H in Arom), 7.20-7.45 (4H, Arom), 7.80-8.40 (4H, Arom); ^{13}C NMR δ 35.7, 113.9, 126.8, 127.1, 127.3, 128.8, 129.7, 133.7, 133.8, 134.6, 134.7, 136.4, 136.7, 137.9, 143.7, 156.9, 157.9, 186.7, 187.4

14: To a mixture of 0.32 g (0.9 mmol) of 17 and 0.01 g of *N,N*-dimethylaminopyridine (DMAP) in 15 mL THF were added 1.17 g (5.36 mmol) of di-*t*-butyldicarbonate and TEA (0.542 g, 5.36 mmol). The resulting mixture was stirred at room temperature for 12 h, concentrated in vacuo, and the residue was subjected to silica gel column chromatography (hexane : ethyl acetate = 9 : 1 by vol.) to give 0.47 (94%) of 14 as a yellow crystalline solid. m.p. 147°C; ^1H NMR (200 MHz, CDCl_3) δ 1.40-1.78 (m, 18H in *t*-butyl) 4.1 (s, 2H in bridge), 5.20-5.80 (2H, CH_2 in vinyl), 6.70 (q, 1H in vinyl), 7.20 (s, 1H in Arom), 7.20-7.40 (4H, Arom), 7.80-8.40 (4H, Arom); ^{13}C NMR δ 27.8, 35.8, 84.5, 114.0, 126.6, 126.9, 127.0, 127.2, 129.7, 133.6, 133.7, 134.2, 134.3, 136.5, 136.6, 137.1, 144.0, 146.6, 148.1, 150.6, 151.2, 181.9, 182.4.

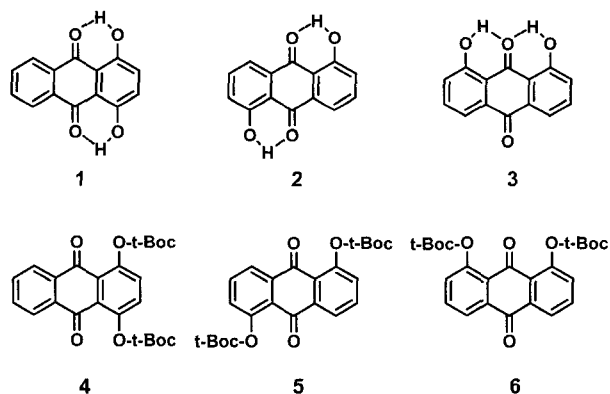
P(*t*BQSt/CSOMI) 16: A solution containing the precursor monomer 14 (0.25 g, 0.45 mmol), the comonomer CSOMI (0.147 g, 0.45 mmol), AIBN (0.01 g, 7 mol%), and 1,4-dioxane (1 mL) in an ampoule was subjected to repeated freeze-thaw cycles before the ampoule was sealed under vacuum. The sealed ampoule was heated at 55°C for 12 h. The solvent was removed under reduced pressure and the polymerization mixture was dissolved in THF and precipitated into methyl alcohol. The polymer thus obtained was purified further by reprecipitation from THF into methanol to give 0.21 g (52%) of the polymer P(*t*BQSt/CSOMI) 16.

Fluorescence Imaging. A typical example of obtaining patterned fluorescence images is as follows. A cyclohex-

anone solution containing poly(methyl methacrylate) (69 wt%), and the *t*-Boc-protected quinizarin 4 (30 wt%), and a photoacid generator, triphenylsulfonium triflate (1 wt%) was filtered with a membrane filter of 0.2- μm pore size. The filtrate was spincoated with 2,000 rpm for 40 sec using a Headway spincoater and prebaked on a hot plate at 100°C for 1 min to make a ca. 0.5 μm thick film. The prebaked film was contactwise exposed to 250 nm-UV for 5 sec (70 mJ/cm^2) through a photomask followed by PEB at 120°C for 60 sec. The fluorescent image pattern was photographed with a fluorescence microscope, Zeiss Epifluor.

Results and Discussion

Precursor Design and Synthesis. The strategic basis for designing a precursor molecule for functional imaging in the polymer film is as follows. The precursor molecule is nonfluorescent and/or colorless in its protected form, however becomes fluorescent and/or reveals color by photoinduced deprotection of the protecting groups. Among many possible candidate molecules which would meet the required criteria, our current investigation focused on dihydroxyanthraquinone systems. As displayed in Scheme III, quinizarin (1) and its regioisomers, anthrarufin (2) and 1,8-dihydroxyanthraquinone (3) have two hydroxy groups which form intramolecular hydrogen bonds with adjacent carbonyl groups. Due to the quasi-aromatic nature brought about by the intramolecular hydrogen bonding, quinizarin (1) and its regioisomers 2 and 3 have maximum absorption wavelengths in the visible regions (Figure 1). Interestingly, among the regioisomers, quinizarin (1) has an absorption maximum ($\lambda_{\text{max}} = 479 \text{ nm}$, $\epsilon = 7,700$) at much longer wavelength than that of 2 ($\lambda_{\text{max}} = 418 \text{ nm}$, $\epsilon = 4,000$) or 3 ($\lambda_{\text{max}} = 430 \text{ nm}$, $\epsilon = 7,800$). Introduction of *t*-Boc groups into the dihydroxyanthraquinones removes the possibility of the intramolecular hydrogen bonding. Accordingly, the UV absorption maxima of the *t*-Boc-protected anthraquinones 4, 5, and 6 shift to significantly shorter wavelength near



Scheme III. Dihydroxyanthraquinones and corresponding *t*-Boc-protected precursors.

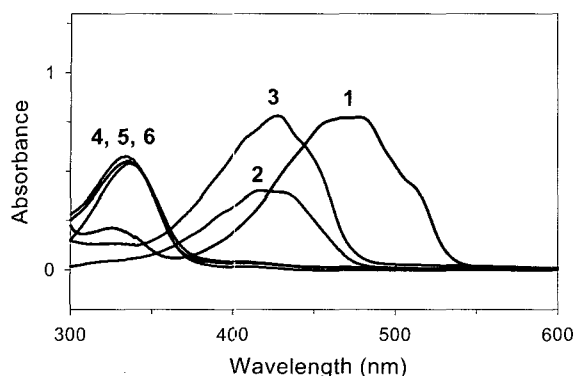


Figure 1. UV-visible absorption spectra of 1×10^{-4} M solution of dihydroxyanthraquinones and *t*-Boc-protected precursors in MeCN (1(quinizarin), 2(anthrarufin), 3(1,8-dihydroxyanthraquinone), 4(*t*-Boc-protected quinizarin), 5(*t*-Boc-protected anthrarufin), 6(*t*-Boc-protected 1,8-dihydroxyanthraquinone)).

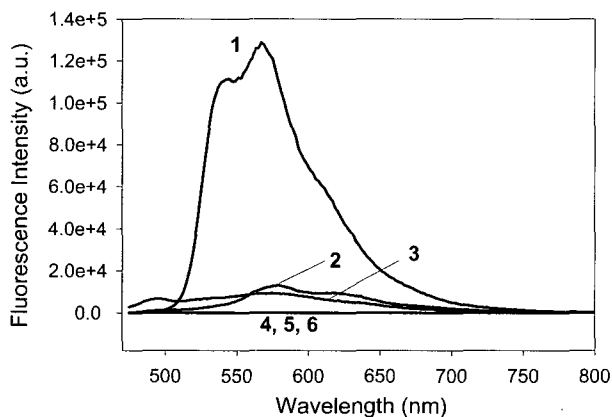


Figure 2. Fluorescence spectra of 1×10^{-4} M solution (MeCN) of dihydroxyanthraquinones and *t*-Boc-protected precursors. The spectra were observed by excitation at their maximum absorption wavelengths.

320 nm.

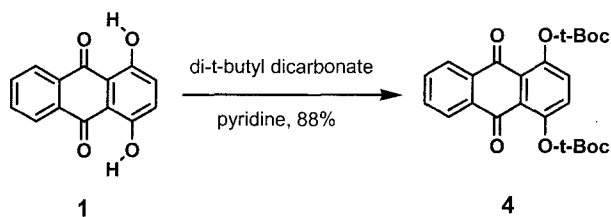
More interesting results were deduced from comparison of their fluorescent spectra in solution (Figure 2). When the fluorescence of the unprotected and *t*-Boc-protected dihydroxyanthraquinones were measured after excitation at their maximum absorption wavelengths, surprising results were obtained. The unprotected quinizarin (1) shows a strong fluorescence emission around 560 nm. The regioisomers 2 and 3 show very weak fluorescence. The fluorescence, however, is virtually absent in the case of *t*-Boc-protected dihydroxyanthraquinones.

The results described above have very intriguing consequences and indicate that the UV absorption maximum and fluorescence of a molecule can be readily altered and manipulated simply by blocking the intramolecular hydrogen bonds. Among the three dihydroxyanthraquinone iso-

mers, quinizarin (1) was found to undergo most dramatic changes in both UV absorption and fluorescence emission spectra. Accordingly, we focused on the generation of functional images with the *t*-Boc-protected quinizarin and its derivatives.

The precursor used in the initial phase of current study were readily prepared by reacting quinizarin (1) with di-*tert*-butyl dicarbonate to give the *t*-Boc-protected quinizarin 4 (Scheme IV). Typically, the reaction was carried out in pyridine solution and formation of the product was easily identified by monitoring the color of the reaction mixture. Reactions were terminated when the orange-red color of the reaction mixture became pale yellow. Pouring of the reaction mixture into cold water resulted in the precipitation of the product. Recrystallization from ethanol gave the pure product. The *t*-Boc-protected quinizarin was found to have a good solubility in common organic solvents such as chloroform, ethyl acetate, dimethyl formamide, acetone.

Photoinduced Regeneration of Quinizarin from the Precursor Molecules. Since the *t*-Boc groups of the precursor 4 are acid labile, the protecting groups are expected to be readily removed during the chemical amplification process. Accordingly, regeneration of quinizarin moieties should result in recovery of color and fluorescence in the exposed regions of the polymer film. In order to test the above possibility, a thin polymethyl methacrylate (PMMA) film of 1.0- μ m thickness containing the *t*-Boc-protected quinizarin 4 (20 wt%) and a photoacid generator, triphenylsulfonium triflate (TPSOTf, 5 wt%), were prepared by spin-coating a cyclohexanone solution on a quartz substrate. The polymer film, then, was exposed to 250 nm-UV and the progress was monitored by UV absorption spectroscopy. As displayed in Figure 3, absorption at the wavelength maxima for the protected quinizarin 4 (335 nm) decreased upon 2 sec irradiation and a new band (480 nm) which is in the region expected for quinizarin (1) appeared. Complete conversion of the precursor 4 to the unprotected quinizarin was observed when the film was irradiated for 2 sec. Additional evidence for the formation of quinizarin in the polymer film was deduced from comparison of the color of the film before and after irradiation. When the lightly yellow, transparent polymer film was exposed to UV for 2 sec, a highly transparent, orange-red film was obtained. These results demonstrate that the transiently protected precursor molecule 4 can be efficiently transformed to the unprotected



Scheme IV. Preparation of the precursor 4.

original molecule **1** by CA process.

In order to get more information about the nature and scope of acid-catalyzed deprotection of *t*-Boc group in the polymer films, the process was monitored by IR spectroscopy (Figure 4). The characteristic peak of *t*-Boc group at 1790 cm^{-1} decreased after irradiation for 1 sec (70 mJ/cm^2) followed by post exposure bake (PEB) at 120°C for 60 sec. Under these conditions, approximately 70% of *t*-Boc groups present in the polymer film were removed. The complete conversion was observed when higher doses (2 sec irradiation) of UV (140 mJ/cm^2) were employed. Further irradiation (5 sec irradiation) did not cause any spectral change.

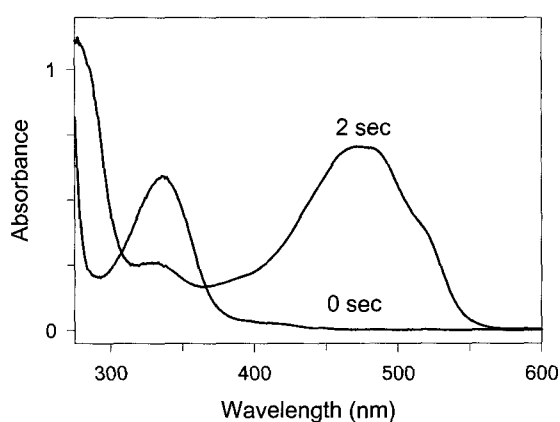


Figure 3. UV visible absorption spectra of a $1.0\text{-}\mu\text{m}$ thick spin-coated PMMA film containing **4** (20 wt%) and TPSOTf (5 wt%) and of the film after 254 nm UV exposure for 2 sec (140 mJ/cm^2) followed by PEB for 1 min at 100°C .

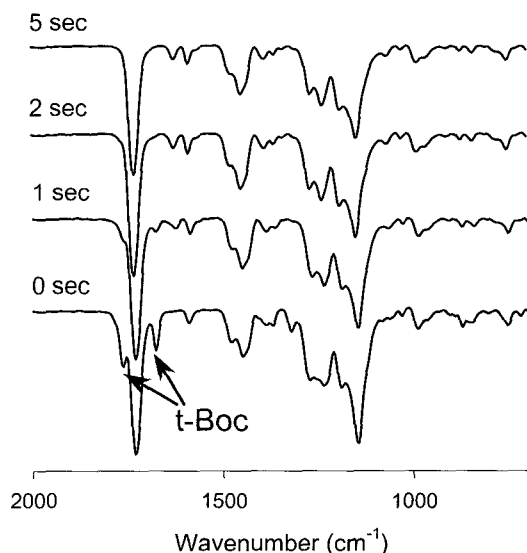
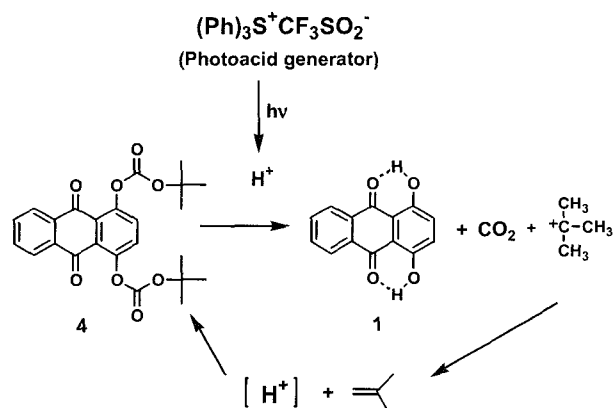


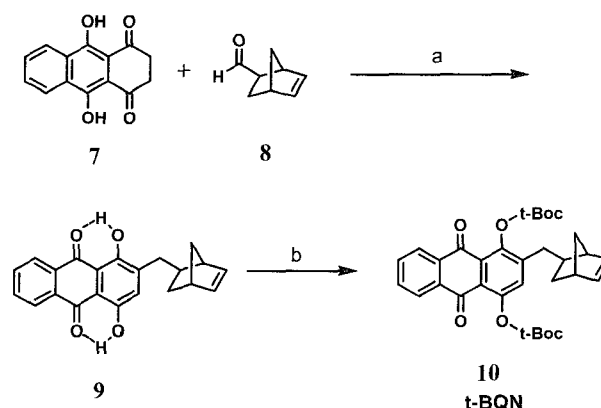
Figure 4. FT-IR spectra of $1.0\text{-}\mu\text{m}$ thick spin-coated film on a NaCl plate containing PMMA (75 wt%), the precursor **4** (25%), and TPOSTf (5 wt%) before and after irradiation followed by PEB at 120°C for 1 min.

Formation of quinizarin (**1**) from the photoinduced deprotection of the *t*-Boc groups of the precursor **4** in the polymer film follows general features of mechanistic pathways involved in the chemical amplification process (Scheme V). Thus, photoinduced decomposition of triphenylsulfonium triflate generates strong acids which catalyze the deprotection of the *t*-Boc groups during PEB process in the polymer film. It is known that one molecule of acid can catalyze approximately 2,000 cycles of the deprotection process. The byproducts from the CA process are only gaseous carbon dioxide and isobutylene.

Polymer-Bound Precursors. One obvious way to make the *t*-Boc-protected precursor more suitable for practical application is to incorporate the precursors into a polymer chain as pendant groups since simple mixture of the *t*-Boc-protected quinizarin **4** and a polymer such as PMMA may lead to the phase separation after long period of time. For this purpose, a norbornene monomer **10** which has pendant *t*-Boc-protected quinizarin moieties was prepared (Scheme VI). The *t*-Boc-protected norbornene monomer **10** was pre-



Scheme V. Mechanism of regeneration of quinizarin by chemical amplification in the polymer film.



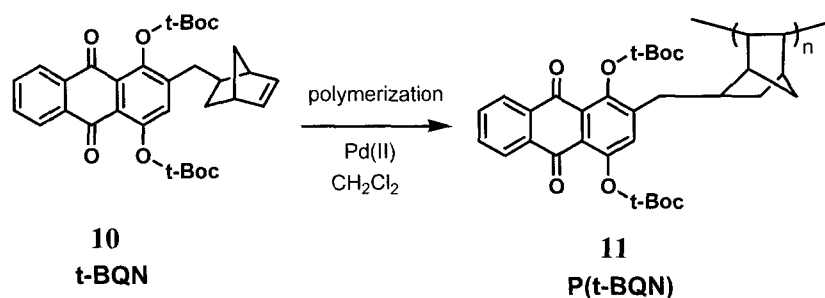
Scheme VI. Synthesis of precursor-containing norbornene monomer **10**. (a) piperidium acetate, isopropanol, reflux, 6 h, 88%. (b) di-*t*-butyl dicarbonate, cat. DMAP, TEA, THF, 25°C , 4 h, 93%.

pared in two steps. Marschalk condensation of leucoquinizarin (**7**) with 5-norbornene-2-carboxaldehyde (**8**) provided intermediate **9** in 88% yield. Conversion of the intermediate **9** to the desired monomer *t*-BQN **10** was achieved by protection of phenol groups with di-*tert*-butyl dicarbonate in the presence of catalytic amount of 4-dimethylaminopyridine (DMAP) in THF (93% yield). The ratio between *endo* and *exo* isomers in the monomer **10** was found to be 8 : 2 by ¹H NMR analysis.

Polymerization of the norbornene-derived monomer *t*-BQN **10** was carried out in the presence of organo palladium catalyst $\{(\eta^3\text{-allyl})\text{Pd}(\text{SbF}_6)\}$ (1 mol% based on the monomer) in methylene chloride (Scheme VII). The polymerization was initiated by adding the organo palladium catalyst solution to the monomer under N₂ atmosphere. The resulting mixture was stirred at 20 °C for 48 h and poured into excess MeOH to give the polymer as a precipitate. The homopolymer P(*t*-BQN) **11** after precipitation into methanol was obtained as a pale orange powder in 45% yield. The polymer **11** had a weight-average molecular weight (*M_w*) of 29,000 with the polydispersity of 1.87. Both *endo* and *exo* isomers of the monomer **11** was converted to polymer. This was evidenced by examining ¹H NMR spectrum of the filtrate after collecting the polymer by precipitating into MeOH.

The next phase of our efforts focused on making the thin polymer films and regeneration of the quinizarin moieties on solid substrates. In order to test the above possibility, thin polymer films of 1.1 μm thickness containing P(*t*-BQN) **11** (95 wt%) and a photoacid generator, triphenylsulfonium triflate (TPSOTf, 5 wt%), were prepared by spin-coating a dioxane solution on quartz substrates. When the nearly colorless polymer film was exposed to 250 nm-UV for 10 sec (140 mJ/cm²), a transparent red film was obtained after PEB at 120 °C for 60 sec. The regeneration of quinizarin moieties in the polymer was confirmed by analysis of UV spectra of the exposed film, as shown in Figure 5. The absorption at the wavelength maximum for *t*-Boc protected quinizarin group (335 nm) decreased and a new absorption at 480 nm corresponding to free quinizarin appeared.

Single Component Imaging System. In order to remove the *t*-Boc-protecting groups of the polymer **11** by CA pro-



Scheme VII. Preparation of homopolymer P(*t*-BQN) **11**.

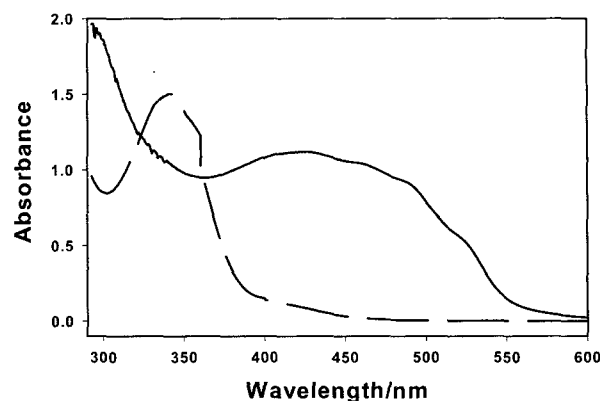


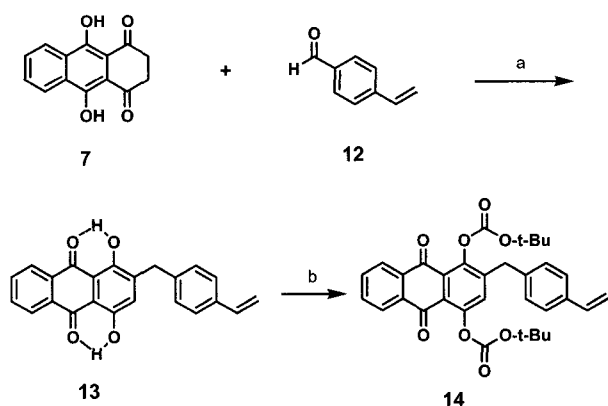
Figure 5. UV visible absorption spectra of a 1.1-μm thick spin-coated film containing P(*t*-BQN) **11** (95 wt%) and TPSOTf (5 wt%) (dashed line) and of the film after UV exposure for 10 sec followed by PEB at 120 °C for 1 min (solid line).

cess, a photoacid generator is required in the polymer film. If the photoacid generator as well as the precursor molecule can be incorporated in the polymer chain, it would no longer be necessary to add the photoacid generator. The polymer system which have both the precursor and PAG is called “single component system”. For this purpose, we have designed a new precursor monomer. The strategy is as follows. Styrene is well known to form an alternating copolymer with maleimide derivative by AIBN-initiated radical polymerization.¹⁹ Camphorsulfonyloxymaleimide (CSOMI) has been used as a monomer for photoacid generation.²⁰ Accordingly, it was expected that the styrenic monomer **14** would polymerize with CSOMI to make an alternating copolymer. The monomer **14** was prepared from leucoquinizarin (**7**) and 4-vinylbenzaldehyde (**12**) in two steps (Scheme VIII). Condensation of leucoquinizarin with 4-vinylbenzaldehyde in toluene under Marschalk conditions gave the intermediate 2-(4-vinylbenzyl)quinizarin (**13**) in 32% yield. When the condensation reaction was carried out in isopropyl alcohol, a routine solvent for Marschalk reaction, only trace amount of the product was isolated. The intermediated **13** was further treated with di-*tert*-butyl dicarbonate in the presence of catalytic amount of 4-dimethylaminopyridine (DMAP) in THF to give the desired

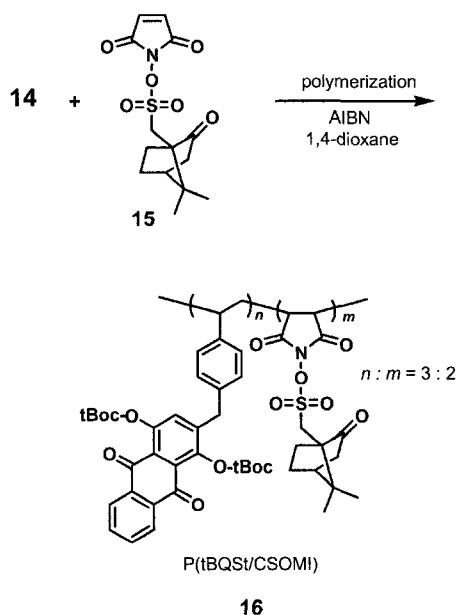
monomer **14** in high yield.

Copolymerization of the *t*-Boc-protected quinizarin monomer **14** with camphorsulfonyloxymaleimide (CSOMI) **15** was carried out with 1 : 1 molar feed ratio in 1,4-dioxane using AIBN as a radical initiator (Scheme IX). The copolymer P(*t*BQSt/CSOMI) **16**, after precipitation into methanol was obtained as pale yellow powders in 47% yield. The polymer has an average molecular weight (M_w) of 15,000 compared to a polystyrene standard by gel permeation chromatography (GPC) (PD = 3.9). The composition of the obtained copolymer P(*t*BQSt/CSOMI) **16** was confirmed to have 3 to 2 molar ratio between the precursor monomer and CSOMI by ^1H NMR and thermal analysis.

It is expected that irradiation of the copolymer P(*t*BQSt/



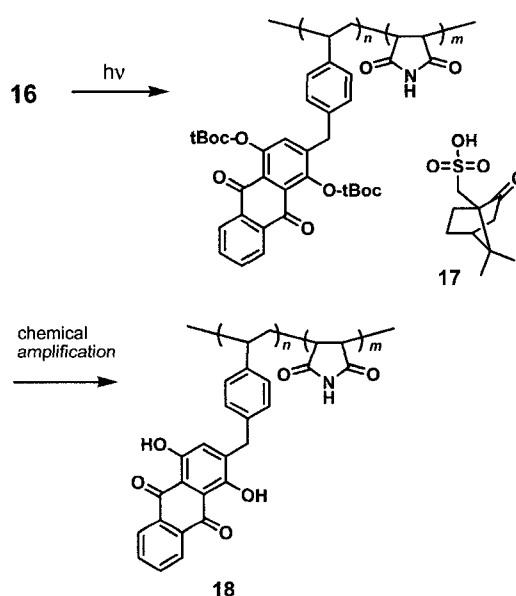
Scheme VIII. Synthesis of precursor-containing styrene monomer **14**. (a) piperidium acetate, toluene, reflux, 10 h, 32%. (b) di-*t*-butyl dicarbonate, cat. DMAP, TEA, THF, 25 °C, 12 h, 94%.



Scheme IX. Synthesis of copolymer **16** by AIBN-initiated radical polymerization.

CSOMI) **16** would cleave the weak N-O bond in CSOMI moieties and generate strong acid, camphorsulfonic acid. The strong acid should catalyze deprotection of the *t*-Boc groups of the precursor molecules and regenerate quinizarin moieties in the polymer film (Scheme X). In order to test the above possibility, the copolymer P(*t*BQSt/CSOMI) **16** was spincoated on a quartz substrate to make a thin film (0.4 μm) and irradiated with 254 nm UV-light. As shown in Figure 6, irradiation of the polymer film for 60 sec allowed regeneration of quinizarin moieties.

Patterned Fluorescence Imaging. In order to generate patterned fluorescent images, thin polymer films on a silicon wafer containing the precursor molecules and a photo-acid generator, triphenylsulfonium triflate, were prepared.



Scheme X. Regeneration of quinizarin moieties by photo-induced chemical amplification.

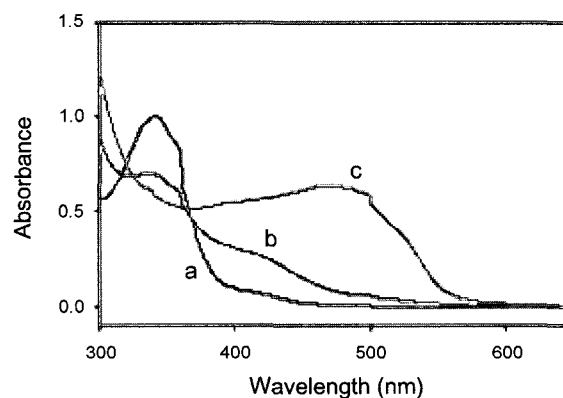


Figure 6. UV visible absorption spectra of a 0.3- μm thick spin-coated film containing **16** after UV exposure for 0 sec (a), 10 sec (b), and 60 sec (c) followed by PEB at 120 °C for 1 min, respectively.

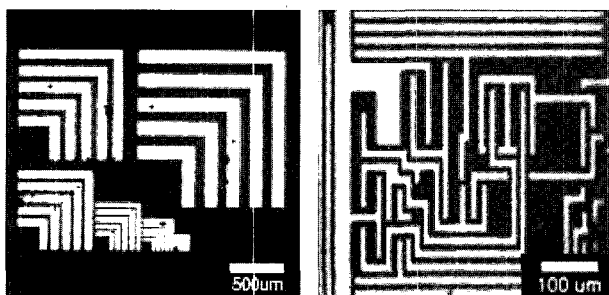


Figure 7. Fluorescence image patterns obtained with precursors **4** (left) and **11** (right).

In the case of the copolymer **16**, the photoacid generator is not required. The polymer films, then, were irradiated with UV light through a photomask. The silicon wafer was then placed on a hotplate for post exposure bake at 120°C for 1 min. We were able to observe patterned fluorescent images under fluorescence microscopy. Figure 7 shows patterned fluorescence images obtained using the precursors **4** and **11**. Although we were able to obtain patterned images with the precursor **16**, the precursors **4** and **11** were found to give better images. The bright areas are portions exposed through the photomask.

Conclusions

We have developed novel precursors for color and fluorescent imaging. The temporarily-protected quinizarin precursors were readily converted to quinizarin moieties in the polymer film during a chemical amplification process and regenerated original properties of quinizarin. Accordingly, a large bathochromic shift and generation of fluorescence were observed. When the polymer film was exposed to UV through a photomask, well resolved fluorescent image patterns were readily obtained in high sensitivity without any further wet development. The simple and straightforward strategy described above for generation of patterned images via CA process should be useful in the design of new imaging materials.

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