

Photochromism of A Styrene-Derived Polymer Having Pendant Phenoxyanthraquinones

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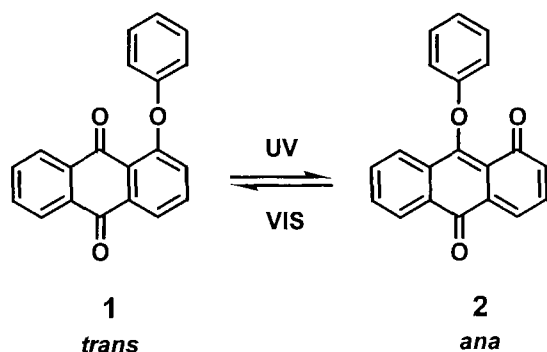
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A Styrene-derived polymer having pendent phenoxyanthraquinones for photochromism was prepared by AIBN-initiated radical polymerization. Synthesis of the monomers was straightforward and the polymer was obtained in 65% yield. Photoinduced rearrangement from the “*trans*” quinone forms to the “*ana*” quinone forms readily occurred both in solution and in film when the polymer was irradiated with UV light.

key words: Photochromism, Polymer, Phenoxyanthraquinone

INTRODUCTION

The development of efficient photochromic compounds has gained much attention in fundamental and applied research areas. Among numerous photochromic compounds, certain phenoxy quinone derivatives are attractive molecules due to their excellent properties such as low fatigue as well as negligible thermal interconversion at room temperature. [1,2,3] For example, the “*trans*”-quinone form of 1-phenoxyanthraquinone undergoes a photochemical rearrangement to the “*ana*”-quinone form upon irradiation with UV light (Scheme 1) [4] The reverse conversion of “*ana*”-quinone to “*trans*”-quinone form readily occurs with visible light.



Scheme 1. Photoisomerization of 1-phenoxyanthraquinone.

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. Recently, we reported synthesis of a norbornene-derived polymer having pendent phenoxyanthraquinone by transition metal-catalyzed addition polymerization. [5] Since the synthesis of the monomer required multisteps and the polymerization was carried out in a glove box under nitrogen condition, we felt it would be more practical if we could reduce the required synthetic procedures for the monomer and simplify the polymerization condition. In this communication, as a part of our continuing efforts for the development of photoinduced color/fluorescence changing polymers, [6,7,8,9,10] we report the synthesis of styrene-derived polymers having pendant phenoxyquinones for photochromism.

MATERIALS AND METHODS

General. ¹H and ¹³C NMR spectroscopic measurements were carried out with a Varian 200 Spectrometer using tetramethylsilane (TMS) as an internal standard in CDCl₃. UV-visible spectra were recorded with a JASCO V-530 spectrophotometer. IR spectra were obtained with a ATI Genesis Series FTIR spectrophotometer. Number and weight average molecular weights (M_n and M_w, respectively) and the molecular weight distribution (M_w/M_n) were estimated by gel permeation chromatography (GPC) using THF as eluent at a flow rate of 1 mL(min⁻¹, calibrated with polystyrene standards.

Materials. 2,2'-Azobisisobutyronitrile (AIBN, Tokyo Kasei Kogyo) was recrystallized from methanol before use. 1-Chloroanthraquinone was purchased from Aldrich and used as received. 4-Acetoxy styrene was purchased from Hoechst Celanese.

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^1H NMR spectra of the copolymer **7** (Figure 1(b)).

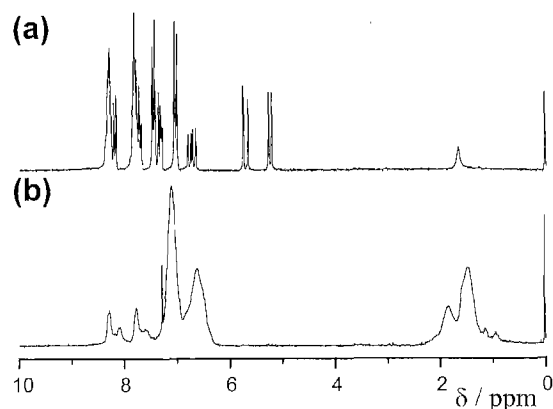


Figure 1. ^1H NMR spectra of (a) monomer VPAQ **5**, (b) copolymer P(VPAQ/ST) **7** in CDCl_3 .

In order to investigate the possibility of photoinduced rearrangement of the chromophores, a solution containing the polymer **7** in toluene was irradiated with 360 nm UV light (Figure 2). As displayed in Figure 2(A), the copolymer **7** having pendant phenoxyanthraquinone moieties shows typical photochromic properties of a phenoxyanthraquinone. Upon

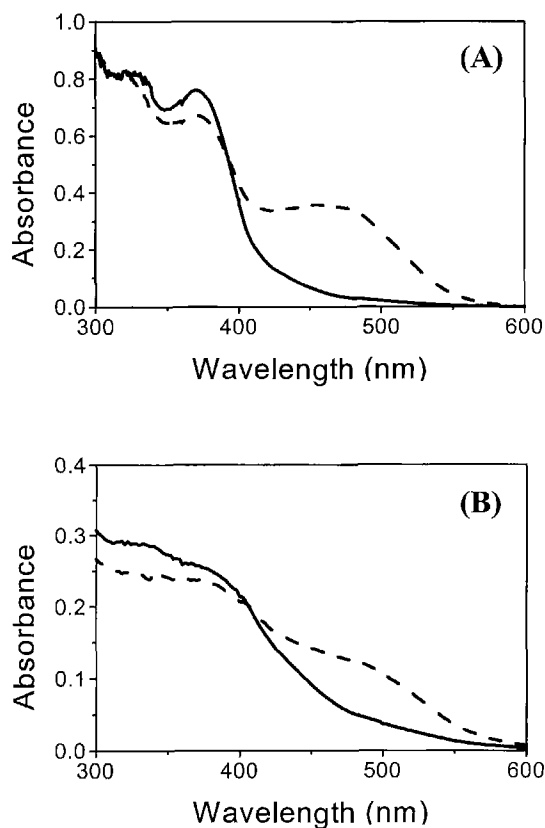


Figure 2. A: UV-visible spectroscopic monitoring of a solution (A) (1.5×10^{-3} M, toluene) and a film (B) ($0.65 \mu\text{m}$ thickness, quartz) containing copolymer **7** before (solid line) and after (dashed line) irradiation for 20 sec with 365 nm UV light.

irradiation of the solution, absorption at around 470 nm which corresponds to “*ana*”-quinone form of the phenoxyanthraquinone increases. Similar results were observed with thin polymer films containing the polymer **7** spin-coated on a quartz plate (Figure 2 (B)). The detailed properties concerning “reversibility” as well as comparison of photoisomerization between solution and film states are under current investigation.

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