

Synthesis and photochromism of polymer-bound phenoxyquinone derivatives

Sang Yong Ju^a, Dae-Ik Kwon^b, Sung-Jun Min^b, Kwang-Duk Ahn^a,
Ki Hong Park^c, Jong-Man Kim^{b,*}

^a Functional Polymer Laboratory, Korea Institute of Science and Technology, P.O. Box 131, Cheongryang, Seoul 130-650, South Korea

^b Department of Chemical Engineering, College of Engineering, Hanyang University,
17 Haengdang-dong, Seongdong-gu, Seoul 133-791, South Korea

^c Electronic Materials and Devices Research Center, Korea Institute of Science and Technology,
P.O. Box 131, Cheongryang, Seoul 130-650, South Korea

Received 6 January 2003; received in revised form 17 March 2003; accepted 22 March 2003

Abstract

Acrylate- and styrene-derived polymers having pendant phenoxyquinones for photochromism were prepared by 2,2'-azoisobutyronitrile (AIBN)-initiated radical polymerization. Synthesis of the monomers were straightforward and the polymers were obtained in high yields in spite of the quinone moieties presented in the monomers, which usually can function as radical scavengers and/or catalysts poison. Photo-induced rearrangement from the "trans"-quinone forms to the "ana"-quinone forms readily occurred when the polymer films were irradiated with UV light.

© 2003 Elsevier Science B.V. All rights reserved.

Keywords: Photochromism; 1-Phenoxynaphthacenequinone; Polymer; Radical polymerization

1. Introduction

Recently, the development of photochromic compounds which can be potentially applicable as memory photodevices has gained much attention in molecular electronics [1]. Among various photochromic compounds prepared and investigated for this purpose, certain phenoxyquinone derivatives have unique properties such as low fatigue as well as negligible thermal interconversion at room temperature [2–15]. For example, 6-phenoxy-5,12-naphthacenequinone is well known to isomerize from the "trans"-quinone form to the "ana"-quinone form upon irradiation with UV light and vice versa by visible light (Scheme 1). The fatigue-resistant photochromic properties of the 6-phenoxy-5,12-naphthacenequinone can be confirmed from the fact that the reversible photo-rearrangement cycles can be repeated over 500 times without decomposition of the material [4].

We have previously reported the first successful direct synthesis of norbornene-derived polymers having pendant phenoxyquinones by transition metal-catalyzed

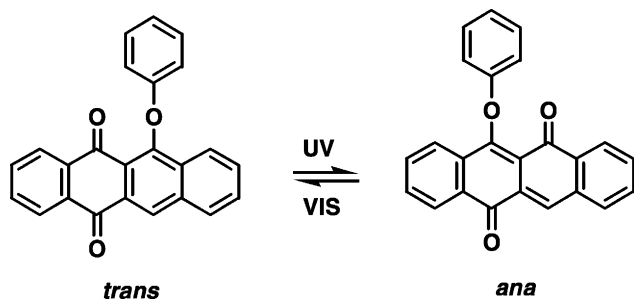
addition polymerization [5]. Since the synthesis of the monomers required multi-steps and the polymerizations were carried out in a glove box under nitrogen condition, we felt it would be more practical if we could reduce the required synthetic procedures for the monomers and simplify the polymerization condition. Accordingly, we have reinvestigated the radical-initiated polymerization of 6-phenoxyquinone derivatives. We have focused polymers having 6-phenoxy-naphthacenequinone derivatives since 6-phenoxy-naphthacenequinone is superior to 1-phenoxyanthracenequinone in terms of photochromic properties as well as its stability [12].

2. Results and discussion

2.1. Preparation of the monomers

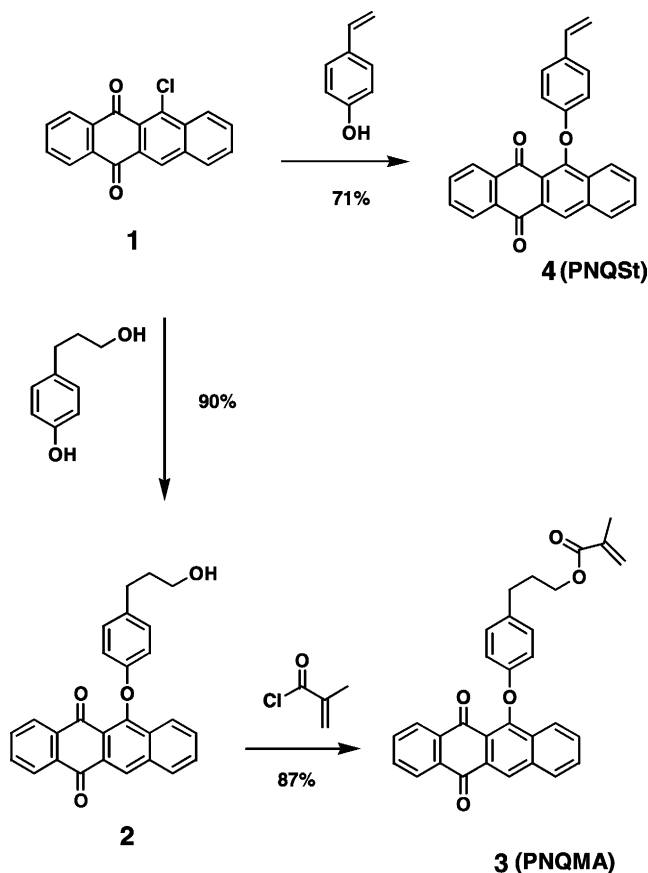
The synthetic sequences employed in the preparation of monomers **3** and **4** are shown in Scheme 2. Aromatic substitution reaction of 6-chloro-5,12-naphthacenequinone (**1**) [4] with commercially available 3-(4-hydroxyphenyl)-1-propanol in the presence of potassium carbonate in DMF gave the intermediate **2** in high yield. Precipitation of the crude

* Corresponding author. Tel.: +82-2-2290-0522; fax: +82-2-2298-4101.
E-mail address: jmk@hanyang.ac.kr (J.-M. Kim).



Scheme 1. Photo-isomerization of 6-phenoxynaphthacenequinone.

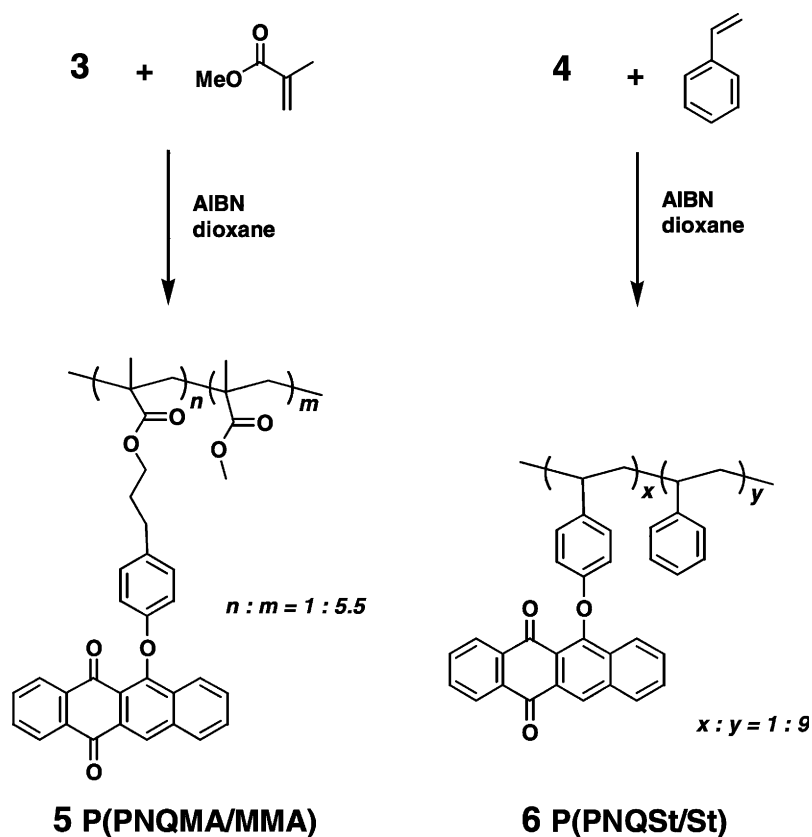
product by pouring the reaction mixture into acidified cold water followed by recrystallization from ethyl acetate/hexane afforded pure product **2**. Coupling of the intermediate **2** with methacryloyl chloride gave the methacrylate monomer **3**. The styrene-derived monomer was readily obtained in one step from 6-chloro-5,12-naphthacenequinone (**1**) and 4-hydroxystyrene, which was prepared from hydrolysis of commercially available 4-acetoxystyrene. The crude product precipitated from acidified cold water was subjected to recrystallization from toluene to afford the desired styrene-derived monomer **4** in good yield.

Scheme 2. Synthesis of 6-phenoxyquinone monomers **3** and **4**.

2.2. Preparation of the copolymers having pendant photochromic chromophore moieties

The main advantage of incorporating photochromic groups into a polymer chain is to facilitate spin-coatability on solid substrates to make thin films. For this purpose, in our previous report [5], we prepared norbornene-derived monomers which can be polymerized by transition metal-catalyzed addition polymerization. The main reason of introducing the palladium-catalyzed polymerization was due to the results described in [4]. Radical-initiated direct polymerization of various acrylate monomers were reported to be failed since the quinone moieties in the photochromic chromophores could act as radical scavengers and/or catalyst poisons. Although the transition metal-catalyzed polymerization afforded the desired copolymers in moderate yields, the polymerization reactions had to be carried out in a N₂ glove box. Accordingly, it would be more practical and useful if polymers having pendant phenoxynaphthacenequinone can be obtained by a simple 2,2'-azoisobutyronitrile (AIBN)-initiated radical polymerization. Previously, we reported [16] synthesis of an acrylate polymer having pendant *tert*-butyloxycarbonyl (*t*-Boc)-protected dihydroxyanthraquinone groups by an AIBN-initiated radical polymerization. Thus, we believed it could also work for phenoxynaphthacenequinone monomers. When the acrylate monomer **3** was copolymerized with methyl methacrylate (MMA) (molar feed ratio, 1:4) under AIBN-initiated radical polymerization, the copolymer, P(PNQMA/MMA) (**5**) was obtained as a yellow powder in 85% yield (Scheme 3). The polymer **5** had a weight-average molecular weight (M_w) of 270,000 with a polydispersity of 11.50. The composition of the obtained copolymer **5** was confirmed to have a 1:5.5 ratio between the chromophore monomer **3** and the comonomer MMA unit by ¹H NMR spectroscopic analysis. Prolonged polymerization over 3 h under this condition led to the gelation of the polymer. Thus, the polymerization was terminated after 2 h.

Copolymerization of the styrene-derived monomer **4** with styrene was carried out with a 1:4 molar feed ratio. The copolymer, P(PNQSt/St) (**6**), after precipitation in methanol, was obtained as a pale yellow powder in 70% yield. The polymer **6** was found to have a weight-average molecular weight (M_w) of 12,000 with a polydispersity of 1.89. The composition of the obtained copolymer **6** was confirmed to have a 1:9 ratio between the chromophore monomer **4** and styrene unit by ¹H NMR spectroscopic analysis. Interestingly, no gelation under extended polymerization was observed in this case. The low molecular weight of the styrene-derived copolymer **6** compared to the copolymer **5** could presumably be due to nearby location of the photochromic chromophore to the polymerizable double bond. The copolymers **5** and **6** are soluble in common organic solvents (such as chloroform, THF and dimethylformamide (DMF)) except for hexane and methanol. ¹H NMR spectra of the monomers **3** and **4** as well as the



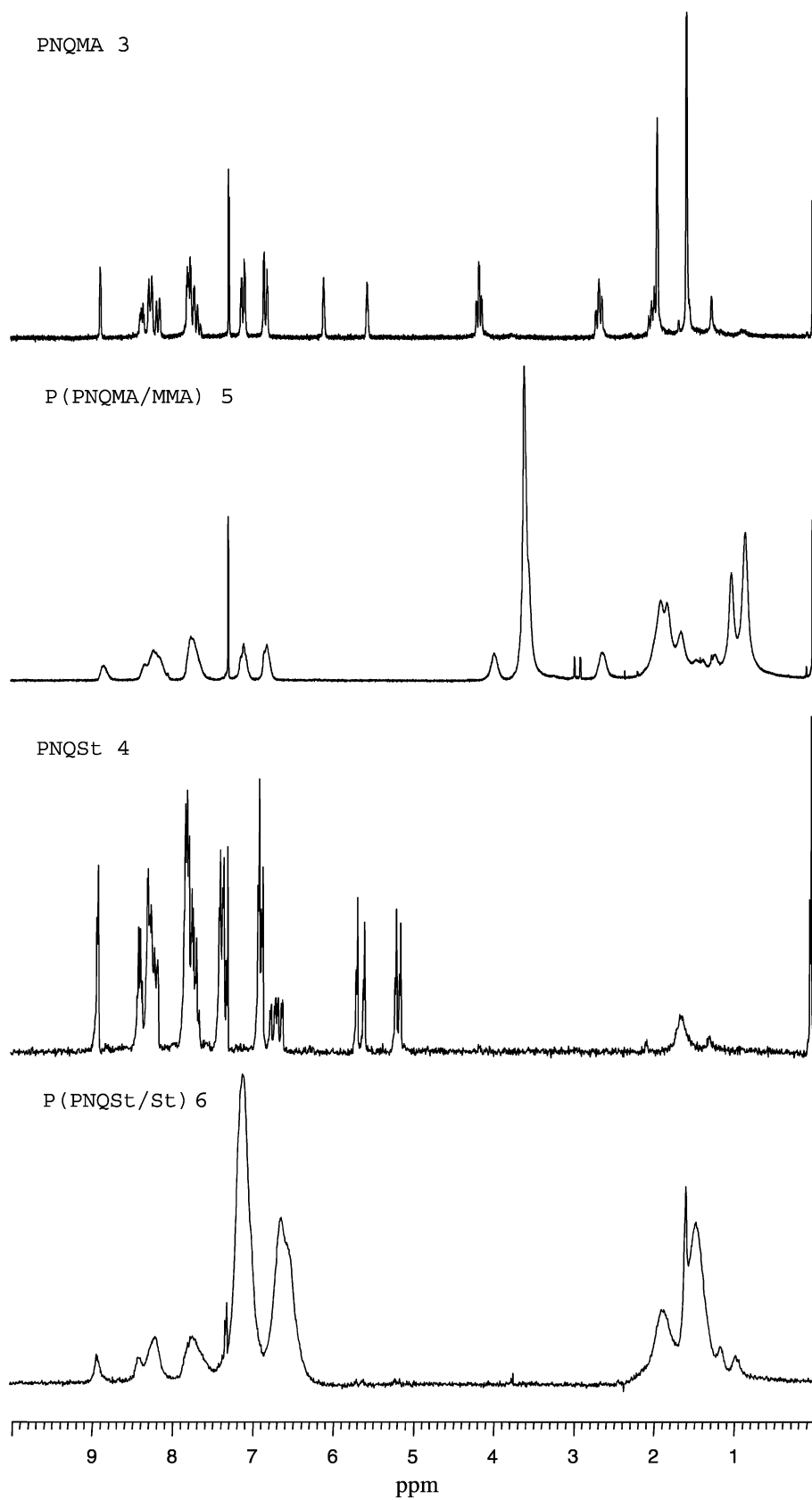
Scheme 3. Synthesis of copolymers **5** and **6** having pendant phenoxyquinones by radical polymerization.

copolymers **5** and **6** are shown in Fig. 1. As can be seen by inspection of these spectra, the vinylic protons of the monomers **3** and **4** disappeared in the corresponding spectra for the polymers **5** and **6**. This observation confirms the radical-initiated polymerizations are successfully carried out.

2.3. Photochromic properties in thin polymer films

In order to investigate the feasibility and degree of photo-induced rearrangement of the chromophores, thin polymer films (ca. 0.5 μm thickness) were prepared by spin coating a dioxane solution containing the copolymer **5** or **6** on quartz substrates. The polymer films were exposed to either UV light (365 nm) for *trans*-to-*ana* transformation or visible light (>410 nm) for *ana*-to-*trans* rearrangement. The progress, then, was monitored with an UV-Vis spectrometer (Fig. 2). As displayed in Fig. 2A and C, copolymers **5** and **6** show typical photochromic properties of a 6-phoxynaphthacenequinone. Upon irradiation of the polymer films containing the copolymer **5** or **6** with 365 nm UV light, characteristic double peaks of the “*ana*”-quinone form of the phoxynaphthacenequinone at 450 and 478 nm increase (Fig. 2A and C). Transformation from “*trans*”-quinone form to “*ana*”-quinone form in the polymer **5** or **6** was found to be efficient, observing

drastic increase of the peaks at 450 and 478 nm with 5 s irradiation of the polymer film. The transformation from “*trans*”-quinone form to “*ana*”-quinone form reached to the saturation after 20 s for both polymers. In order to test reversibility of the rearrangement, the polymer films pre-exposed with 365 nm UV light were irradiated with visible light (>410 nm) and the results are shown in Fig. 2B and D. Upon irradiation with visible light, decrease of the peaks at 450 and 478 nm was observed. As displayed in Fig. 2B and D, the transformation from “*ana*”-quinone to “*trans*”-quinone induced by visible light, however, was found to be less efficient than UV light-induced *trans*-to-*ana* conversion in the polymer films. Thus, complete conversion to the “*trans*”-quinone form was not observed. The acrylate copolymer **5** has slightly higher conversion (63%) than the styrene-derived copolymer **6** (55%). This is presumably due to the lack of flexibility in the case of styrene-derived copolymer **6** in which the photochromic chromophore is directly attached to the main chain backbone of the polymer. Accordingly, migration of the phenoxy group to the adjacent carbonyl group can be affected by steric bulkness of the main chain backbone of the polymer. In the case of acrylate polymer **5**, the polymer has alkyl chain between main chain backbone and the photochromic chromophore, providing some flexibility to the migrating groups.

Fig. 1. ^1H NMR spectra of monomers and polymers in CDCl_3 .

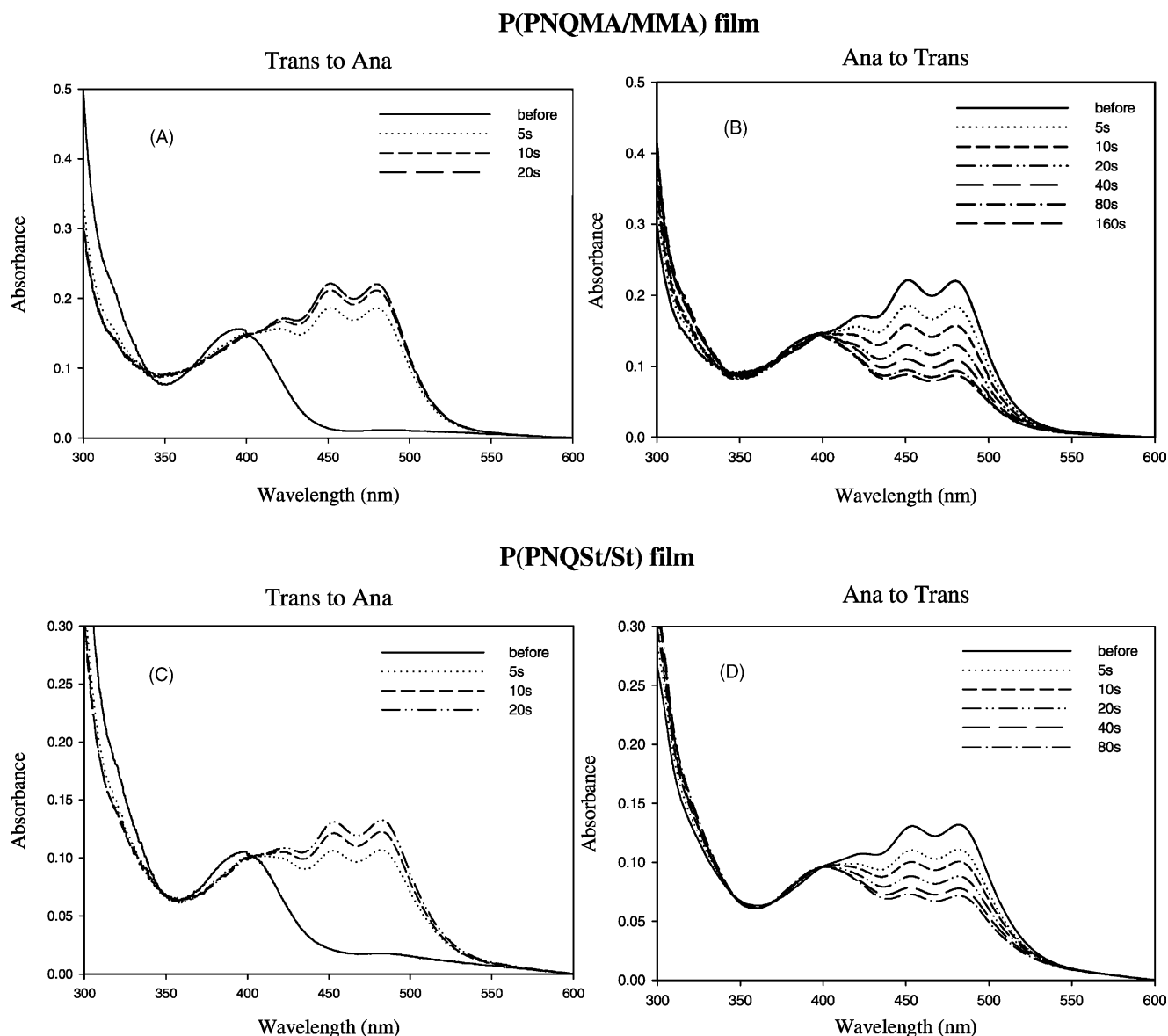


Fig. 2. Time course revealed by UV-Vis spectroscopic monitoring of thin films of P(PNQMA/MMA) and P(PNQSt/St) upon irradiation with 365 nm UV light (A and C) and visible light (>410 nm) (B and D).

3. Conclusion

Copolymers having pendant photochromic groups have been prepared by AIBN-initiated radical polymerization. Synthesis of the monomers were straightforward and the radical-initiated polymerizations with the acrylate- and styrene-derived monomers were conducted without any difficulty in spite of the quinone moieties presented in the monomers. The polymers obtained were readily dissolved in common organic solvents such as chloroform, dioxane, THF, and DMF. Spin-casting of the polymer solution afforded thin polymer film on a quartz substrate. Photo-rearrangement from “*trans*”-quinone forms to “*ana*”-quinone forms occurred when the polymer film was exposed to 365 nm UV light. Although complete reversibility was not observed

with the polymers, the “*ana*”-quinone forms were transformed to “*trans*”-quinone forms by irradiation with visible light. The simple and straightforward strategy described above for the preparation of polymers having pendant photochromic quinone moieties should be useful in the design of polymer-bound photochromic materials.

4. Experimental

4.1. General

2,2'-Azobisisobutyronitrile (Tokyo Kasei Kogyo) was recrystallized from methanol before use. 3-(4-Hydroxyphenyl)-1-propanol, 4-acetoxystyrene, styrene, methyl methacry-

late, and methacryloyl chloride were purchased from Aldrich and used as received. ^1H and ^{13}C NMR spectroscopic measurements were carried out with a Varian 200 Spectrometer using tetramethylsilane (TMS) as an internal standard in CDCl_3 . UV-visible spectra were recorded with a JASCO V-530 spectrophotometer. IR spectra were obtained with an 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. Photo-irradiation was carried out using a 500 W high-pressure mercury lamp. Light of the appropriate wavelength was selected by using either a monochromator or a cut-off optical filter.

4.2. Material synthesis

6-Chloro-5,12-naphthacenequinone (**1**) was prepared as described in [4].

4.2.1. 4-Hydroxystyrene

A mixture containing 4-acetoxystyrene (20.0 g, 0.12 mol) and potassium hydroxide (17.0 g, 0.31 mol) in 170 ml of H_2O was stirred until the suspension of 4-acetoxystyrene disappeared. White crystalline 4-hydroxystyrene was obtained by bubbling the solution with CO_2 gas (yield: 14.6 g, 99%). mp: 68°C ; ^1H NMR (CDCl_3 , 200 MHz): δ 7.35 (d, 2H), 6.85 (d, 2H), 6.68 (t, 1H), 5.6 (d, 2H), 5.2 (d, 1H); IR (KBr, cm^{-1}): 3340, 1609, 1510, 1257, 992, 899, 839.

4.2.2. 6-[(4-(3-Hydroxypropyl)phenoxy)]-5,12-naphthacenequinone (**2**)

A mixture of 6-chloro-5,12-naphthacenequinone (0.2 g, 0.68 mmol), potassium carbonate (0.82 g, 2.05 mmol), and 3-(4-hydroxyphenyl)-1-propanol (0.13 g, 0.82 mmol) in 10 ml of DMF was stirred at 110°C for 6 h. The resultant mixture was cooled to room temperature, poured into acidified cold water. The precipitate was collected, dried, and recrystallized from ethyl acetate/hexane to give 0.24 g (90%) of a yellow crystalline product **2**. mp $204\text{--}205^\circ\text{C}$; ^1H NMR (CDCl_3 , 200 MHz): δ 8.90 (s, 1H), 8.36 (t, 1H), 8.23 (d, 2H), 8.19 (d, 1H), 7.75 (m, 4H), 7.18 (d, 2H), 6.85 (d, 2H), 3.65 (t, 2H), 2.66 (t, 2H), 1.87 (quintet, 2H); ^{13}C NMR: δ 182.9, 181.1, 157.5, 152.6, 136.0, 135.5, 135.2, 134.3, 133.6, 131.8, 130.3, 130.1, 129.9, 129.5, 127.6, 127.1, 127.0, 125.0, 114.8, 62.3, 34.2, 31.2, 29.7; IR (KBr, cm^{-1}): 3471, 3045, 2929, 2856, 1668, 1581, 1498, 1425, 1398, 1344, 1272, 1213, 1168, 1106, 1054.

4.2.3. 6-[(4-(3-Methacryloyloxypropyl)phenoxy)]-5,12-naphthacenequinone (**3**)

To a mixture of naphthacenequinone **2** (0.4 g, 0.98 mmol), triethylamine (0.15 g, 1.47 mmol) in 7 ml of THF was added

methacryloyl chloride (0.15 g, 1.47 mmol) over 30 min at -5°C . The resultant mixture was stirred at ambient temperature for 6 h, filtered, and the filtrate was concentrated in vacuo. The residue was purified by column chromatography eluting with hexane/ethyl acetate (3:1 by volume) to give 0.35 g (87%) of the desired monomer **3**. mp 97°C ; ^1H NMR (CDCl_3 , 200 MHz): δ 8.89 (s, 1H), 8.12–8.42 (m, 4H), 7.65–7.85 (m, 4H), 7.19 (d, 2H), 6.83 (d, 2H), 6.12 (s, 1H), 5.58 (s, 1H), 4.19 (t, 2H), 2.73 (t, 2H), 2.05 (m, 5H); ^{13}C NMR: δ 183.6, 181.9, 168.3, 158.3, 153.3, 137.1, 136.8, 136.3, 135.4, 135.1, 134.5, 134.3, 132.5, 131.5, 131.0, 130.6, 130.4, 128.4, 127.9, 127.6, 126.1, 125.8, 121.8, 115.5, 32.0, 30.9, 19.1; IR (KBr, cm^{-1}): 3397, 3336, 3064, 2931, 2329, 1886, 1714, 1671, 1585, 1500, 1425, 1394, 1270, 1166, 1110, 1022.

4.2.4. 6-[(4-Vinylphenoxy)]-5,12-naphthacenequinone (**4**)

A mixture containing 4-hydroxystyrene (1.44 g, 12.0 mmol), 6-chloro-5,12-naphthacenequinone (**1**) (2.43 g, 10.0 mmol), and K_2CO_3 (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%) of the desired product **4**. mp: 94°C ; ^1H NMR (CDCl_3 , 200 MHz): δ 8.95 (s, 1H), 8.15–8.50 (m, 4H), 7.65–7.90 (m, 4H), 7.25–7.5 (d, 2H), 6.90 (d, 2H), 6.65–6.85 (t, 1H), 5.65 (d, 1H), 5.18 (d, 1H); ^{13}C NMR (CDCl_3): 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.

4.2.5. Preparation of copolymer P(PNQMA/MMA) (**5**)

A solution containing the acrylate monomer **3** (223 mg, 0.47 mmol), MMA (188 mg, 1.88 mmol), AIBN (2 mol% based on total monomers), and 1,4-dioxane (2 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 2 h. After polymerization, the product was precipitated into excess methanol. Polymers were filtered off and dried to give 349 mg (85%) of P(PNQMA/MMA) (**5**) as a yellow powder.

4.2.6. Preparation of copolymer P(PNQSt/St) (**6**)

A solution containing the styrene-derived monomer **4** (0.75 mg, 2.0 mmol), styrene (0.83 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. Polymers were filtered off and dried to give 1.10 g (70%) of P(PNQSt/St) (**6**) as a yellow powder.

4.2.7. Film preparation and photo-isomerization experiment

A solution containing the polymer **5** or **6** (10 wt.%) in 1,4-dioxane was filtered with a membrane filter of 0.2 μm pore size. The filtrate was spin-coated with 400 rpm for 20 s followed by 2000 rpm for 20 s using a Headway spin-coater to give a ca. 0.5 μm thick film. The film was exposed to 365 nm UV or visible light with cut-off filter (410 nm). The progress was monitored using a JASCO V-530 spectrophotometer.

Acknowledgements

This research was supported by Korea Research Foundation Grant (KRF-2001-003-E00301).

References

- [1] J.C. Crano, R.J. Guglielmetti (Eds.), *Organic Photochromic and Thermochromic Compounds*, vols. 1 and 2, Plenum Press, New York, 1999.
- [2] A. Doron, E. Katz, M. Portnoy, I. Willner, *Angew. Chem. Int. Ed. Engl.* 35 (1996) 1535.
- [3] M. Lahav, E. Katz, A. Doron, F. Patolsky, I. Willner, *J. Am. Chem. Soc.* 121 (1999) 862.
- [4] F. Buchholtz, A. Zelichenok, V. Krongauz, *Macromolecules* 26 (1993) 906.
- [5] J.-M. Kim, H.-Y. Shin, K.H. Park, T.-H. Kim, S.Y. Ju, D.K. Han, K.-W. Ahn, *Macromolecules* 34 (2001) 4291.
- [6] A.J. Myles, N.R. Branda, *Tetrahedron Lett.* (2000) 3785–3788.
- [7] J. Malkin, J. Zelichenok, V. Krongauz, A.S. Dvornikov, P.M. Rentzepis, *J. Am. Chem. Soc.* 116 (1994) 1101.
- [8] A. Doron, M. Portnoy, M. Lion-Dogan, E. Katz, I. Willner, *J. Am. Chem. Soc.* 118 (1996) 8937.
- [9] Y. Yokoyama, S. Fukui, Y. Yokoyama, *Chem. Lett.* (1996) 355–356.
- [10] Z. Fang, S. Wang, Z. Yang, B. Chen, F. Li, J. Wang, S. Xu, Z. Jiang, T. Fang, *J. Photochem. Photobiol., A* 88 (1995) 23.
- [11] A. Zelichenok, F. Buchholtz, E. Fischer, J. Ratner, V. Krongauz, H. Anneser, C. Bräuchle, *J. Photochem. Photobiol., A* 76 (1993) 135.
- [12] A.V. El'tsov, A.I. Ponyaev, E.R. Zakhs, D. Klemm, E. Klemm, in: A.V. El'tsov (Ed.), *Organic Photochromes*, Consultants Bureau, New York, 1990, p. 177.
- [13] N.P. Gristan, L.S. Klimenko, *J. Photochem. Photobiol., A* 70 (1993) 103.
- [14] Y.E. Gerasimenko, A.A. Parshutkin, N.T. Poteleschenko, V.P. Poteleschenko, V.V. Romanov, *Zh. Prikl. Spectrosk.* 30 (1979) 954 (in Russian).
- [15] Y.E. Gerasimenko, N.T. Poteleschenko, *Zh. Org. Khim.* 7 (1971) 2412 (in Russian).
- [16] J.-M. Kim, T.-E. Chang, J.-H. Kang, D.K. Han, K.-D. Ahn, *Adv. Mater.* 11 (1999) 1499.