Norbornene-Derived Quinizarin Dye Molecules for Photoimaging in Polymer Film Based on Chemical Amplification

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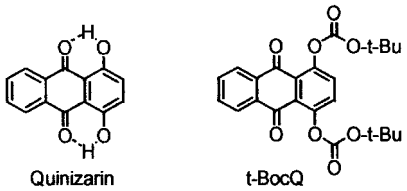
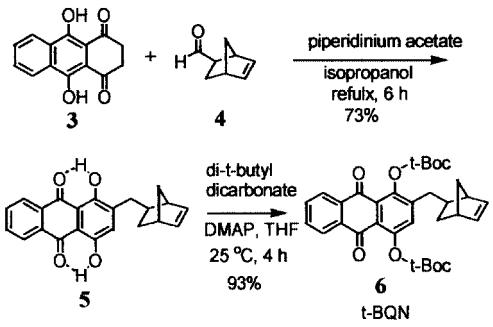
A novel photoimaging process in thin films has been disclosed by taking advantage of photolithographic techniques based on chemical amplification concept. The key materials utilized in the process are norbornene-derived quinizarin dye molecules protected with acid-labile *tert*-butoxycarbonyl (*t*-Boc) blocking groups.

Since the pioneering discovery of chemical amplification (CA) concept by IBM researchers two decades ago, it has been key technology for photolithographic generation of patterned images in polymer film.[1–3] 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 protecting groups in the polymer film, typically during the post-exposure bake (PEB) process. This process allows rapid removal of the protecting group at lower temperature than the required thermal deprotection temperature. *tert*-Butyl and *tert*-butoxycarbonyl (t-Boc) are typical protecting groups used in the chemically amplified process and are removed selectively in the exposed regions of the polymer film. The different chemical and physical properties between the exposed and unexposed regions of the film can lead to generation of patterned images in various ways.

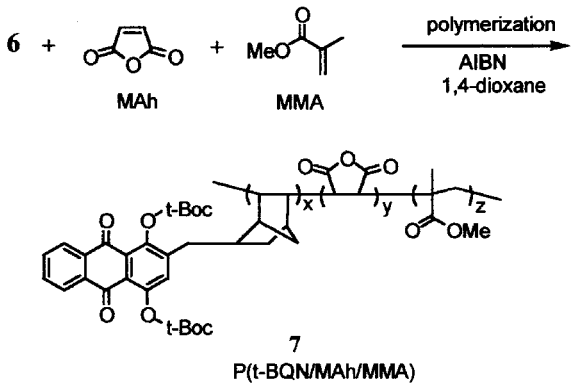


We have been interested in application of this novel technology to nonlithographic photoimaging areas. Recently, we reported synthesis of t-Boc-protected quinizarin **2** from quinizarin **1** for color and fluorescent imaging in the polymer film.[4] Quinizarin **1** has a maximum absorption wavelength in the visible region and is strongly fluorescent due to the intramolecular hydrogen bonding. Removal of the possibility of the intramolecular hydrogen bonding with t-Boc groups causes shift of the maximum absorption wavelength to UV region and the t-Boc-protected quinizrin **2** is nonfluorescent. By converting the t-Boc-protected quinizarin **2** to quinizarin by chemical amplification, we were able to generate color and fluorescence images in the polymer film. Very recently, we reported synthesis of a copolymer with a methacrylate monomer and fluorescence imaging which has pendent t-Boc-protected quinizarin precursors.[5] Since the synthesis of methacrylate monomer requires four steps, we felt it would be more practical if we could reduce the required synthetic procedures. We now report efficient synthesis of novel polymer having t-BOC-protected quinizarin moieties and more fine fluorescence image patterns with a new monomer **6** derived from norbornene. The t-Boc-protected norbornene monomer **6** was prepared in two steps. Marschalk condensation[6] of leucoquinizarin (**3**) (Aldrich Chemical Co.) with 5-norbornene-2-carboxaldehyde (**4**) provided intermediate **5** in 73% yield. Conversion of the intermediate to the desired monomer t-BQN **6** 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).[7]

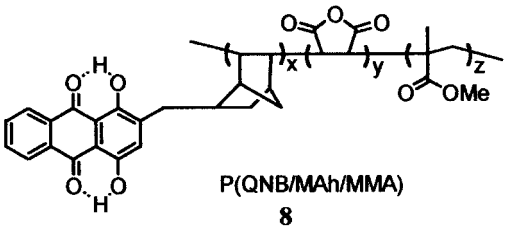


Scheme 1. Synthesis of t-Boc-protected norbornene monomer **6**.

Generally, t-BQN is hardly homopolymerizable but the monomer readily copolymerized with strongly electron-accepting monomers such as maleic anhydride (MAh) by virtue of electron-donor-acceptor (EDA) polymerization. Accordingly, radical copolymerization of tBQN and MAh with methyl methacrylate (MMA) was carried out with a 1:1:2 molar feed ratio in 1,4-dioxane using 2,2'-azobis(isobutyronitrile) (AIBN) as a radical initiator at 60 °C for 24 h. The terpolymer, P(t-BQN/MAh/MMA) **7**, after precipitation in methanol, was obtained as a pale yellow powder in 62% yield. The polymer has an average molecular weight (M_w) of 12000 compared to a polystyrene standard by GPC (polydispersity = 1.72). The composition of the terpolymer obtained was confirmed to have a P(t-BQN/MAh/MMA = 1:1:6) ratio by ^{1}H NMR and thermal analysis.



Scheme 2. Preparation of terpolymer P(t-BQN/MAh/MMA) **7**.



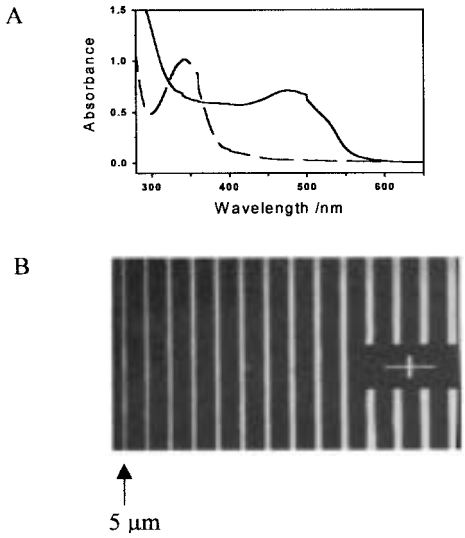


Figure 1. A: UV absorption spectra of a 0.95 μm thick spin-coated film containing P(t-BQN/Mah/MMA) 7 (95 wt%) and TPSOTf (5 wt%) (dashed line) and of the film after UV exposure for 10 s followed by PEB at 120 °C for 1 min (solid line); B: Fluorescence image patterns obtained with 1.3 μm thick film containing the polymer **7** as described above after irradiation with a photomask.

The next phase of our efforts focused on making the thin polymer films and regeneration of the quinizarin moieties on solid substrates. Since the t-Boc group of the polymer P(t-BQN/MAh/MMA) **7** is acid labile, the protecting groups are expected to be readily removed during the CA process only liberating gaseous by products of CO_2 and isobutene. Accordingly, regeneration of quinizarin moieties as in **8** should result in recovery of color and fluorescence in the exposed regions of the polymer film.

In order to test the above possibility, thin polymer films of 0.95 μm thickness containing P(t-BQN/MAh/MMA) **7** (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 250nm-UV for 10 s (140 mJ/cm^2), a transparent red film was obtained after PEB at 120 °C for 60 s. The regeneration of quinizarin moieties in the polymer was confirmed by analysis of UV spectra of the exposed film, as shown in Figure 1A. 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. When a 1.3-μm thick film containing same composition which was spin-coated on a silicon wafer was irradiated with 250 nm UV for 10 s (140 mJ/cm^2) through a photomask fine fluorescent image patterns with 5 μm resoultion under fluorescence microscopy were obtained after PEB at 120 °C for 60 s (Figure 1B). The bright areas are portions exposed through the photomask.

In summary, we have prepared a novel polymer having quinizarin precursor pendants for color and fluorescent imaging. The t-Boc protected precursors of the polymer were converted to the quinizarin moieties during a chemical amplification process in the polymer film 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 in the presence of a photoacid generator through a photomask, finely-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.

References and Notes

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7 ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.62 (1H, m), 1.22 (1H, m), 1.41 (1H, m), 1.60 (18H, s), 1.91 (1H, m), 2.39 (1H, m), 2.47–2.50 (2H, m), 2.71–2.80 (2H, m), 6.02–6.22 (2H, m), 7.40 (1H, s), 7.70 (2H, m), 8.10-8.22 (2H, m); ^{13}C NMR δ 27.7, 32.2, 35.1, 42.1, 45.4, 50.0, 84.1, 124.3, 126.3, 132.4, 133.4, 137.9, 144.9, 151.0, 182.1.