

Communications

The First Synthesis of a Transition Metal-Catalyzed Homopolymer Having Pendent *t*-Boc-Protected Quinizarin for Patterned Fluorescence Images

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Abstract: A homopolymer having pendent *t*-Boc-protected quinizarin moieties has been prepared for patterned fluorescence images. The homopolymer P{*t*-BQN (2-norbornenylmethyl di-*tert*-butoxycarbonylquinizarin)} **5** was prepared by palladium-catalyzed addition polymerization. The *t*-Boc-protecting groups of the polymer were efficiently removed during chemical amplification process and revealed original properties of quinizarin, allowing patterned fluorescence images in the polymer film.

Keywords: patterned fluorescence image, homopolymer, chemical amplification, addition polymerization.

Introduction

Recently, synthesis of norbornene-derived polymers having pendent functional groups has been extensively studied in fundamental and applied research areas. In general, norbornene monomers can be polymerized by (1) AIBN-initiated radical polymerization,¹⁻⁴ (2) ring opening metathesis polymerization (ROMP),⁵⁻⁷ or (3) transition metal-catalyzed addition polymerization.⁸⁻¹² Among these, the ROMP and the transition metal-catalyzed addition polymerization are the two most common methods for the preparation of polymers derived from norbornene monomers. The polymers obtained by ROMP, however, contain double bonds in the main chain of the polymers which may effect long term stability of the polymers if light-sensitive pendent functional groups are to be incorporated. Thus, many researchers have

attempted to prepare norbornene-derived polymers with pendent functional groups using the transition metal-catalyzed addition polymerization. However, the majority of results reported to dates are limited to simple functional groups such as esters. This is mainly because most transition metal catalysts rapidly react with functional groups and become inactive for polymerization. As part of our on going efforts for the development of photoinduced color/fluorescence changing polymers,¹³⁻¹⁹ we now report the first successful transition metal-catalyzed synthesis of norbornene-derived homopolymers having pendent *t*-Boc-protected quinizarin moieties for patterned fluorescence images.

Experimental

Materials. Leucoquinizarin, 5-norbornene-2-carboxaldehyde, di-*t*-butyl dicarbonate and allylpalladium chloride dimer were purchased from Aldrich and used as received.

Synthesis of Norbornene-derived Monomer *t*-BQN (2-

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norbornenylmethyl di-*tert*-butoxycarbonylquinizarin) 5.

A solution containing leucoquinizarin (**1**) (30.0 g, 0.124 mol), 5-norbornene-2-carboxaldehyde (**2**) (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 **3** as red crystals, m.p 141.8°C (DSC). IR (KBr): 725.1, 1239.6, 1435.8, 1587.5, 1622.3, 2964.7 cm⁻¹. 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. Anal. Calcd. for C₂₂H₁₈O₄: C 76.29 H 5.24 O 18.48; Found C 76.21 H 5.50 O 18.29.

To a solution containing **3** (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 **4** (15.0 g, 93%) as a yellow crystal. IR (KBr): 716.3, 1258.9, 1370.9, 1476.9, 1594.2, 1676.2, 1759.5, 2977.0 cm⁻¹. 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). ¹³C NMR (CDCl₃): 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. Anal. Calcd. for C₃₂H₃₄O₈: C 70.31 H 6.27 O 23.42; Found C 70.18 H 7.09 O 22.74.

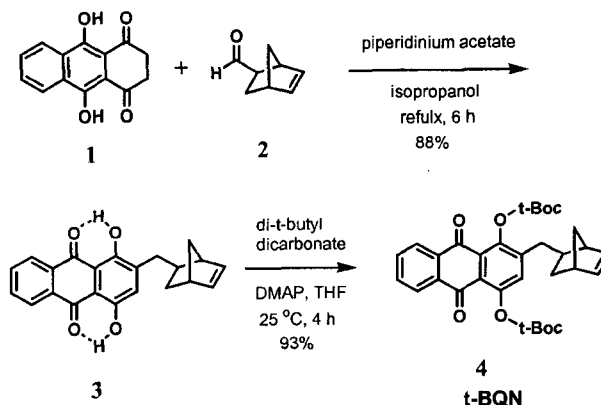
Preparation of Homopolymer P(*t*-BQN) 5. A mixture containing [(η³-allyl)PdCl]₂ (22.0 mg, 0.06 mmol) and AgSbF₆ (50.0 mg, 0.15 mmol) in 1.3 mL of CH₂Cl₂ was stirred at 20°C for 30 min and filtered. To the clear yellow solution was added *t*-BQN **4** (3.3 g, 6.00 mmol). The reaction mixture was stirred 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) **5**.

Fluorescence Imaging. A solution containing the polymer P(*t*-BQN) **5** (95 wt%) and a photoacid generator, triphenylsulfonium triflate (TPSOTf, donated by Kumho Co.) (5 wt%) in 1,4-dioxane (1 mL) was filtered with a membrane filter of 0.2-μm pore size. The filtrate was spincoated with 2,500 rpm for 60 sec using a Headway spincoater and prebaked on a hot plate at 100°C for 1 min to make a 1.1 μm thick film. The prebaked film was contactwise exposed to 250 nm-UV for 10 sec through a photomask followed by PEB at 120°C for 60 sec. The fluorescent image pattern was photographed with a fluorescence microscope, Zeiss Epifluor.

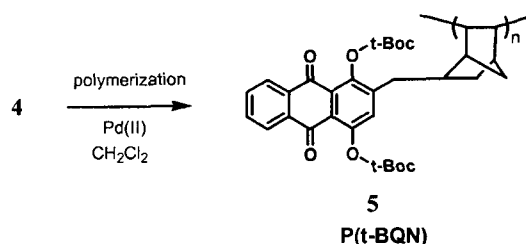
Results and Discussion

The *t*-Boc-protected norbornene monomer **4** was prepared in two steps. Marschalk condensation²⁰ of leucoquinizarin (**1**) (Aldrich Chemical Co.) with 5-norbornene-2-carboxaldehyde (**2**) provided intermediate **3** in 88% yield. Conversion of the intermediate to the desired monomer *t*-BQN **4** 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 The ratio between *endo* and *exo* isomers in the monomer **4** was found to be 8:2 by ¹H NMR analysis.

Polymerization of the norbornene-derived monomer *t*-BQN **4** was carried out in the presence of organo palladium catalyst {(η³-allyl)Pd(SbF₆)} (1 mol% based on the monomer) in methylene chloride (Scheme II). 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 **5** P(*t*-BQN) after precipitation into methanol was obtained as a pale orange powder in 45% yield. The polymer **5** 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 **4** was converted to polymer. This was evidenced by examining ¹H NMR spectrum of the filtrate after collecting



Scheme I. Synthesis of *t*-Boc-protected norbornene monomer *t*-BQN **4**.



Scheme II. Preparation of homopolymer P(*t*-BQN) **5**.

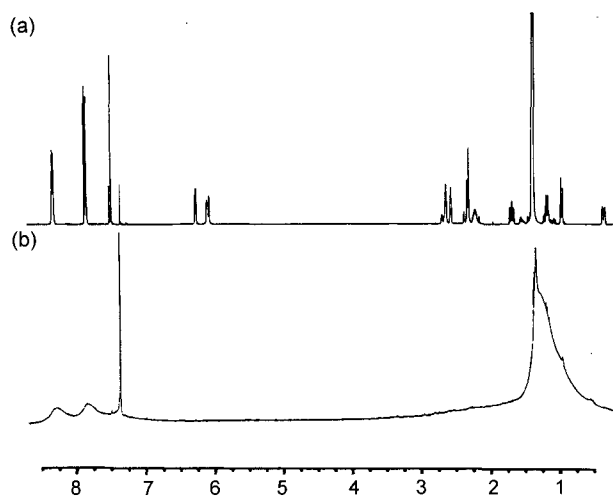
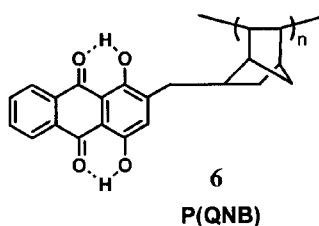


Figure 1. ^1H NMR spectra of (a) monomer *t*-BQN **4** and (b) polymer P(*t*-BQN) **5** in CDCl_3 .

the polymer by precipitating into MeOH.

^1H NMR spectra of the monomer as well as the polymer are displayed in Figure 1. As can be seen by inspection of these data, the peaks at around 6.1 ppm for the characteristic norbornene resonances for the monomers **4** (Figure 1(a)) completely disappeared in ^1H NMR spectra of the polymers **5** (Figure 1(b)).

The next phase of our efforts focused on making the thin polymer films and regeneration of the quinizarin moieties on solid substrates. For these purposes, a photolithographic method called 'chemical amplification (CA) process' has been employed.²¹⁻²⁴ 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 *t*-Boc protecting groups in the polymer film, typically during the post-exposure bake (PEB) step. Since the *t*-Boc group of the polymer P(*t*-BQN) **5** 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 **6** 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 1.1 μm thickness containing P(*t*-BQN) **5** (95 wt%) and a

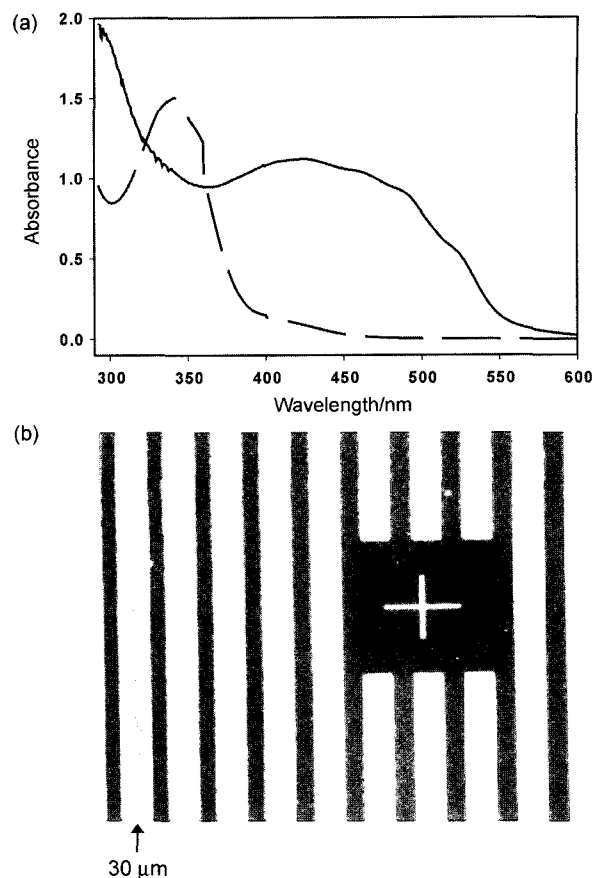


Figure 2. (a) UV absorption spectra of a 1.1 μm thick spin-coated film containing P(*t*-BQN) **5** (95 wt%) and TPSOTf (5 wt%) (dashed line) and of the film after UV exposure for 10 sec followed by PEB at 120°C for 1 min (solid line); (b) Fluorescence image patterns obtained with 1.2 μm thick film containing the polymer **5** after irradiation with a photomask.

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/cm^2), 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 2(a). 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 1.2- μm thick film containing same composition which was spin-coated on a silicon wafer was irradiated with 250 nm UV for 10 sec (140 mJ/cm^2) through a photomask fine fluorescent image patterns with 30 μm resolution under fluorescence microscopy were obtained after PEB at 120°C for 60 sec (Figure 2(b)). The bright areas are portions exposed through the photomask.

In summary, we have prepared a novel homopolymer having quinizarin precursor pendants derived from a transition

metal-catalyzed addition polymerization. As expected, 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.

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