Nonsalt 1-(Arylmethyloxy)pyrene Photoinitiators Capable of Initiating Cationic Polymerization

Naoki Uchida, Haruka Nakano, Tetsutaro Igarashi, Tadamitsu Sakurai

Department of Material and Life Chemistry, Faculty of Engineering, Kanagawa University, Kanagawa-ku, Yokohama 221-8686, Japan
Correspondence to: T. Sakurai (E-mail: sakurt01@kanagawa-u.ac.jp)

ABSTRACT: Analysis of photoproducts derived from 1-(methoxynaphthalen-1-ylmethyloxy)pyrene initiators and polymer end groups demonstrated that methoxynaphthalen-1-ylmethyl carbocation is involved in the initiation steps for both styrene (St) and cyclohexene oxide (CHO) polymerization. Charge transfer from the pyrenyloxy oxygen atom to the methoxynaphthalen-1-ylmethyl chromophore in the singlet excited state is assumed to be responsible for the efficient generation of the carbocation species, which also initiates the copolymerization of St and CHO. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 40510.

INTRODUCTION

Various functional initiators have been developed for use in photochemistry.[1] Recent research has focused on hybrid-type photoinitiators that promote the initiation of both radical and cationic polymerization[2–8] because such photoinitiators enable the production of hybrid polymers composed of radical- and cation-derived polymer units.

Although certain salt-type photoinitiators can initiate both radical and cationic polymerization,[2–5,8–10] they have limited industrial applications because they have low monomer solubility and are, in general, metal- or halogen-containing inorganic compounds. To overcome these limitations, nonsalt photoinitiators have been developed. Unfortunately, these photoinitiators are limited in their ability to induce hybrid polymerization.[6,7,11,12] Therefore, the development of highly efficient nonsalt organic photoinitiators that can effectively induce hybrid polymerization is a significant research goal.

A novel approach based on the intramolecular charge separation in the singlet excited state of *O*-substituted aryl alcohols, which assists the heterolytic and homolytic cleavage of specific covalent bonds, led to the design of arylmethyloxyanthraquinone and arylmethyloxyanthracene initiators as novel, high-performance, and hybrid-type photoinitiators.[13,14] These initiators exhibited intense absorption bands near the visible region and underwent rapid photodecomposition to induce bulk polymerization of both styrene (St) and cyclohexene

oxide (CHO). In addition, the relative yields of polystyrene (PSt) and poly(cyclohexene oxide) (PCHO) depended on the structure of the aromatic rings bonded to the arylmethyloxy oxygen atom in the above initiators, leading to the possibility of controlling the yield by using different aryl substituents, i.e., anthryl and pyrenyl. If this proves to be true, based on the aryl substituent, the development of a multifunctional photoinitiator with the ability to initiate radical, cationic, or hybrid polymerization could be possible.

Thus, because pyrene rings in the singlet excited state show a stronger tendency to form excimers or exciplexes than anthracene rings,[15] 1-(methoxy-substituted naphthalene-1-ylmethyloxy)pyrene photoinitiators **1a** and **1b** were synthesized and their photolytic behavior and ability to initiate the polymerization of St and CHO (Figure 1) were investigated. The results of this study are reported herein.

EXPERIMENTAL

Materials and Solvents

St and CHO monomers were purified by vacuum distillation before use. All other chemicals were obtained from commercial sources at the highest grade available. 1-Hydroxypyrene was synthesized by treating a dichloromethane solution of 1-pyrenecarboxaldehyde with *m*-chloroperbenzoic acid, a saturated NaHCO₃ solution, and then a KOH solution according to the procedure by Sehgal and Kumar.[16] The 1-(methoxy-substituted naphthalene-1-ylmethyloxy)pyrene derivatives (**1a** and **1b**) were synthesized using the following procedure. After
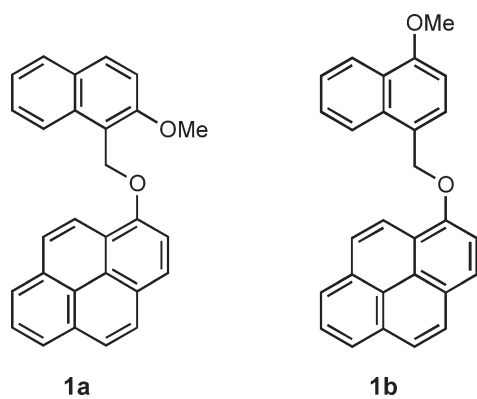
Figure 1. Structures of **1a** and **1b**.

sodium hydride (60% purity) was slowly added to an N,N-dimethylformamide (DMF) solution of 1-hydroxypyrene with stirring, 1-chloromethyl-2-methoxynaphthalene and 1-chloromethyl-4-methoxynaphthalene, obtained via chlorination of the corresponding methoxy-substituted 1-hydroxymethylnaphthalene with thionyl chloride, was allowed to react with the hydroxypyrene-derived sodium salt for 5 h at room temperature. The reaction mixture was then poured into ice-chilled water, and the precipitated solid was extracted with ethyl acetate. The ethyl acetate solution was washed several times with water and dried over anhydrous $MgSO_4$. The residual solid obtained after solvent removal under reduced pressure was purified by column chromatography on silica gel (70–230 mesh; eluent, $CHCl_3$: hexane = 1 : 1 v/v) to afford analytical grade product of **1a** and **1b** in 51% (**1a**) and 65% (**1b**) yield. The authentic sample 2-methoxy-1-methoxymethylnaphthalene was synthesized by treating a DMF solution of 1-hydroxymethyl-2-methoxynaphthalene, obtained from the reduction of 2-methoxy-1-naphthaldehyde with sodium borohydride in methanol, with sodium hydride (60% purity) and then with methyl iodide. The crude product was purified by column chromatography on silica gel (70–230 mesh; eluent, $CHCl_3$: hexane = 1 : 1 v/v) to afford an analytical grade authentic sample in 49% yield. The spectroscopic data for 1-hydroxypyrene, **1a**, **1b**, and 2-methoxy-1-methoxymethylnaphthalene are as follows:

1-Hydroxypyrene. δ_H [500 MHz, $CDCl_3$, tetramethylsilane (TMS) as internal standard, ppm]: 8.34 (1H, d, $J = 9.0$ Hz), 7.91–8.10 (7H, m), 7.47 (1H, d, $J = 8.0$ Hz), 5.58 (1H, s). δ_C (125 MHz, $CDCl_3$, ppm): 151.4, 132.8, 132.0, 131.2, 128.7 (2C), 128.0 (2C), 125.9 (2C), 125.7 (2C), 125.3, 125.1, 120.6, 106.3.

1a. δ_H (500 MHz, $CDCl_3$, TMS as internal standard, ppm): 8.34 (1H, d, $J = 9.0$ Hz), 8.21 (1H, d, $J = 8.5$ Hz), 8.15 (1H, d, $J = 8.5$ Hz), 8.06 (1H, d, $J = 8.5$ Hz), 8.04 (1H, d, $J = 8.5$ Hz), 7.97 (1H, d, $J = 9.5$ Hz), 7.86–7.95 (5H, m), 7.83 (1H, d, $J = 8.0$ Hz), 7.49 (1H, dd, $J = 7.5$, 8.0 Hz), 7.38 (1H, dd, $J = 7.5$, 8.0 Hz), 7.35 (1H, d, $J = 9.0$ Hz), 5.93 (2H, s), 4.01 (3H, s). δ_C (125 MHz, $CDCl_3$, ppm): 155.6, 153.3, 133.9, 131.69, 131.66, 131.0, 129.2, 128.3, 127.2, 127.1, 126.2, 126.0, 125.8, 125.44, 125.36, 125.0, 124.9, 124.1, 124.0, 123.9, 123.8, 121.6, 120.8, 117.3, 113.3, 109.9, 62.0, 56.8. MALDI TOF-MS m/z calcd for $C_{28}H_{20}NaO_2$ [M + Na]$^+$: 411.15. Found: 411.08.

1b. δ_H (500 MHz, $CDCl_3$, TMS as internal standard, ppm): 8.39 (1H, d, $J = 9.0$ Hz), 8.37 (1H, d, $J = 8.0$ Hz), 8.15 (1H, d, $J = 8.0$ Hz), 8.14 (1H, d, $J = 8.5$ Hz), 8.09 (1H, d, $J = 8.0$ Hz), 8.08 (1H, d, $J = 8.0$ Hz), 7.98 (1H, d, $J = 9.0$ Hz), 7.94 (1H, d, $J = 9.0$ Hz), 7.93 (1H, dd, $J = 8.0$, 8.0 Hz), 7.90 (1H, d, $J = 9.0$ Hz), 7.76 (1H, d, $J = 8.5$ Hz), 7.62 (1H, d, $J = 7.5$ Hz), 7.56 (1H, dd, $J = 7.5$, 8.0 Hz), 7.54 (1H, dd, $J = 7.5$, 8.0 Hz), 6.82 (1H, d, $J = 7.5$ Hz), 5.76 (2H, s), 4.04 (3H, s). δ_C (125 MHz, $CDCl_3$, ppm): 156.2, 153.0, 132.9, 131.7 (2C), 127.5, 127.2, 127.1, 126.4, 126.1, 126.0, 125.9, 125.5, 125.4, 125.3, 125.1, 124.9, 124.5, 124.3, 124.2, 123.9, 122.7, 121.5, 120.8, 109.8, 102.9, 69.9, 55.6. MALDI TOF-MS m/z calcd for $C_{28}H_{20}NaO_2$ [M + Na]$^+$: 411.15. Found: 411.69.

2-Methoxy-1-methoxymethylnaphthalene. δ_H (500 MHz, $CDCl_3$, TMS as internal standard, ppm): 8.06 (1H, d, $J = 8.3$ Hz), 7.71 (1H, d, $J = 8.3$ Hz), 7.70 (1H, d, $J = 8.3$ Hz), 7.46 (1H, dd, $J = 8.3$, 8.9 Hz), 7.29 (1H, dd, $J = 8.3$, 8.9 Hz), 7.13 (1H, d, $J = 8.3$ Hz), 4.93 (2H, s), 3.81 (3H, s), 3.39 (3H, s). δ_C (125 MHz, $CDCl_3$, ppm): 155.3, 133.6, 130.1, 128.9, 128.0, 126.6, 123.5, 123.3, 118.1, 112.9, 64.1, 57.6, 56.3.

Measurements

Changes in the ultraviolet (UV) absorption spectra for **1a** and **1b** (1.0×10^{-4} mol dm^{-3}) were observed at room temperature in nitrogen-saturated toluene or 1,2-dimethoxyethane (25 mL) following irradiation with a 500 W high-pressure Hg lamp [Corning 0-52 (NY) and Toshiba IRA-25S (Tokyo, Japan) glass filters] at wavelengths greater than 340 nm. The irradiation intensity was 170 mW cm^{-2}.

For the analysis of photoproducts derived from **1a** (1.0×10^{-3} mol dm^{-3}), a solution of the photoinitiator in nitrogen-saturated toluene or 1,2-dimethoxyethane (25 mL) in a Pyrex vessel was irradiated with a 500 W high-pressure Hg lamp at room temperature for 30–60 s at wavelengths greater than 340 nm. The irradiated solution was then subjected to high-performance liquid chromatography (HPLC) analysis (mobile phase, MeCN : THF : H_2O = 40 : 30 : 30 v/v; detection wavelength, 240 or 290 nm). The structures of the photoproducts were determined by comparing the HPLC data (retention times and shapes of the HPLC signals) of the products with those of commercially available and independently synthesized authentic samples.

For polymerization with St or CHO, a specified amount of **1** was dissolved in St or CHO in a glass tube. The resulting solution was degassed using three freeze–pump–thaw cycles. The sealed glass tube was maintained at a given temperature and irradiated by a 500 W high-pressure Hg lamp at wavelengths greater than 340 nm for a given period of time. The solution was then poured into aqueous methanol or hexane–methanol, and the resultant polymer that precipitated was filtered and dried *in vacuo* at 40°C. The polymer yield was gravimetrically estimated using an average of more than two measurements.

^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded on a JEOL JNM-A500 spectrometer (Tokyo, Japan) at 500 and 125 MHz, respectively, in $CDCl_3$ with TMS as the internal standard. The irradiation intensity was measured using
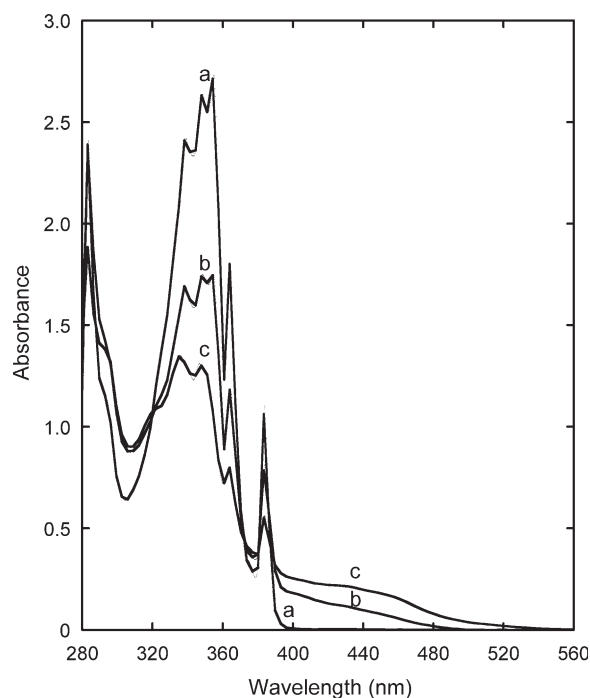
Figure 2. Ultraviolet (UV) absorption spectral changes following irradiation ($\lambda > 340$ nm) of **1a** (1.0×10^{-4} mol dm^{-3}) in nitrogen-saturated toluene at room temperature. Irradiation times were 0 s (curve a), 5 s (curve b), and 25 s (curve c).

a UV-M03 intensity meter equipped with a UV-SN35-M10 photodetector (Tokyo, Japan). UV absorption and fluorescence spectra were collected on a Hitachi U-3300 spectrophotometer and a Hitachi F-4500 spectrofluorimeter (Tokyo, Japan), respectively. HPLC analyses were conducted on a Shimadzu LC-10AT$_{VP}$ HPLC system (Kyoto, Japan) equipped with a 4.6×250 mm ODS (Zorbax) column and a Shimadzu SPD-10A$_{VP}$ UV detector. The molecular weight distribution of the polymers was estimated by gel permeation chromatography (GPC) using a Tosoh model HLC-8020 GPC unit (Tokyo, Japan) equipped with a refractive index detector on two TSK-gel columns (Multipore H$_{XL}$-M $\times$ 2) with tetrahydrofuran as an eluent. A calibration curve for molecular weights ranging from 500 to 1.11×10^6 was obtained under conditions similar to those used for standard PSt.

RESULTS AND DISCUSSION

Photoreactivity of 1

When a nitrogen-saturated toluene solution of **1a** (1.0×10^{-4} mol dm^{-3}) was irradiated for a given period of time at wavelengths greater than 340 nm ($\lambda > 340$ nm) using a 500 W high-pressure Hg lamp at room temperature, absorption bands originating from the pyrenyloxy chromophore decreased and a new absorption band appeared in the 400–500 nm range. A typical example is shown in Figure 2. Similar changes in the UV absorption spectra were observed in the more polar solvent, 1,2-dimethoxyethane, and for the photoinitiator **1b**. Because the irradiated light ($\lambda > 340$ nm) is exclusively absorbed by the pyrenyloxy chromophore in the initiator **1**, the decrease in the absorbance at 350 nm at each second during the initial stage of

the photolysis of this initiator could be used as a substitute for the quantum yield for initiator photolysis, and thus, as a measure of the photoreactivity of **1**. This value for **1a** (0.19 in toluene and 0.15 in 1,2-dimethoxyethane) was greater than that for **1b** (0.014 and 0.015, respectively), indicating that the 2-methoxy-substituted pyrene initiator **1a** was more reactive than its isomer **1b** by a factor of ~10 in these two solvents. The order of photoreactivity for **1a** and **1b** is consistent with that for the corresponding anthracene photoinitiators.[14]

Previously, we found that photoproduct analysis can reliably distinguish the mode of bond cleavage for bichromophoric photoinitiators.[11–14] Therefore, in this study, pyrene initiator **1a** was chosen as the model, and the **1a**-derived product distribution was examined by comparing the HPLC data for the photoproducts with those for the commercially available and independently synthesized authentic samples. As depicted in Scheme 1, irradiation of a nitrogen-saturated toluene solution of **1a** (1.0×10^{-3} mol dm^{-3}) at wavelengths greater than 340 nm afforded 1-formyl-2-methoxynaphthalene (**2a**, 12% HPLC yield), pyrene (**3**, 1%), 1-hydroxymethyl-2-methoxynaphthalene (**4a**, 16%), and 1-hydroxypyrene (**5**, 34%) at 44% conversion. Approximately same product composition was obtained from photolysis in 1,2-dimethoxyethane: **2a** (15%), **3** (4%), **4a** (25%), and **5** (25%) at 50% conversion. On the basis of the criteria for the bond cleavage mode established in our previous studies,[11–14] it can be concluded that heterolysis of the CH$_2$–OAr bond (leading to **4a** and **5**) occurs more readily than the homolysis of the CH$_2$O–Ar bond (leading to **2a**, **3**, and **4a**), even in the nonpolar solvent, toluene. The addition of 10 vol% methanol in toluene and 1,2-dimethoxyethane led to the formation of 2-methoxy-1-methoxymethylnaphthalene (**6a**) in 2% HPLC yield in the former solvent and 3% yield in the latter (Scheme 1). This photoproduct must be formed by capture of the 2-methoxynaphthalen-1-ylmethyl carbocation by methanol, which supports the above conclusion. It should be noted that minor additional HPLC signals were observed in the chromatogram along with **1a**, **2a**, **3**, **4a**, and **5**. Control experiments confirmed that a few of these minor signals could be attributed to the **5**-derived secondary photoreactions. The high electrophilicity of the arylmethyl carbocation also enabled this reactive intermediate to form adducts with toluene and 1,2-dimethoxyethane,
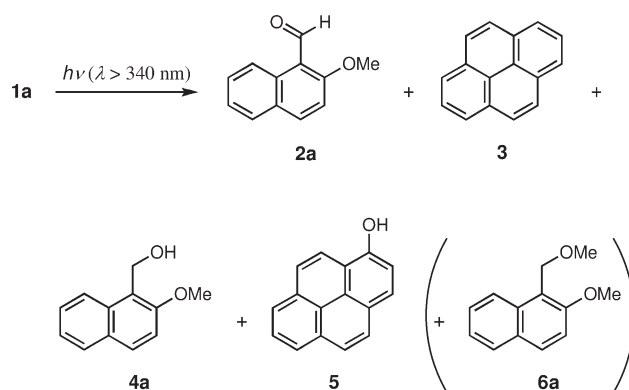
Scheme 1. Product distribution derived from the photolysis of **1a** in toluene at room temperature.
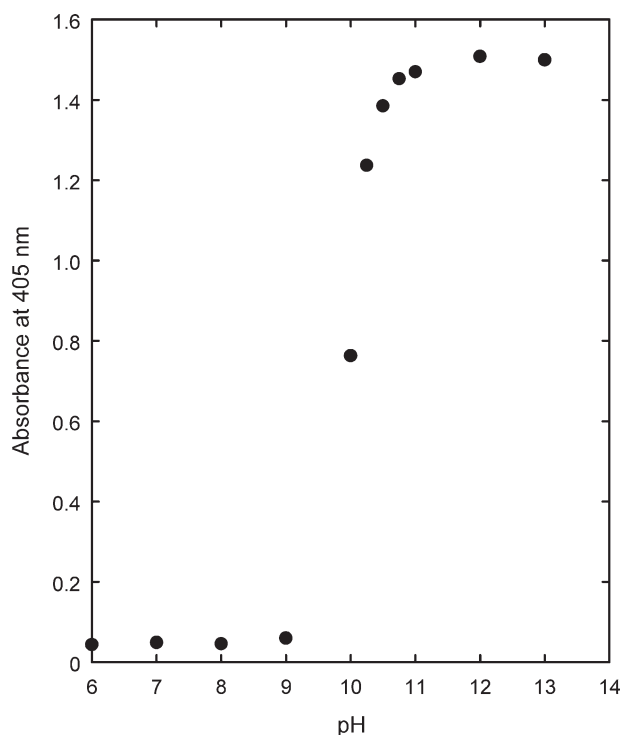
Figure 3. Absorbance of 1-hydroxypyrene (1.0×10^{-4} mol dm^{-3}) at 405 nm in water containing KCl (0.10 mol dm^{-3}) at room temperature as a function of pH.

resulting in a decrease in the material balance of the photoproducts **2a–5**. In addition, the fact that pyrene (**3**) was detected in a much lower yield than expected strongly suggested the minor contribution of hydrogen abstraction by the pyrenyl radical. These considerations led to the conclusion that 1-hydroxypyrene (**5**) and 1-hydroxymethyl-2-methoxynaphthalene (**4a**) were formed from the hydrolytic reaction of the pyren-1-yloxy anion and 2-methoxynaphthalen-1-ylmethyl carbocation in toluene and 1,2-dimethoxyethane, which usually contain trace amounts of water.

The bond cleavage mode observed for **1a** suggested that a strong charge-transfer interaction between the methoxynaphthalene and pyrenyloxy chromophores in the excited state preferentially induced heterolytic CH$_2$—OAr bond cleavage even in the nonpolar solvent, toluene. On the basis of the pH dependence of the UV absorption and fluorescence spectra of 1-hydroxypyrene in water containing 0.10 mol dm^{-3} KCl (Figures 3 and 4, respectively), pKa in the singlet ground and excited states were estimated to be 10.0 and 9.6, respectively. ΔpKa of 0.4 revealed that a charge-separated state was not attained during the excited-state lifetime; thus, the excited-state acidity of 1-hydroxypyrene was only slightly enhanced. On the other hand, as previously reported, dissociation constant of 1-hydroxyanthracene in its singlet excited state was increased by approximately five orders of magnitude (ΔpKa = 5.4) because of a significant influence of the charge-separated state on the excited-state acidity of this derivative. Therefore, it can be concluded that a difference in the excited-state interaction modes between 2-methoxynaphthalen-1-ylmethyl and pyren-1-yloxy chromophores in pyrene initiator **1a** and between 2-methoxynaphthalen-1-ylmethyl and anthracen-1-

yloxy chromophores in the corresponding anthracene initiator is likely responsible for the significantly different modes of CH$_2$—O bond cleavage in toluene.

Photopolymerization with 1

The photoproduct analysis described above confirmed that the 1-(arylmethyloxy)pyrene initiators generate the arylmethyloxy radical and arylmethyl carbocation via photolysis, allowing them to function as either hybrid or cationic photoinitiators in the polymerization of St and CHO. The data summarized in Table 1 show that the pyrene initiator **1a** with the 2-methoxy substituent less efficiently induced bulk photopolymerization of St and CHO than its isomer **1b**, despite the fact that the former is more reactive than the latter. This result suggests the involvement of the pyrene ring in the initiation step of these polymerization reactions. In addition, the unexpected finding that both **1a** and **1b** induced the photopolymerization of St to produce PSt with considerably lower number average molecular weight (M_n) and much lower yield than the corresponding anthracene initiators, which induce the exclusive radical polymerization of St, led us to propose an ionic mechanism for this photopolymerization.[14] Thus, to ascertain whether the St polymerization proceeded via an ionic or radical mechanism, the effect of 2,2,6,6-tetramethylpiperidinyl-1-oxy (TEMPO) on polymer yield after irradiation at 60°C for 8 h was examined. The presence of 0.2 mol % TEMPO in St exerted a negligible effect on the yields of PSt (4.8% for **1a**/TEMPO and 6.0% for **1b**/TEMPO), indicating the major participation of the former mechanism in the photopolymerization of St. Because the corresponding anthracene
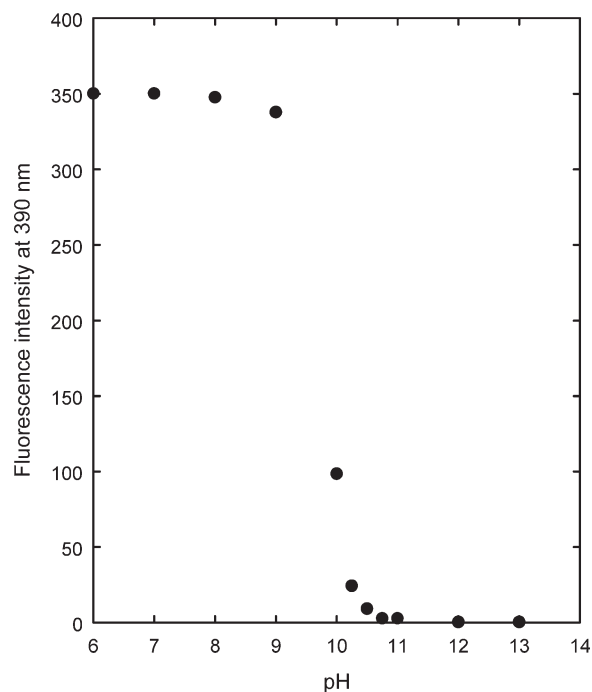
Figure 4. Fluorescence intensity of 1-hydroxypyrene (1.0×10^{-4} mol dm^{-3}) at 390 nm in water containing KCl (0.10 mol dm^{-3}) at room temperature as a function of pH. The excitation wavelength was the isosbestic point (354 nm) as determined by evaluating the ultraviolet (UV) absorption spectra at different pH.

Table 1. Photopolymerization of Styrene (St) and Cyclohexene Oxide (CHO) with **1a** and **1b** as Initiators[a]

| Initiator	Time (h)	Temperature (°C)	PSt (PCHO)		
			Yield (%)	$M_n \times 10^{-3}$	M_w/M_n
1a	8	RT[b]	<1 (5.3)	— (15)	— (1.7)
	8	60	5.0 (18)	5.4 (21)	1.8 (1.6)
	12	60	8.0 (23)	5.6 (19)	2.3 (1.5)
1b	8	RT[b]	4.4 (9.4)	4.7 (16)	1.9 (1.5)
	8	60	5.9 (32)	4.7 (24)	2.5 (1.7)
	12	60	9.5 (36)	4.6 (24)	2.8 (1.7)

[a] [Initiator]/[St] = [Initiator]/[CHO] = 0.2 mol %. The initiator was irradiated with $\lambda > 340$ nm.
[b] RT represents room temperature.

initiator-derived radical pair (exclusively formed in the St monomer) efficiently induced the radical polymerization of this monomer,[14] this finding confirms that the arylmethyl carbocation/pyren-1-yloxy anion pair generated in the St monomer had much greater reactivity than the arylmethyloxy radical/pyrenyl radical pair. As shown in Table 1, the observation of the much lower M_n and yield (of PSt) than anticipated might be due to the much lower rate of the propagation reaction for the St monomer-derived cation as compared with that for the St monomer-derived radical. This decreased rate of the propagation reaction is likely to result in an acceleration of the termination reaction for the cationic polymerization of St; thus, decreasing M_n and yield of PSt. On the other hand, the pyrene initiator **1** induced the cationic polymerization of CHO to afford PCHO in a yield comparable with that of the polymer obtained using the corresponding anthracene initiator. The difference in the CHO polymerization behavior of these two photoinitiators can be explained by the fact that anthracene initiators, which are photochemically more reactive, have a strong tendency to produce larger amounts of PCHO,[14] while the reverse tendency is observed for pyrene initiators. It is likely that the pyren-1-yloxy anion exists in close vicinity to the arylmethyl carbocation (in the initiation reaction between the photochemically generated ion pair and St or CHO monomer) and sterically hinders the initiation reaction.

To analyze the polymer end groups, ^1H NMR spectra were recorded for PSt and PCHO produced via the photopolymerization with **1a** at 60°C. However, an attempt to synthesize PSt and PCHO with low M_n (suitable for the analysis of the polymer end groups) was unsuccessful. In addition, the proton signals of these polymer end groups could not be detected in any NMR spectra of PSt ($M_n = 5.4 \times 10^3$) and PCHO ($M_n = 2.1 \times 10^4$) obtained from the 8 h irradiation (Table 1). On the other hand, the fact that the methoxynaphthalene and pyrene chromophores show intense fluorescence allowed us to expect a rapid detection of these chromophores attached to polymer ends.[17] As expected, both the **1a**-derived polymers exhibited very similar fluorescence profiles near 370 and 400 nm (Figure 5) and possessed the same chromophores at their polymer ends. The 370 and 400 nm emission bands were virtually consistent with those of 2-methoxy-1-methoxymethylnaphthalene (360 nm) and 1-hydroxypyrene (390 and 410 nm) shown in Figure 6 under the same conditions,

respectively, indicating that the methoxynaphthalen-1-ylmethyl group predominantly existed at one polymer end with the pyren-1-yloxy group at the other end. Intramolecular and intermolecular interactions between the same end groups and between different end groups, including the polymer side chains are considered to be responsible for differences in the position and shape of the observed fluorescence bands. Therefore, it was concluded that the arylmethyl carbocation was preferentially involved in the initiation steps of all polymerization reactions. The finding that **1a** and **1b** also function as cationic photoinitiators for St suggested that the initiator **1** could induce the copolymerization of St with CHO. Therefore, a St—CHO
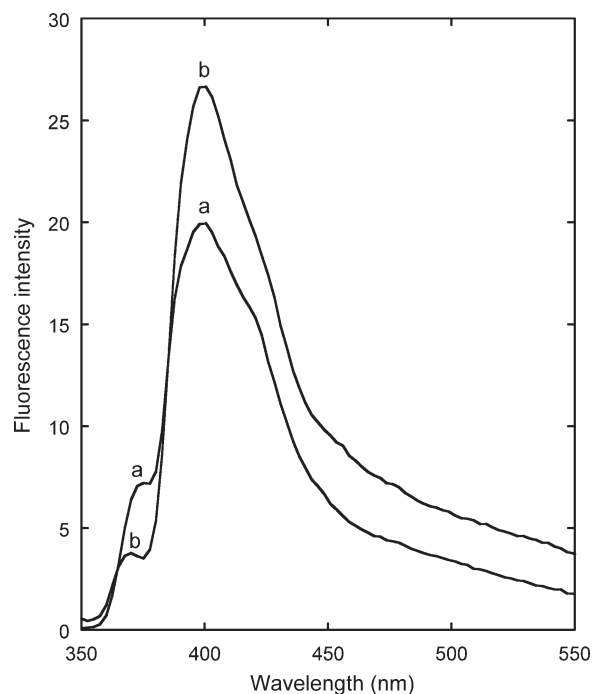
Figure 5. Fluorescence spectra of polystyrene (PSt) (curve a, 0.50 g dm^{-3}) and poly(cyclohexene oxide) (PCHO) (curve b, 0.50 g dm^{-3}) obtained following irradiation ($\lambda > 340$ nm) of styrene (St) and cyclohexene oxide (CHO), respectively, in the presence of 0.2 mol % **1a** at 60°C in nitrogen-saturated chloroform at room temperature. The excitation wavelength was 283 nm.
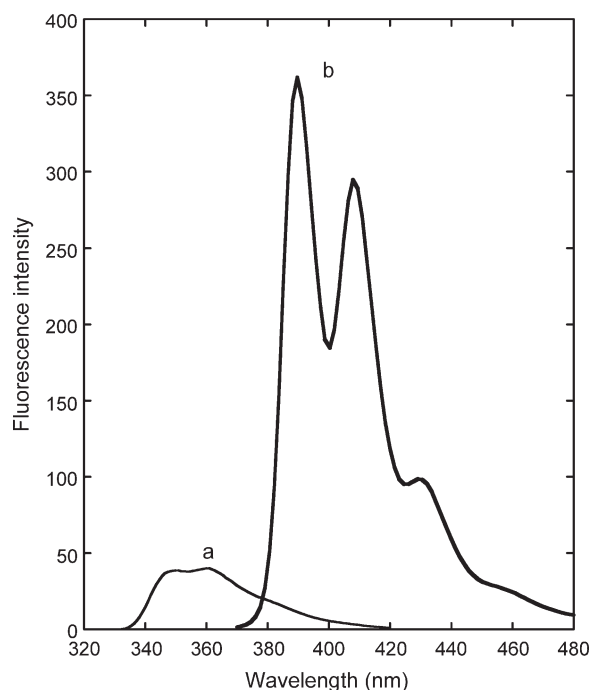
Figure 6. Fluorescence spectra of 2-methoxy-1-methoxymethylnaphthalene (curve a, 1.0×10^{-4} mol dm^{-3}) and 1-hydroxypyrene (curve b, 1.0×10^{-4} mol dm^{-3}) in nitrogen-saturated chloroform at room temperature. The excitation wavelength was 283 nm.

mixture (mole ratio = 1 : 1) in the presence of 0.2 mol % **1a** was irradiated for 12 h at 60°C and a polymer with $M_n = 4500$ and $M_w/M_n = 2.2$ (M_w = mass average molecular weight) was obtained in 5.2% yield. The ^{1}H NMR spectral analysis of the polymer showing a unimodal GPC elution curve revealed that the polymer contained St and CHO units in a 4 : 1 composition ratio, and this ratio was not influenced by repeated reprecipitation from aqueous methanol and hexane–methanol as expected.

CONCLUSIONS

In this study, we demonstrated that the photoinitiator, methoxynaphthalen-1-ylmethyloxypyrene, underwent rapid photodecomposition to afford an arylmethyl carbocation/pyrenyloxy anion pair preferentially over an arylmethyloxy radical/pyrenyl radical pair, even in a highly nonpolar St monomer. The significantly increased reactivity of the pyrene-photoinitiator-derived ion pair in this monomer was assumed to be responsible for

the predominant cationic polymerization of St. In addition to inducing the cationic polymerization of both St and CHO, the novel photoinitiator enabled the copolymerization of these two monomers.

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