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Communications to the Editor

Synthesis of Norbornene-Derived Polymers Having Pendant Phenoxyquinones for Photochromism

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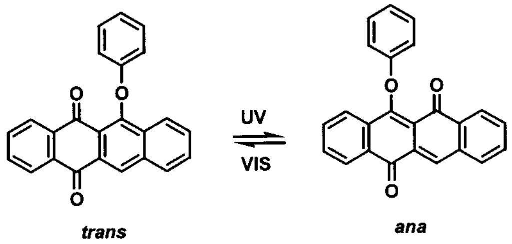
The development of efficient photochromic compounds has gained much attention in fundamental and applied research areas. Among numerous photochromic compounds, certain phenoxynaphthacenequinone derivatives are attractive molecules due to their excellent properties such as low fatigue as well as negligible thermal interconversion at room temperature.[1] For example, the "*trans*"-quinone form of 1-phenoxy-5,12-naphthacenequinone undergoes a photochemical rearrangement to the "*ana*"-quinone form upon irradiation with UV light (Scheme 1).[1a] The reverse conversion of "*ana*"-quinone to "*trans*"-quinone form readily occurs with visible light. It was reported that the photochemical rearrangement process could be repeated 500 times without decomposition of the material.[1a]

One obvious way to make the photochromic compound more suitable for practical application is to incorporate the chromophore into a polymer chain as pendant groups since polymers can be spin-coated on solid substrates to make thin films. It is surprising that not many results have been reported on the synthesis of polymer bound phenoxyquinone derivatives in light of their novel properties. To the best of our knowledge, only one published result on the synthesis of polymer-bound phenoxynaphthacenequinones has been described.[1a] In the literature, the phenoxynaphthacenequinone derivatives were incorporated into the polymer chain by coupling the modified chromophores with hydroxysuccinimide-activated polymers. Direct radical polymerizations of various acrylate monomers were failed due to the quinone moieties which presumably acted as radical scavengers and/or as catalyst poisons. In this communication, as part of our continuing efforts for the development of photoinduced color/fluorescence changing polymers,[2] we report the first successful direct synthesis of norbornene-derived polymers having pendant phenoxyquinones.

Scheme 1. Photoisomerization of 1-Phenoxynaphthacenequinone



The synthetic sequences employed in the preparation of monomers **5** and **6** are shown in Scheme 2. The phenoxyanthracene monomer **6** was also prepared to compare its photochromic properties with the polymer derived from the naphthacenequinone monomer **5**. The monomers **5** and **6** were readily obtained in two steps from 1-chloro-5,12-naphthacenequinone (**1**)[1a] and commercially available 1-chloroanthracenequinone (**2**), respectively. In the first step, the chloroquinone **1** or **2** was treated with 3-(4-hydroxyphenyl)-1-propanol in the

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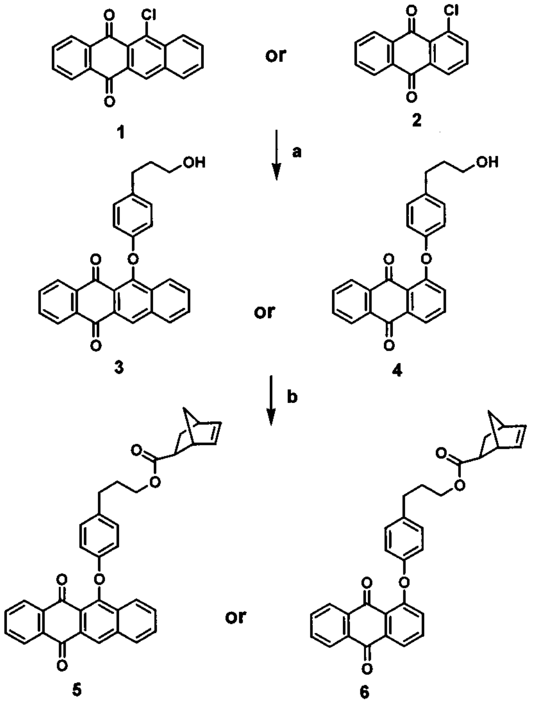
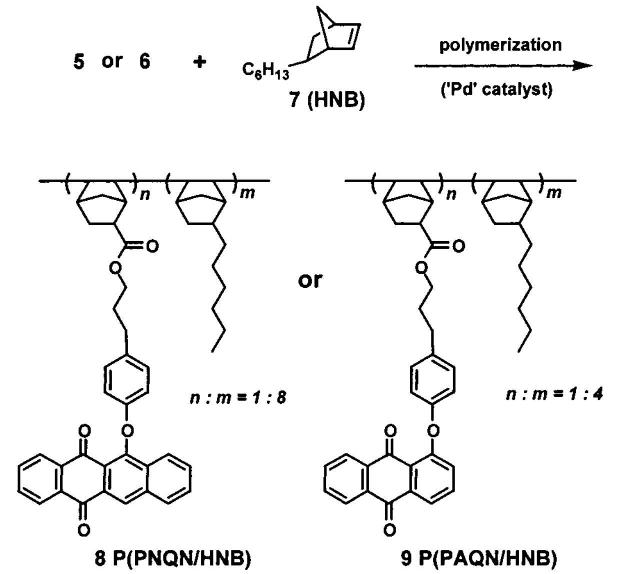
Scheme 2. Synthesis of Phenoxyquinone Monomers 5 and 6: (a) 3-(4-Hydroxyphenyl)-1-propanol, K_2CO_3, DMF, 110 °C, 3 h, 90% for 3 and 85% for 4, Respectively; (b) 5-Norbornene-2-carboxylic Acid Ethyl Ester, Dibutyltin Oxide, Toluene, Reflux, 3 h, 88% for 5 and 87% for 6, Respectively



presence of K_2CO_3 in DMF. Pouring of the crude reaction mixture into acidic water led to the precipitation of the product. Recrystallization of the product from ethyl acetate−hexane afforded pure phenoxyquinone **3** (90%) or **4** (85%) in good yield. The intermediate **3** or **4** was converted to the desired monomer **5** (88%) or **6** (87%) by tin-catalyzed transesterification with 5-norbornene-2-carboxylic acid ethyl ester[3] in toluene. The monomers were obtained as mixtures of *endo* and *exo* isomers.

In general, norbornene monomers can be polymerized by (1) AIBN-initiated radical polymerization,[4] (2) ring-opening methathesis polymerization (ROMP),[5] or (3) transition-metal-catalyzed addition polymerization.[6] Among these, the transition-metal-catalyzed addition polymerization was employed in this study since the radical polymerization with acrylate monomers was reported to be unsuccessful with phenoxyquinone derivatives in the literature.[1a] Besides, polymers obtained by ROMP contain double bonds in the main chain of the polymers which may effect long-term stability of these light-sensitive polymers. To facilitate the polymerization and to enhance solubility of the resulting polymers in organic solvents, *n*-hexylnorbornene (HNB), **7**,[7] was employed as a comonomer. Copolymerizations were carried out with a 1:3 molar feed ratio of the chromophore monomer and HNB in the presence of organopalladium catalyst $\{(\eta^3\text{-allyl})Pd(SbF_6)\}$[8] (1 mol % based on total monomers) in toluene (Scheme 3). The polymerizations were initiated by adding the organopalladium catalyst to the monomer solution under N_2 atmosphere at room temperature. After polymerization for 12 h at room temperature, the catalyst was quenched by bubbling the reaction mixture with H_2 gas for 30 min. Removal of the solid precipitate by filtering followed by pouring the filtrate into excess MeOH gave the polymers as precipitates. The copolymer **8** P(PNQN/HNB) or **9** P(PAQN/HNB) after precipitation into methanol was obtained as a yellow powder in 63% or 72% yield, respectively. Polymer **8** had a weight-average molecular weight (M_w) of 39 000 with a polydispersity of 4.29. The compositions of the obtained copolymers were confirmed to have a 1:8 for **8** and 1:4 for **9** ratios between the chromophore monomer and HNB unit by ^1H NMR spectroscopic analysis. Both *endo* and *exo* isomers of the monomers **5** and **6** as well as the comonomer HNB were converted to polymers. This was evidenced by examining ^1H NMR spectrum of the filtrate after collecting the polymers by precipitating into MeOH. The polymers prepared as described above had maximum absorption wavelengths at 400 and 368 nm for **8** and **9**, respectively, due to the phenoxyquinone groups. The polymers were readily dissolved in common organic solvents such as $CHCl_3$, toluene, cyclohexanone, THF, and DMF and were insoluble in MeOH and hexane.

Scheme 3. Synthesis of Copolymers 8 and 9 Having Pendant Phenoxyquinones by Addition Polymerization



To investigate the feasibility and degree of photo-induced rearrangement of the chromophores, solutions containing polymer **8** or **9** in toluene were irradiated with 360 nm UV light (Figure 1). As displayed in Figure 1A, copolymer **8** having pendant phenoxynaphthcenequinone moieties shows typical photochromic properties of a phenoxynaphthacenequinone. Upon irradiation of the solution, characteristic double peaks of the "*ana*"-quinone form of the phenoxynaphthacenequinone at 450 and 478 nm increase with isosbestic points at 400, 366, and 340 nm. In the case of polymer **9**, irradiation of a solution containing the polymer resulted in the photo-induced rearrangement to the "*ana*"-quinone form (Figure 1B). However, the "*ana*"-quinone form of the phenoxyanthraquinone moieties in polymer **9** was found to be relatively unstable and decomposed upon prolonged irradiation (above 5 min, data not shown). The poor stability of the "*ana*"-quinone form of the phenoxyanthraquinone was previously described in the litherature.[1i] When the solutions containing the "*ana*"-quinone forms obtained with irradiation of UV light were irradiated with visible light (>450 nm), the "ana"-quinone forms were readily isomerized to the "trans"-quinone forms. Similar results were observed with thin polymer films

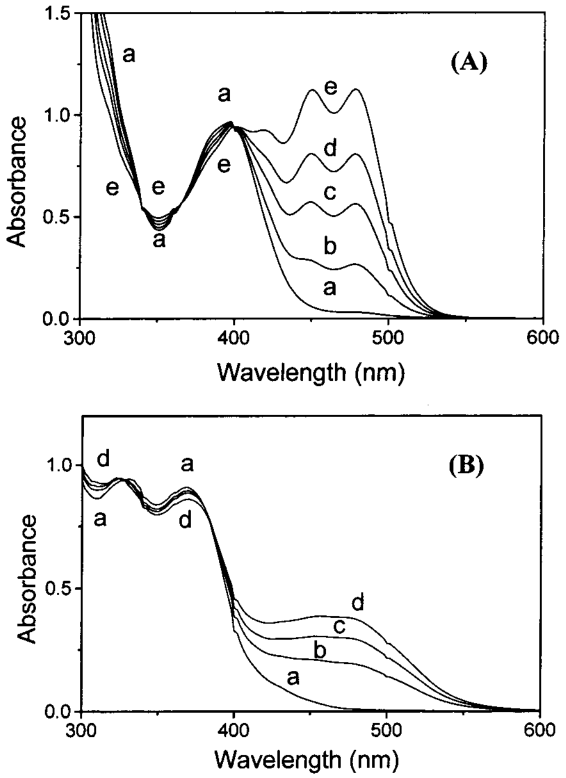


Figure 1. Time course revealed by UV–vis spectroscopic monitoring of solutions containing (A) copolymer **8** (1.5×10^{-4} M) or (B) copolymer **9** (2.0×10^{-4} M) in toluene upon irradiation with 365 nm UV light. Spectra were recorded at (a) 0 s, (b) 10 s, (c) 1 min, (d) 5 min, and (e) 20 min time periods for copolymer **8** and at (a) 0 s, (b) 30 s, (c) 1 min, and (d) 5 min time periods for copolymer **9**.

containing polymer **8** or **9** spin-coated on a quartz plate. The detailed properties concerning "reversibility" as well as comparison of photoisomerization between solution and film states are under current investigation.

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