

Effects of Oxygen on the Photochemical Behaviors of Methacrylic Homopolymer Containing Anthracene Groups

Yong Woon Kim and Kyu Ho Chae*

Faculty of Applied Chemistry and The Polymer Science & Technology Research Center,
Chonnam National University, Kwangju 500-757, Korea

A homopolymer containing anthracene groups, poly[6-(9-anthryloxy)hexyl methacrylate] (PAn) was prepared and the effect of oxygen on its photochemical reaction was studied by UV and IR absorption spectroscopy in order to understand its photochemical behavior. Photochemical reaction of the PAn in THF solution under an atmosphere of air resulted in the formation of endoperoxide at the beginning stage of reaction followed by photodimerization reaction after all the oxygen was consumed, whereas photodimerization and endoperoxide formation took place concomitantly in the film state. The photoreversible reaction of the anthracene photodimer groups in the polymer by photolysis with 254 nm UV light was not efficient. The IR absorption spectral changes of the PAn film upon irradiation indicate that various photooxidation products were produced in the atmosphere of air.

key words: photosensitive polymer, anthracene homopolymer, photodimerization, photooxidation

INTRODUCTION

Anthracene derivatives are interesting compounds because of their versatile photochemical applications. Owing to their diverse photophysical and photochemical properties, anthracene and its derivatives have been used in many systems such as energy migration probes in polymers, triplet sensitizers, molecular fluorosensors, electron acceptor or donor chromophores in artificial photosynthesis, photochromic substrates in 3D memory materials, etc. [1].

Polymers containing anthracene groups have been prepared and their photochemistry also have been studied. For example, photophysical properties of anthracene polymers [2], photochemical cross-linking reaction of anthracene-containing polyesters [3], and photochemistry of polymers containing anthrylmethyl vinyl ketone [4] have been reported. Irradiation of polymers containing anthracene groups photo-induces cross-linking due to the formation of [4+4] cycloadducts across the 9,10-positions of anthracene groups, while in the presence of oxygen, 9-10-endoperoxide is predominately formed.

The photochemical reactions of the anthracene groups in the polymer induce considerable changes in their physical properties, for instance, refractive index, absorption, or the degree of solubility etc., which enables them to apply various optoelectronic materials. Thus, the macromolecules or polymers containing anthracene groups have been used to develop light-switched chromic devices [5,6], electroluminescent devices [7-9], photoresist and channel waveguide applications [10],

optoelectronic materials [11], and others.

We are interested in the photonic applications of the polymer bearing anthracene (An) groups because of their versatile photoreactivity and various applications. In this paper, we prepared a new homopolymer containing oxyanthracene groups and studied the effect of oxygen on its photochemical behavior in solution and at film state.

EXPERIMENTAL

Materials and instruments

6-Bromo-1-hexanol and methacrylic anhydride were purchased from Aldrich Chemical Company, and anthraquinone was obtained from Junsei Chemical Company. Anthrone was prepared by the reported procedure [12]. Ultra-violet (UV) spectra were taken on a Jasco model V-530 spectrophotometer. Infrared (IR) spectra were obtained with the use of Shimadzu model FTIR-8300 spectrometer. ¹H nuclear magnetic spectra were recorded on a Bruker 300 MHz ASX-32 FT-NMR spectrometer. Irradiations were carried out on a Rayonet photochemical reactor (The Southern New England UV Company model 208) equipped with 365 or 254 nm fluorescent lamps. One module of the photochemical reactor was placed in a horizontal position and irradiated. Light intensity was measured by a Vilber Lourmat radiometer model VLX-3W. An Able model ASS-301 spin coater was used for the preparation of polymer films.

Synthesis of 6-(9-anthryloxy)hexane-1-ol (1)

A mixture of anthrone (5.00 g, 25.8 mmol), K₂CO₃ (4.30 g, 31 mmol), and 6-bromo-1-hexanol (4 mL, 31 mmol) in acetone

*To whom correspondence should be addressed.

E-mail : khochae@chonnam.ac.kr

Received October 1, 2002; accepted November 1, 2002

(30 mL) was refluxed for 48 hours with stirring. The salt formed was removed by filtration from the reaction mixture. After concentration by evaporation of the solvent under reduced pressure, the product was isolated by silica gel column chromatography and purified by crystallization from petroleum ether. The yield and melting point were 35% (2.65 g) and 66–68°C, respectively.

IR (KBr pellet, cm^{-1}): 3261 (s; -OH), 3051 (s; aromatic C-H), 2935 (s, aliphatic C-H), 1620 (s; anthracene C=C), 1338, 1085 (s; C-O-C), 739. $^1\text{H-NMR}$ (chloroform- d , δ , ppm): 8.29–7.43 (9H, m, anthracene ring), 4.20 (2H, t, An-O-CH₂-), 3.71 (2H, m, -CH₂-OH), 2.08 (2H, m, An-O-CH₂-CH₂-), 1.77–1.55 (6H, m, HO-CH₂-(CH₂)₃-CH₂-CH₂-O-An).

Synthesis of 6-(9-anthryloxy)hexyl methacrylate (2)

Methacrylic anhydride (0.73 mL, 4.9 mmol) in 5 mL of benzene was added dropwise to a mixture of compound **1** (1.2 g, 4.1 mmol), pyridine (1.32 mL, 8.2 mmol), triethylamine (2.28 mL, 5.2 mmol), hydroquinone (3 mg), and benzene (40 mL), which was refluxed for 3 hours with stirring. After addition of methacrylic anhydride, the reaction mixture was refluxed for 3 days. The reaction mixture was washed with distilled water three times and was dried with MgSO_4 . MgSO_4 was removed by filtration, and the filtrate was concentrated by evaporation of the solvent under reduced pressure. A yellow crystalline solid was isolated by silica gel column chromatography. The product was purified by crystallization in petroleum ether. The yield and melting point were 35% (0.52 g) and 32–34°C, respectively.

IR (KBr pellet, cm^{-1}): 3044 (s; aromatic C-H), 2941 (s; aliphatic C-H), 1724 (s; ester C=O), 1637 (s; anthracene C=C), 1416, 1340, 1088 (s; C-O-C), 740. $^1\text{H-NMR}$ (chloroform- d , δ , ppm): 8.28–7.43 (9H, m, anthracene ring), 6.12, 5.55 (2H, d, CH₂=C), 4.22–4.12 (4H, m, C(=O)-O-CH₂- and O-CH₂-), 2.07 (2H, m, O-CH₂-CH₂-), 1.95 (3H, s, -CH₃), 1.82–1.53 (6H, m, An-O-CH₂-CH₂-(CH₂)₃-).

Preparation of PAn

A mixture of compound **2** (1.00 g, 2.76 mmol) and azobisisobutyronitrile (AIBN) (9.2 mg, 2 mole%) in THF (5 mL) was purged with N_2 gas for twenty minutes, and the polymerization was carried out at 60°C for twenty hours. After concentrating the reaction mixture by evaporation of the solvent under reduced pressure, the resulting polymer was purified by double precipitation in methanol (yield 57%).

IR (KBr pellet, cm^{-1}): 3051 (aromatic C-H), 2939 (aliphatic C-H), 1724 (C=O), 1624 (anthracene C=C), 1340 (aromatic C-O), 1261, 1153, 1090. $^1\text{H-NMR}$ (CDCl_3 , δ , ppm): 7.2–8.4 (9H, anthracene), 3.8–4.2 (4H, O-CH₂-), 0.8–2.2 (13H, -CH₂-, -CH₃).

Film preparation

PAn (0.1 g) was dissolved in 1 mL of THF, and it was filtered with a Milipore filter. The polymer solution was spin

coated on a quartz plate (3.5×1.3 cm) by a spin coater with 1000 rpm for 10 seconds at 1st run and 2000 rpm for 10 seconds at 2nd run, respectively. The film on a quartz plate was dried at room temperature for 1 hour followed by drying at 50°C for 4 hours under vacuum.

Measurement

UV absorption spectral changes: The PAn was dissolved in THF and the absorbance of the solution at 371 nm was adjusted to 1.0–1.2. The polymer solution was placed in two quartz tubes. One tube was purged with N_2 for 10 minutes in order to remove dissolved oxygen, and the other was in an atmosphere of air. The two tubes were irradiated with 365 nm UV light (light intensity; 0.67 mW/cm^2) and UV absorption spectral changes upon irradiation were observed.

Two PAn films on the quartz plate were prepared. One in an atmosphere of N_2 and the other in an atmosphere of air were placed under the UV lamp and irradiated. UV absorption spectral changes upon irradiation with 350 nm UV light (light intensity; 1.6 mW/cm^2) were observed.

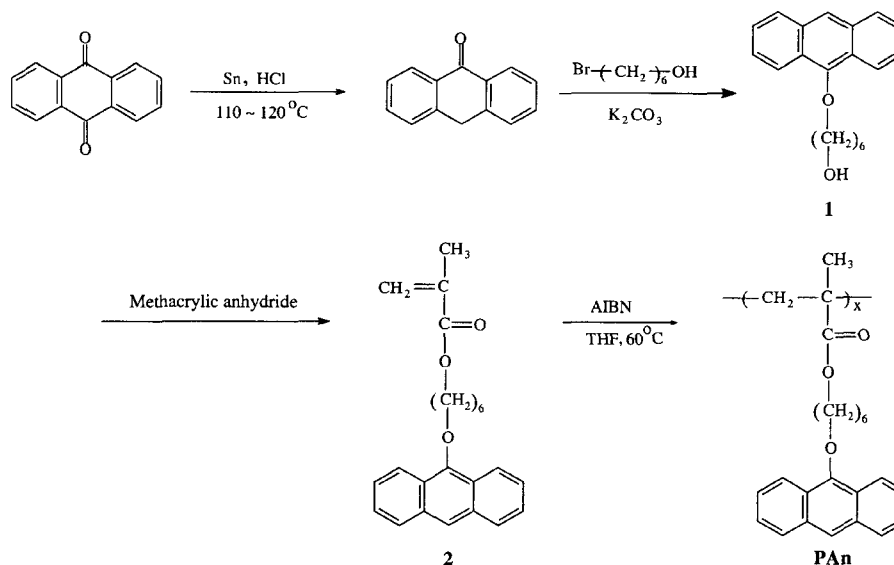
IR absorption spectral changes: A 10 wt% of the PAn solution in THF was cast on a KBr pellet which was pre-dried at 110°C for 24 hours. The film on a KBr pellet was dried at 50°C for 4 hours and was sealed in a quartz tube under an atmosphere of N_2 . Two films, one in an atmosphere of N_2 and the other in an atmosphere of air were irradiated with 350 nm UV light, and IR absorption spectral changes upon irradiation were observed.

Photoreversibility: The photochemical reversibility of the anthracene groups in the PAn was observed as follows: A PAn film on a quartz plate was irradiated with 350 nm UV light. When the absorbance of the PAn film at 373 nm became minimum, UV absorption spectral changes upon irradiation with 254 nm UV light (light intensity; 1.9 mW/cm^2) were observed.

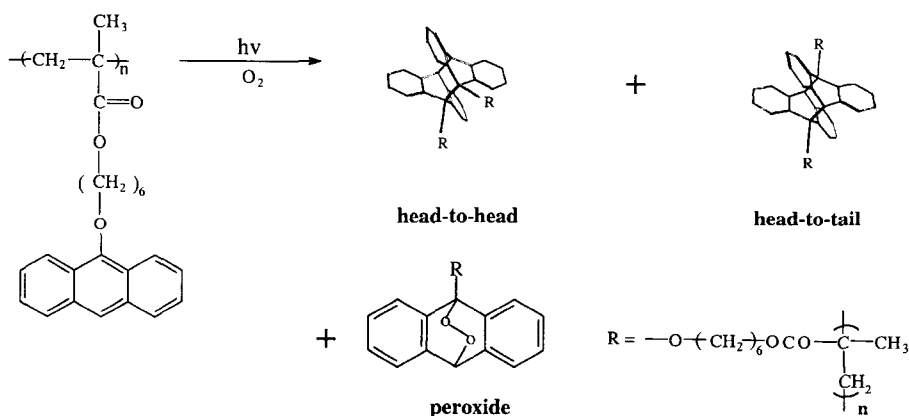
RESULTS AND DISCUSSION

A synthetic route for the preparation of a monomer and a polymer containing anthracene groups is shown in Scheme 1. Anthrone was prepared from the reduction of anthraquinone with tin. 9-Hydroxyanthracene (9-anthrol) exists mainly anthrone due to the keto-enol tautomerization [13] and anthrone easily oxidized to anthraquinone. The compound **1**, a blue fluorescent compound, was prepared from the reaction of anthrone with 6-bromohexanol in the presence of K_2CO_3 in acetone. The compound **2** was prepared through the reaction of compound **1** with methacrylic anhydride followed by the column chromatography and recrystallization. Compound **2** has a blue fluorescence.

PAn, a polymer containing anthracene groups was prepared by polymerization of compound **2** with AIBN. It was soluble in DMF, DMSO, THF, and chloroform, but insoluble in



Scheme 1.



Scheme 2.

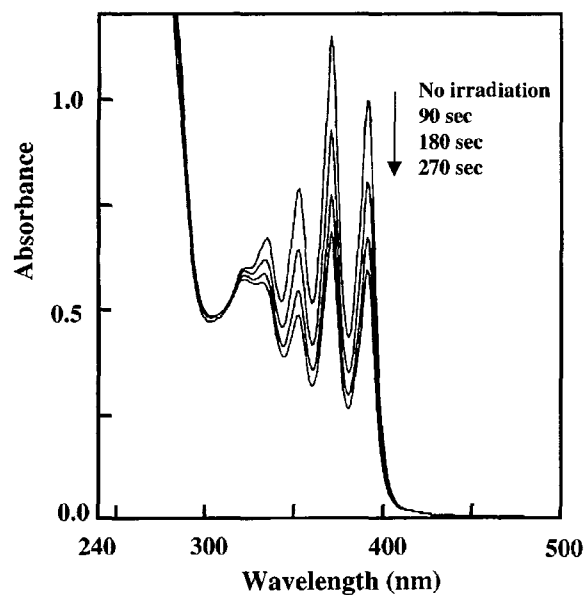
methanol or ether. PAN has a good film forming property on the solid matrix. The number average molecular weight (M_n) and polydispersity of PAN were 6,300 and 1.94, respectively. The glass transition temperature (T_g) measured by DSC and the internal thermal decomposition temperature (T_d) measured by TGA were 50.6 and 300°C, respectively.

The photochemistry of 9-hydroxyanthracene is complicated because of the solvent dependent ground state equilibrium with anthrone and by easy formation of various autooxidation products [14]. Irradiation of 9-hydroxyanthracene yielded 10,10'-bianthrone as well as [4+4] head-to-head and head-to-tail photocyclodimers in methanol [15]. The possible photochemical reaction of the PAN that contains oxyanthracene moieties in the polymer side chain was shown in Scheme 2. The effects of oxygen on the photochemical behaviors of the PAN in solution or in the film state were studied by the UV and IR absorption spectroscopy upon irradiation with 354 nm UV light.

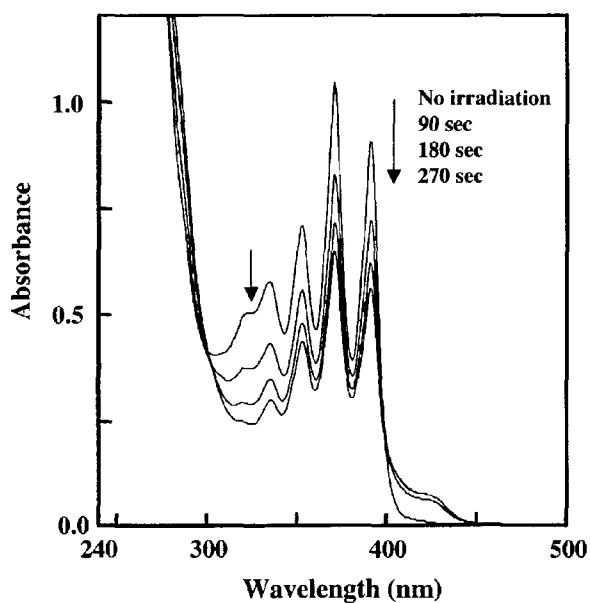
Figure 1 shows UV absorption spectral changes of the PAN

in THF upon irradiation in an atmosphere of air (a) and that of N_2 (b), respectively. The rate of decrease in the absorption band at 300~350 nm was faster in N_2 than that in air. Since the fine splitting of the absorption band at around 300~400 nm is due to the absorption of anthracene groups in the polymer, the result indicates that photochemical transformation of anthracene groups was favored in an atmosphere of N_2 over that of air. However, the absorption band at around 400~450 nm did not change when the polymer solution was irradiated in an atmosphere of air, while it increased slightly in an atmosphere of N_2 . It should be noted that the absorption band at around 400~450 nm comes from the anthracene dimer that was produced by the photodimerization of anthracene [16]. The result indicates that the photodimerization of anthracene groups in the PAN was favored in an atmosphere of N_2 .

Figure 2 shows plots of the A_t/A_0 of the PAN in THF solution upon irradiation with 354 nm UV light as a function of irradiation time. The A_0 and A_t is the absorbance at the



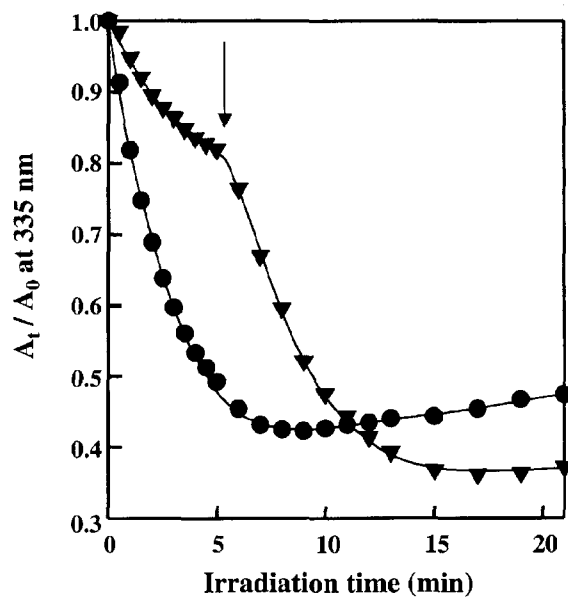
(a)



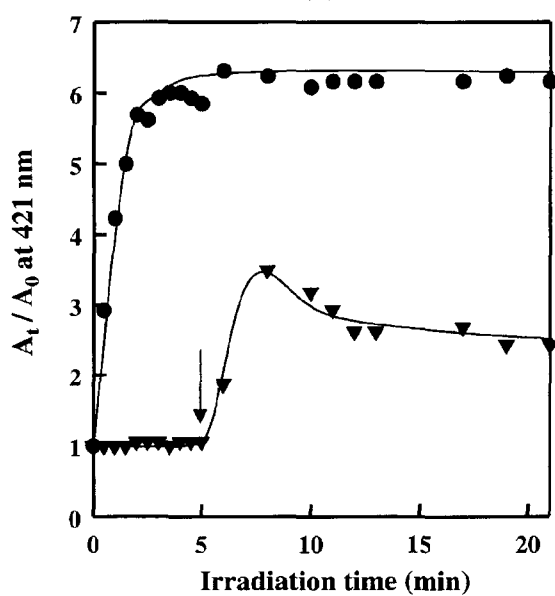
(b)

Figure 1. UV absorption spectral changes of PAN in THF upon irradiation with 350 nm UV light in an atmosphere of air (a) and N_2 (b).

irradiation time of 0 and t min at 335 and 421 nm, respectively. Figure 2(a) shows the plots of the A_t/A_0 at 335 nm in an atmosphere of N_2 and that of air. When irradiations were carried out in an atmosphere of N_2 , the absorbance ratio (A_t/A_0) at 335 nm decreased drastically from 1.0 to 0.45 within five minutes of irradiation time. However, in the presence of oxygen, the absorbance ratio fell from 1.0 to 0.8 during five minutes of irradiation time, and then decreased steadily below 0.4 upon irradiation. Figure 2(b) shows plots of the A_t/A_0 at



(a)



(b)

Figure 2. Plots of the A_t/A_0 of PAN in THF as a function of irradiation time at (a) 335 and (b) 421 nm in an atmosphere of N_2 (●) and air (▼), respectively. Irradiations were carried out with 350 nm UV light.

421 nm as a function of irradiation time. The ratio of absorbance increased sharply within 5 min of irradiation time, and then leveled out in the nitrogen atmosphere. However, in an atmosphere of air it remained constant at the beginning five minutes of irradiation time, and then it began to increase somewhat upon irradiation.

The above result indicates that endoperoxide was formed at the beginning five minutes of irradiation time in the presence of oxygen. After all the dissolved oxygen in solution was

consumed by the endoperoxide formation, the photodimerization of anthracene groups in the polymer side chain began to take place. However, in the nitrogen atmosphere, the photodimerization reaction of anthracene groups took place at the beginning stage of the reaction because endoperoxide could not be formed.

Figure 3 shows the plot of the A_t/A_0 of a PAn film at (a) 335 and (b) 421 nm as a function of irradiation time in an atmosphere of N_2 or air. The relative decrease in absorbance at 335 nm in an atmosphere of N_2 was smaller than that in air. This seems to be due to that the photodimerization of the anthracene

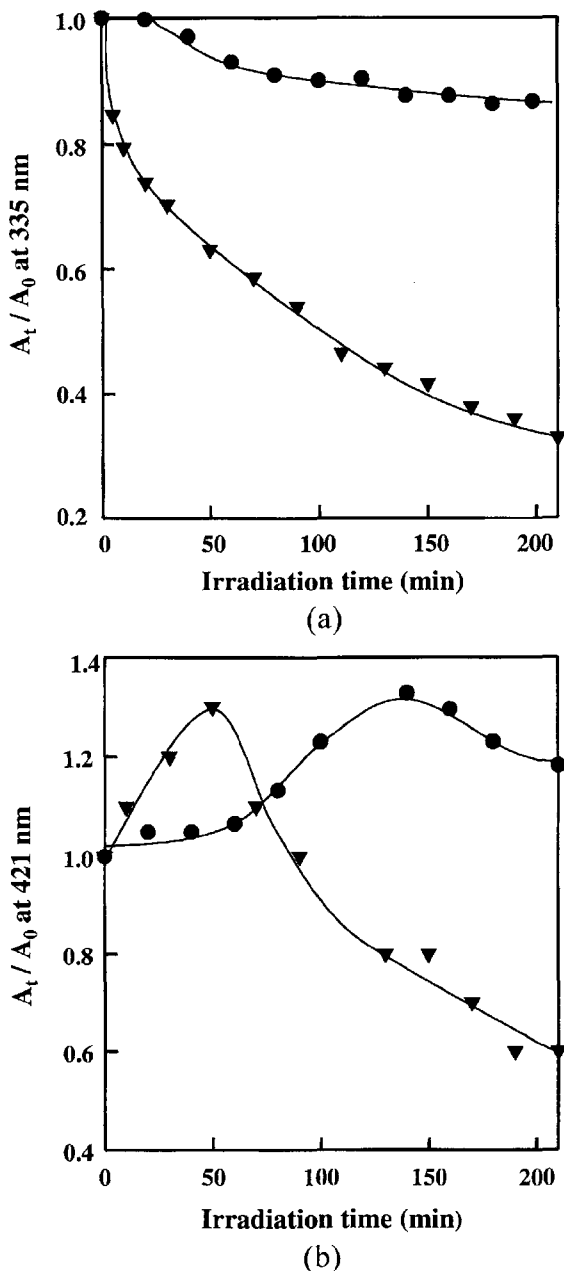


Figure 3. Plots of the A_t/A_0 of a PAn film as a function of irradiation time at (a) 335 and (b) 421 nm in an atmosphere of N_2 (●) and air (▼), respectively.

groups in the polymer is the only photochemical reaction in the nitrogen atmosphere, while the endoperoxide formation as well as photodimerization took place concomitantly in an atmosphere of air. The absorbance ratio of the PAn film at 421 nm in an atmosphere of N_2 increased slightly upon irradiation. However, in the presence of oxygen, it increased slightly during the beginning 50 minutes of irradiation time, and then steadily decreased as a result of photooxidation of anthracene groups.

The photochemical reaction of the PAn at the film was slower than that in solution. This seems to be due to that the photochemical reactions of anthracene groups in the PAn film hardly took place compared to those in solution because of the low mobility of anthracene groups in the polymer chain at the temperature of below T_g (50.6°C). In solution state, the endoperoxide was formed at the beginning stage of the reaction and then photodimerization reaction took place after all the dissolved oxygen was consumed in solution. However, in the film state, the photodimerization and endoperoxide formation occurred concomitantly.

It was well known that the photodimers of anthracene derivatives were photosplitted thermally or photochemically into the original anthracene derivatives [17,18]. Photo or thermal reversibility of the anthracene groups in the PAn film was studied from the UV absorption spectral changes upon irradiation. Figure 4 shows the ratio of the absorbance at 373 nm as a function of irradiation time upon irradiation with 350 and 254 nm UV light, alternatively. It decreased with irradiation, and the rate of decrease in air was faster than that in N_2 . After the ratio of the absorbance of the PAn film at 373 nm became minimum by irradiation with 350 nm UV light, irradiation of

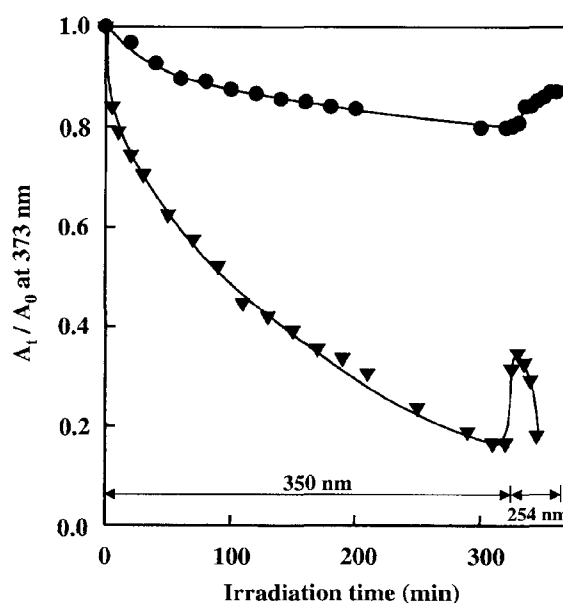


Figure 4. Plot of the A_t/A_0 of a PAn film at 373 nm as a function of irradiation time in an atmosphere of N_2 (●) and air (▼) upon irradiation with 350 nm followed by 254 nm of UV light, alternatively.

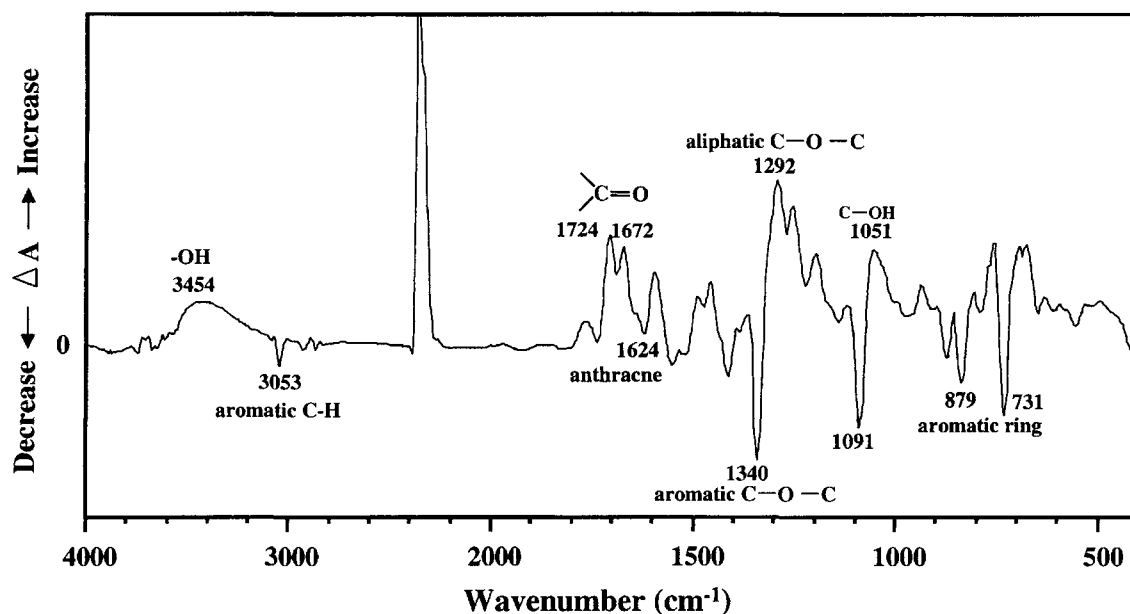


Figure 5. A difference FT-IR spectrum of a PAn film on a KBr pellet between before and after irradiation with 350 nm UV light over two hours in an atmosphere of air.

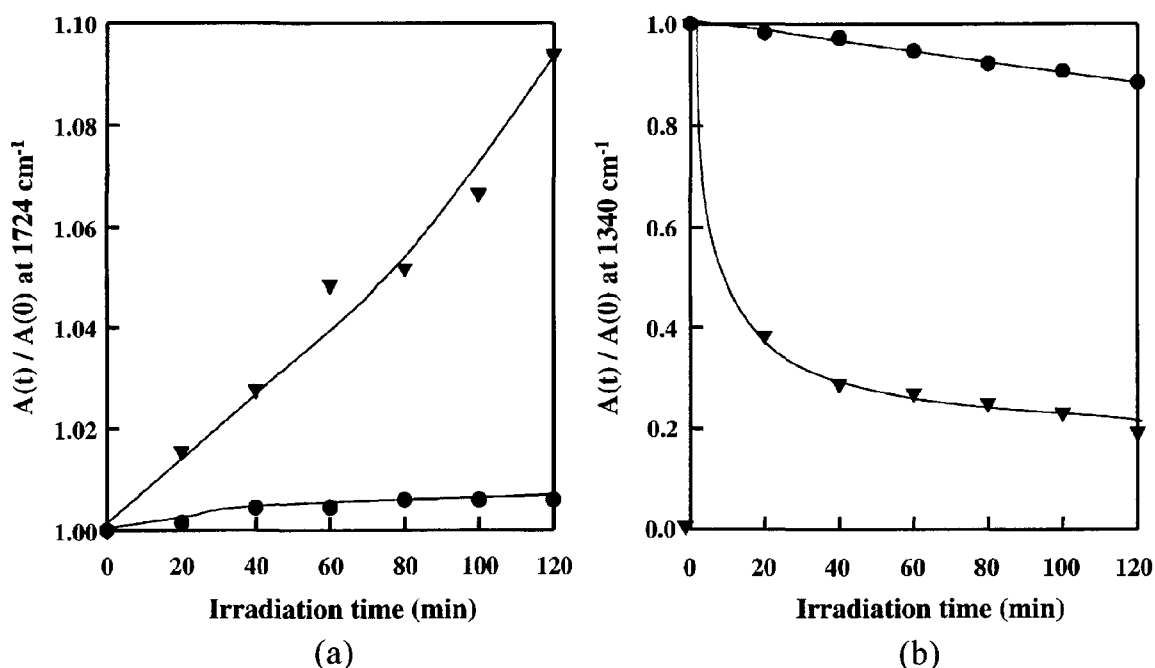


Figure 6. Plots of a PAn film on a KBr pellet as a function of irradiation time at (a) 1724 and (b) 1340 cm^{-1} in an atmosphere of N_2 (●) and air (▼), respectively.

254 nm UV light resulted in the increase of absorbance at 373 nm due to the photosplitting of the anthracene photodimer groups. The absorbance at 373 nm restored up to 35% in an atmosphere of N_2 by irradiation with 254 nm UV light, while it increased up to 23% and then quickly decreased in an atmosphere of air. This seems to be due to the photooxidation of the anthracene groups, which were produced by the

photosplitting of the anthracene photodimer groups in the polymer chain.

Figure 5 shows the difference IR spectrum of the PAn film on a KBr pellet between before and after irradiation with 254 nm UV light over 2 hours in air. The absorption band at 3454, 1724, 1292, and 1051 increased upon irradiation indicating the formation of -OH, C=O, aliphatic C-O-C, and C-OH groups,

respectively. The absorption band at 3053, 1340, 879, and 731 decreased due to the formation of aliphatic C-H, C-C, and aromatic C-O-C groups through the photodimerization or endoperoxide formation of the anthracene groups.

Figure 6 shows the ratio of absorbance of the PAN film on a KBr pellet at (a) 1724 and (b) 1340 cm^{-1} as a function of irradiation time. The absorbance at 1724 cm^{-1} due to the formation of carbonyl groups increased in an atmosphere of air, while that in an atmosphere of N_2 did not change significantly with irradiation. A similar result was obtained at 3454 cm^{-1} . The absorbance at 1340 cm^{-1} due to the aromatic C-O-C groups decreased upon irradiation as a result of the formation of aliphatic C-O-C groups by the photodimerization and endoperoxide formation of the anthracene groups.

CONCLUSION

A anthracene homopolymer, the PAN was soluble in various organic solvents and has a good film forming property on the solid matrix. Irradiation of 354 nm UV light to the PAN in THF in an atmosphere of air resulted in the endoperoxide formation at the beginning stage of reaction followed by the photodimerization reaction after all the oxygen in solution was consumed. However, the photodimerization and endoperoxide formation took place concomitantly at the film state. The photosplitting reaction of anthracene photodimer groups into the original anthracene groups in the polymer side chain was not efficient when irradiations were carried out with 254 nm UV light.

Acknowledgements – This work has been supported by the Korea Science and Engineering Foundation (Grant No. 98-05-01-03-01-3) and by the Brain Korea 21 Project in 2001.

REFERENCES

1. Bouas-Laurent, H., A. Castellan, J. P. Desvergne and R. Lapouyade (2000) Photodimerization of anthracenes in fluid solution: structural aspects. *Chem. Soc. Rev.* **29**, 43-55.
2. Hargreaves, J. S. and S. T. Webber (1984) Photophysics of anthracene polymers: fluorescence, singlet energy migration, and photodegradation. *Macromolecules*, **17**, 235-240.
3. Jones, J. R., C. L. Liotta, D. M. Collard and D. A. Schiraldi (2000) Photochemical cross-linking of poly(ethylene terephthalate-co-2,6-anthracenedicarboxylate). *Macromolecules*, **33**, 1640-1645.
4. Modi, P. J. and J. E. Guillet (1995) The photochemistry of polymers containing anthrylmethyl vinyl ketone. *J. Polym. Sci., Polym. Chem.* **33**, 197-201.
5. Deng, G., T. Sakaki and S. Shinkai (1993) Light-Switched Chromophoric Device Designed from an Ionophoric Calix [4]arene. *J. Polym. Sci., Polym. Chem.* **31**, 1915-1919.
6. Tsudera, T., A. Ikeda and S. Shinkai (1997) Light-switched metal-tunneling across a π -basic tube of 1,3-alternate-calix [4]arenes. *Tetrahedron*, **53**, 13609-13620.
7. Aguiar, A., L. Akcelrud, and F. E. Karasz (1995) Electroluminescent devices based on modified polystyrene II. Pendant anthracenyl groups as light emitters. *Synthetic Metals*, **71**, 2189-2190.
8. Suzuki, H., S. Satoh, Y. Kimata and A. Kuriyama (1995) Synthesis and properties of poly(methylphenylsilane) containing anthracene units. *Chem. Lett.* 451-452.
9. Satoh, S., H. Suzuki, Y. Kimata and A. Kuriyama (1996) Optical and electroluminescence properties of poly (methylphenylsilane) containing an anthracene unit. *Synthetic Metals*, **79**, 97-102.
10. Paul, S., O. Halle, H. Einsiedel, B. Menges, K. Müllen, W. Knoll and S. Mittler-Neher (1996) An anthracene-containing PMMA derivative for photoresist and channel waveguide applications. *Thin Solid Films*, **288**, 150-154.
11. Tran-Con, Q. (1996) Polarization induced photochromic reactions in polymer solids. *Polymeric Materials Encyclopedia*, J. C. Salamone ed., vol.7: New York; CRC, 5128-5136.
12. Vogel, A. I. *A Textbook of Practical Organic Chemistry*; 3rd ed. Longman: London, p. 740.
13. Koerner, M. and B. Rickborn (1989) Anthrones as reactive dienes in Diels-Alder reactions. *J. Org. Chem.* **54**, 6-9.
14. Dabestani, R., K. J. Ellis and M. E. Sigman (1995) Photodecomposition of anthracene on dry surfaces: products and mechanism. *J. Photochem. Photobiol. A: Chem.* **86**, 231-239.
15. Kim, S. S., C. H. Lim, B. J. Ahn and S. C. Shim (1993) Photochemistry of anthrone and its derivatives. *Bull. Korean. Chem. Soc.* **14**, 663-664.
16. Tung, C. H. and J. Q. Guan (1998) Regioselectivity in the photocycloaddition of 9-substituted anthracene incorporated within Nafion membranes. *J. Org. Chem.* **63**, 5857-5862.
17. Schütz, A. and T. Wolff (1997) Regioselectivity in the photodimerization of 9-hydroxymethylanthracene and 9-anthracene carboxylic acid esters in surfactant systems. *J. Photochem. Photobiol., A: Chem.* **109**, 251-258.
18. Breton, G. W. and X. Vang (1998) Photodimerization of anthracene: A [4 π +4 π] photochemical cycloaddition. **75**, 81-82.