

Photochromism of A Styrene-Derived Polymer Having Pendant Phenoxyanthraquinones

Sang Yong Ju, Kwang-Duk Ahn, Dong Keun Han, Dong Hack Suh¹ and Jong-Man Kim^{1*}
Functional Polymer Laboratory, Korea Institute of Science and Technology, P.O. Box 131,
Cheongryang, Seoul 130-650, Korea

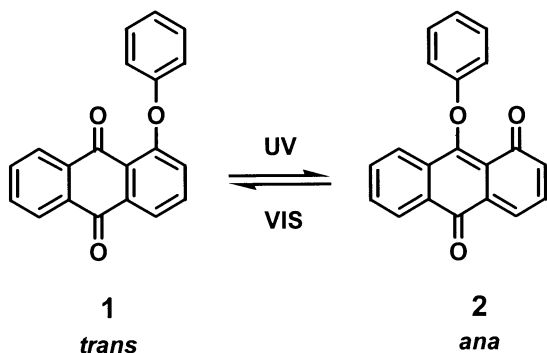
¹Division of Chemical Engineering, Center for Ultra-microchemical Process Systems, Hanyang University,
17 Haengdang-dong, Seongdong-gu, Seoul 133-791, Korea

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'-Azoisobutyronitrile (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.

*To whom correspondence should be addressed.

E-mail : jmk@hanyang.ac.kr

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Preparation of 4-hydroxystyrene (4). A mixture containing 4-acetoxystyrene (20.0 g, 0.12 mol) and potassium hydroxide (17.0 g, 0.31 mol) in 170 mL of H₂O was stirred until the suspension of 4-acetoxystyrene disappeared. White crystalline 4-hydroxystyrene was achieved by bubbling the solution with CO₂ gas (yield: 14.6 g, 99%). Mp: 68 °C. ¹H NMR(CDCl₃, 200MHz): δ = 7.35(2H), 6.85(2H), 6.68(1H), 5.6(2H), 5.2(1H). IR(KBr, cm⁻¹): 3340, 1609, 1510, 1257, 992, 899, 839.

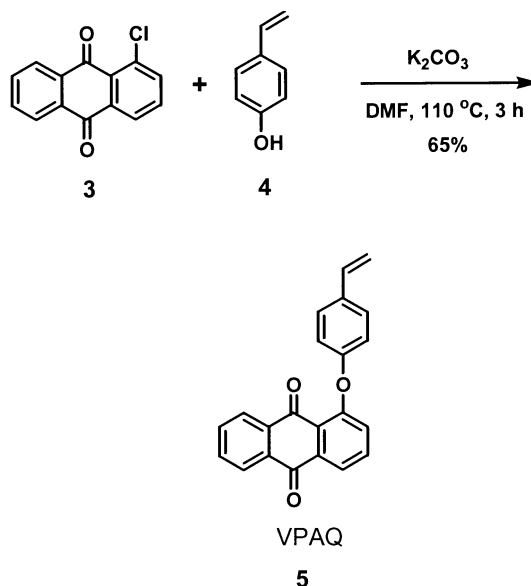
Synthesis of monomer VPAQ 5. A mixture containing 4-hydroxystyrene (1.44 g, 12.0 mmol), 1-chloroanthraquinone (2.43g, 10.0 mmol), and K₂CO₃ (1.80 g, 13.0 mmol) in DMF (50 mL) was stirred at 110 °C for 3 h. The resulting mixture was cooled to room temperature and poured into the acidified ice water. The precipitate was collected, dried, and recrystallized from methanol to give 2.12 g (65%). Mp: 94 °C; ¹H NMR(CDCl₃, 200MHz): δ = 8.25-8.4 (3H), 7.75-7.9 (3H), 7.25-7.5 (2H), 7.05 (2H), 6.65-6.85 (1H), 5.70 (1H), 5.25 (1H); ¹³C NMR(CDCl₃): δ = 181, 180.1, 155.6, 154.8, 134.3, 134.1, 133.2, 133.1, 132.8, 132.0, 131.9, 131.0, 126.2, 125.7, 124.8, 122.5, 121.5, 117.1, 111.6; IR(KBr, cm⁻¹): 1673, 1584, 1503, 1440, 1325, 1254, 1157.

Preparation of copolymer P(VPAQ/St) 7. A solution containing monomer 5 (650.0 mg, 2.0 mmol), styrene (833.0 mg, 8.0 mmol), AIBN (2 mol% based on total monomers), and 1,4-dioxane (8 mL) in an ampoule was subjected to repeated freeze-thaw cycles before the ampoule was sealed under vacuum. The sealed ampoule was heated at 65 °C for 6 h. After polymerization, the product was precipitated into excess methanol. Polymer was filtered off and dried to give 964.0 mg (65%) of P(VPAQ/St) 7.

RESULTS AND DISCUSSION

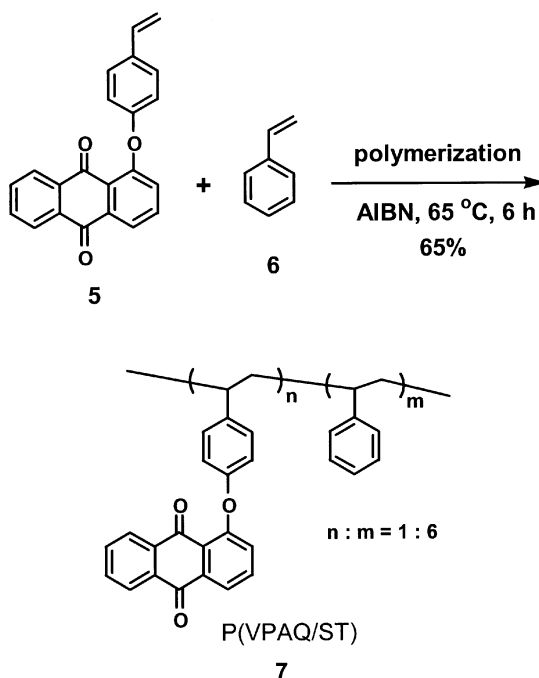
The monomers 5 was readily obtained in one step from commercially available 1-chloroanthraquinone (3) and 4-hydroxystyrene (4) (Scheme 2). 1-Chloroanthraquinone (3) was treated with 4-hydroxystyrene in the presence of K₂CO₃ in DMF. Pouring of the crude reaction mixture into acidic water led to the precipitation of the product. Recrystallization of the product from methanol afforded pure phenoxyquinone monomer 5 in 65% yield.

Copolymerizations were carried out with a 2:8 molar feed ratio of the chromophore monomer 5 and styrene (6) in the presence of AIBN (2 mol% based on total monomers) in dioxane (Scheme 3). After polymerization for 6 h at 65 °C, the mixture was poured into excess MeOH to give the copolymer P(VPAQ/St) 7 as a precipitate in 65% yield. The polymer 7 had a weight-average molecular weight (M_w) of 12000 with the polydispersity of 1.55. The composition of the obtained copolymer was confirmed to have a 1:6 ratio between the chromophore monomer and styrene unit by ¹H NMR spectroscopic analysis. The polymer prepared had a



Scheme 2. Synthesis of styrene-derived phenoxyquinone monomer VPAQ 5.

maximum absorption wavelength at 368 nm due to the phenoxy quinone groups. The polymer 7 was readily dissolved in common organic solvents such as CHCl₃, toluene, cyclohexanone, THF, and DMF and was insoluble in MeOH and hexane.



Scheme 3. Synthesis of a copolymer P(VPAQ/St) 7 having pendant phenoxyquinones by AIBN-initiated radical polymerization.

¹H NMR spectra of the monomer 5 as well as the copolymer 7 are displayed in Figure 1. The peaks at around 5.2, 5.6, and 6.6 ppm for the characteristic vinyl protons of the styrene monomer 5 (Figure 1 (a)) completely disappeared in

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

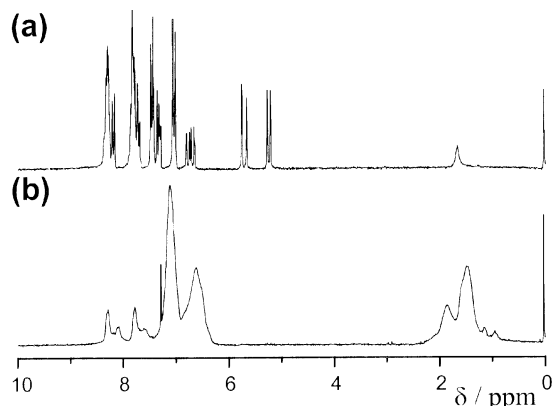


Figure 1. ^1H NMR spectra of (a) monomer VPAQ **5**, (b) copolymer P(VPAQ/ST) **7** in CDCl_3 .

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

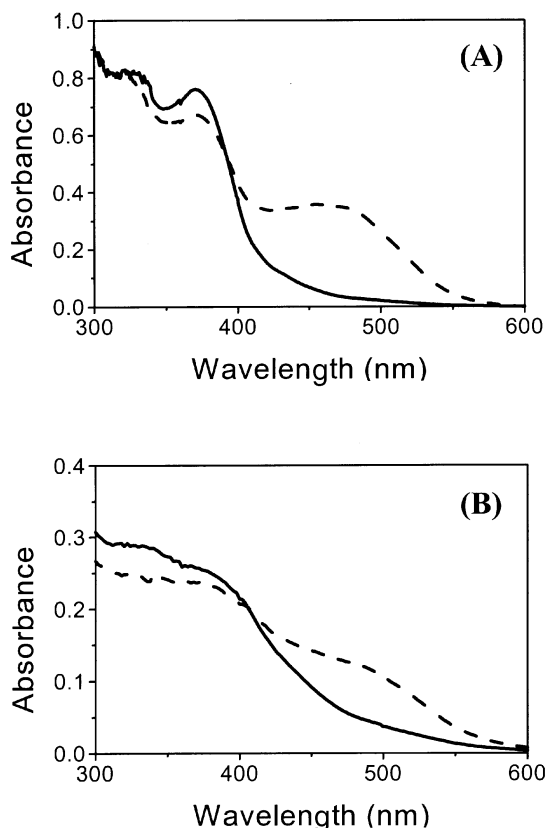


Figure 2. A: UV-visible spectroscopic monitoring of a solution (A) (1.5×10^{-3} M, toluene) and a film (B) (0.65 μm thickness, quartz) containing copolymer **7** before (solid line) and after (dashed line) irradiation for 20 sec with 365 nm UV light.

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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