

Multi-Regulated Color Tuning of a Patterned Polymer Film Incorporating Pendant Phenoxyquinones and Phenolphthaleins

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The development of efficient fluorescent and color changeable compounds has gained much attention in both fundamental and applied research areas. Among numerous photochromic and fluorescent compounds, certain phenoxy-naphthacene-quinone derivatives are attractive molecules due to their excellent properties, such as low fatigue as well as negligible thermal interconversion at room temperature.¹ For example, 6-phenoxy-5,12-naphthacenequinone is well known to isomerize from the *trans*-quinone to the *ana*-quinone upon irradiation with UV light and to isomerize back to the *trans* form with visible light.^{1a} We have previously reported the first successful direct synthesis of norbornene- or styrene-derived photochromic polymers (Figure 1).² In addition, phenolphthaleins are increasingly important as the active components of color change indicators, temperature resistant polymers, and optoelectronic photosensors.³ We have also described chemically amplified photolithography for color imaging using phenolphthalein or quinizarin derived polymers.⁴ In this report, an optical change in the polymer is accompanied by a structural change, *i.e.*, the colorless lactone form of phenolphthalein under alkaline conditions dissociates a proton from its phenol group to form the red-violet colored quinoidal anion form (Figure 1). Mixtures of electron donor and electron acceptor groups often exhibit a new absorption band, attributable to a donor-acceptor complex (DAC), which is not displayed by

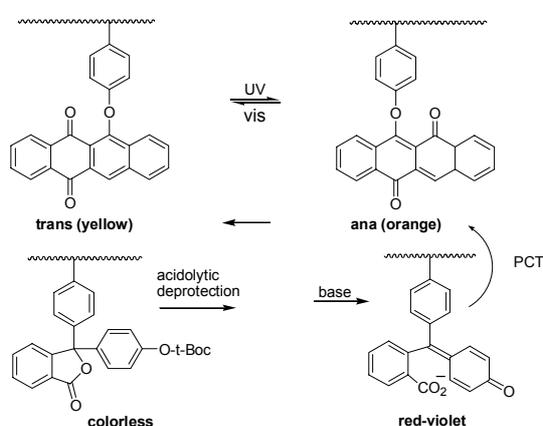


Figure 1. Photo-isomerization/photo-lithography of polymers incorporating chromophores and the proposed PCT pathway by donor/acceptor interactions in the bound polymer.

either component separately. The transition between donor and acceptor is referred to as a charge-transfer (CT) transition, and is generally broad and structureless.⁵ We felt that the absorbed visible light energy could effectively be transferred to the phenoxyquinone moiety to give a photochromic isomerization from the *ana* to the *trans* isomer by a photoinduced charge-transfer (PCT) pathway. In this paper, as part of our continuing effort to develop photoinduced color/fluorescent changing polymers,^{2,4} we report the successful synthesis of a terpolymer incorporating pendant phenoxyquinone and phenolphthalein groups and the multi-regulated color tuning of a patterned polymer film.

To achieve this goal, an attempt was made to prepare a polymer integrating pendant phenoxyquinone and phenolphthalein groups. First, 6-[(4-vinylphenoxy)]-5,12-naphthacenequinone (PNQSt) monomer and a mono *t*-Boc protected phenolphthalein methacrylate (BMPP) monomer were prepared as previously described.² The synthetic sequence employed in the preparation of the terpolymer is shown in Figure 2. When the styrene derived naphthacenequinone monomer (PNQSt) and *t*-Boc protected phenolphthalein monomers (BMPP) were terpolymerized with methylmethacrylate (molar ratio 1:1:2) under AIBN initiated radical polymerization, the terpolymer P(PNQSt/MMA/BMPP) was produced with a weight-average molecular weight (*M_w*) of 350,000 and a polydispersity of 5.7. The terpolymer composition was confirmed to have a 1:8:1 ratio by ¹H NMR spectroscopic analysis. As can be seen by inspection of the spectra, the vinylic protons of the monomers disappear due to the polymerization, as seen in the corresponding spectrum of the polymer; characteristic peaks of the monomers, a singlet at 1.6 ppm for the *t*-Boc group of BMPP, a singlet at 3.5 ppm for the methoxy group of methyl methacrylate and a multiplet at 7.5-8.4 ppm for the aromatic naphthacenequinone group, all

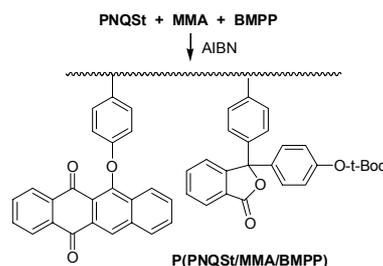


Figure 2. Synthesis of P(PNQSt/MMA/BMPP) by radical polymerization.

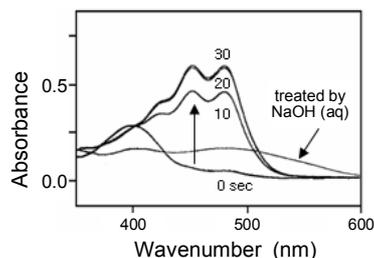


Figure 3. UV-Vis spectra of the P(PNQSt/MMA/BMPP) deprotected polymer containing TPSOTf (5 wt%) after exposure to 250 nm UV light (0 sec), and the time course of the reaction revealed by UV-Vis monitoring of the thin polymer film upon irradiation with 360 nm UV light.

appear in the polymer spectrum. In a FT-IR, characteristic absorption bands corresponding to the carbonyl groups of *t*-Boc, lactone, and ketone at 1760, 1750, and 1740 cm^{-1} were all identified. In TGA/DSC thermograms, the mass loss (*ca.* 8 %) due to cleavage of the *t*-Boc group in the terpolymers was found to be in good agreement with calculated values. The deprotection temperature of the terpolymers was observed at 170 °C, beginning at 150 °C. These observations confirm that the radical-initiated polymerization was successful.

In order to investigate the flexibility and degree of photo-induced transformation properties of the chromophore, thin polymer films were exposed to both UV light (250 nm) for deprotection of the *t*-Boc groups and UV light (360 nm) for the *trans* to *ana* transformation followed by post-exposure baking at 120 °C for 1 min to finish the deprotection process. The progress of the reaction was monitored with an UV spectrometer. As shown in Figure 3, the terpolymer films show typical photochromic properties of phenoxynaphthacene-quinone derivatives. Upon irradiation of the polymer films (yellow color), characteristic double absorption bands of the *ana*-quinone form (orange color) of the phenoxynaphthacene-quinone moieties at approximately 450 and 480 nm increase. In order to reverse the rearrangement from the *ana* to *trans* isomers, the polymer films pre-exposed to 360 nm UV light were irradiated with visible light (> 410 nm), similar to results which have previously been reported.² Interestingly, when the polymer films were treated with an aqueous alkaline solution (1 M NaOH), the peak intensity at approximately 550 nm increased, which suggests there is an accompanying structural change, *i.e.*, the colorless lactone form of phenolphthalein under alkaline conditions dissociated a proton to form a red-violet colored quinoidal anion form. This pH controlled colorimetric transition was reproducible by acid/base chemistry. In addition, peaks of the terpolymer at approximately 420, 450 and 480 nm largely disappeared and broadened upon treatment with an alkaline solution. The exact role played by NaOH in this process is not clear. We believe that the line broadening promoted by the small amount of additional NaOH is attributable not to the phenoxyquinone moiety but to the phenolphthalein moiety, resulting in the corresponding pink color associated with the quinoidal structure. Presumably, PCT from the quinoidal anion electron donor to the adjacent ketone group of the phenoxynaphthacenequinone electron acceptor

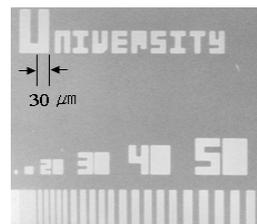


Figure 4. Fluorescent patterns obtained on 0.5 thick P(PNQSt/MMA/BMPP) film containing TPSOTf (5 wt%) cast on a silicone wafer.

can effectively occur between the planar chromophore structures attached directly to the main chain back-bone of the terpolymer. Further mechanistic studies for this photo-rearrangement are required to fully elucidate the PCT mechanism in the presence of alkaline media.

The advantages of using the *t*-Boc protected polymer include superior film-forming properties and clean deprotection of the polymer followed by treatment with alkaline solution to give the significant solubility change needed for the application of classical photolithography technology. We observed that micro-patterned images could be obtained by removing the exposed regions with an appropriate aqueous, alkaline solution (0.1 M, NaOH). The significant solubility changes promoted by NaOH are ascribed to the phenolphthalein moiety converting to the corresponding polar quinoidal structure. These patterned structures were subsequently converted into fluorescent images by transformation of the *trans*- to *ana*-quinone isomer by UV light irradiation (360 nm), as shown in Figure 4.

In summary, we have developed a generic approach to micro-patterned fluorescent images using the terpolymer with side groups containing chromophores such as phenolphthalein and phenoxynaphthacenequinone. We expect this photolithography technology in combination with photochromic pendant materials to be useful in the color sensor area.

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