1-(Arylmethyloxy)-9,10-anthraquinones: Photoinitiators for Radical and Cationic Polymerizations

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An investigation was undertaken to gain understanding of the type of bond cleavage (heterolysis *versus* homolysis) of 1-(methoxy-substituted arylmethyloxy)-9,10-anthraquinones (**1**) as bichromophoric photoinitiators of styrene (St) and cyclohexene oxide (CHO) polymerization to aid development of a novel and efficient hybrid photoinitiator. Results indicated that the 4-methoxynaphthalen-1-ylmethyl-substituted photoinitiator **1** containing no halogen or metal induces radical and cationic polymerization reactions of St and CHO, respectively, to give the corresponding polymers in reasonable yields. This initiator also accomplished hybrid photopolymerization of an equimolar mixture of St and CHO, although the ability to initiate polymerization was reduced. Analysis of the photoproducts derived from specific initiators as well as of the polymer end groups substantiated that the arylmethyloxyl radical and arylmethyl carbocation are major reactive species initiating the polymerization of St and CHO, respectively. In addition, the charge-separated state characteristic of the 9,10-anthraquinon-1-yloxy chromophore in the singlet excited state played a pivotal role in the heterolytic bond-cleavage in the latter monomer.

KEY WORDS: Initiator / Photochemistry / Cationic Polymerization / Radical Polymerization / Substituent Effect /

Various types of functional initiators have been developed for use in photochemistry.[1] Recent research has focused on novel photoinitiators that promote the initiation of both radical and cationic polymerizations,[2–8] because a combination of these two types of polymerizations could produce a hybrid polymer composed of radical- and cation-derived polymer units. For example, interpenetrating network polymers[9–11] that combine the properties of these two polymer units present an attractive research subject due to potential practical applications.

While some salt-type photoinitiators can initiate both cationic and radical polymerizations,[2–5,8,12,13] they have limited industrial application because of problems such as low solubility in monomers and the need for metal- or halogen-containing inorganic initiators. To overcome these problems, nonsalt-type photoinitiators have been developed, but they induce only minor hybrid polymerization.[6,7,14] A systematic study on the photoreactivity of *O*-substituted anthracene-9-methanol derivatives in methanol revealed that an intramolecular charge transfer interaction in their singlet excited states assists heterolytic CH_2–O bond cleavage to generate ion pairs along with radical pairs.[15] Therefore, these derivatives are good candidates for a novel hybrid-type photoinitiator containing no halogen or metal. While *O*-acyl anthracene-9-methanol functioned as a photoinitiator for the radical polymerization of styrene (St), the cationic photopolymerization of cyclohexene oxide (CHO) was induced only to a minor extent.[14] This finding suggests that the much lower polarity of CHO compared with that of methanol results in inefficient heterolytic bond cleavage in the singlet excited state.

Therefore, an investigation was undertaken to develop a hybrid-type photoinitiator that would undergo much more efficient heterolysis in CHO. To accomplish this, 2-arylmethyloxy-6-cyanonaphthalenes were synthesized followed by analysis of the product distribution obtained by the photolysis of these cyanonaphthalene derivatives in toluene and 1,2-dimethoxyethane, which were employed instead of St and CHO, respectively, as monomers.[16] A dramatic increase occurred in the acidity of the naphthol chromophore in the singlet excited state that accelerated the heterolytic CH_2–O bond cleavage reaction.[17] Product analysis revealed that the cyanonaphthalene derivative undergoes both heterolytic and homolytic bond cleavage reactions in 1,2-dimethoxyethane, while the latter reaction proceeds exclusively in toluene. However, the ability to initiate cationic photopolymerization of CHO remained low due to weak absorption of the cyano-substituted naphthol chromophore in the long wavelength region ($\lambda > 320\,nm$). To improve the previous initiator design, the oxyanthracene chromophore (showing strong absorption in the $\lambda > 320\,nm$ region) was introduced instead of the oxynaphthalene, resulting in a dramatic increase in the yields of poly(styrene) (PSt) and poly(cyclohexene oxide) (PCHO).[18] Thus, it is likely that introduction of the oxyaryl group with intense absorption in the visible region as a chromophore for a hybrid photoinitiator enables radical and cationic polymerizations to proceed more efficiently in the presence of a reduced amount of initiator. To develop such a photoinitiator, 1-(methoxy-substituted arylmethyloxy)-9,10-anthraquinones (**1a–d**, Scheme 1) were synthesized followed by an examination of their photoreactivity in toluene and 1,2-dimethoxyethane and their ability to initiate photopolymerization of St and CHO.

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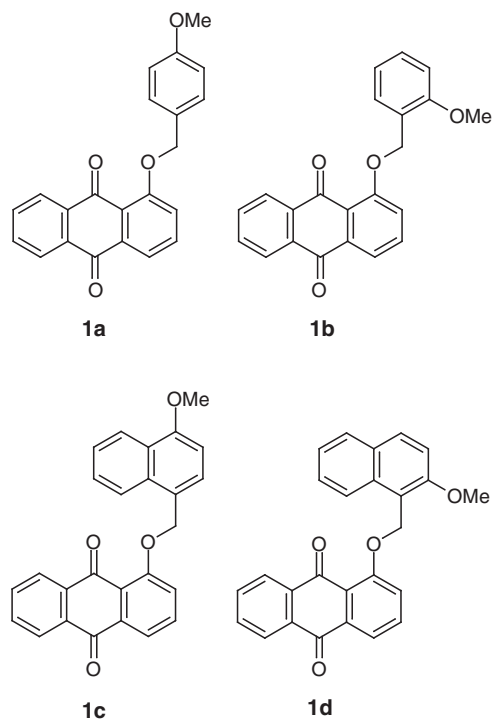
Scheme 1.

EXPERIMENTAL

Materials

1-(Methoxy-substituted arylmethyloxy)-9,10-anthraquinone derivatives (**1a–d**) were prepared according to the following procedures. Sodium hydride (60% purity) was slowly added to a DMF solution of 1-hydroxy-9,10-anthraquinone with stirring followed by drop-wise addition of 4-methoxybenzyl chloride, 2-methoxybenzyl chloride, 1-chloromethyl-4-methoxynaphthalene, or 1-chloromethyl-2-methoxynaphthalene. After the resulting reaction mixture was heated at 80 °C for 6 h, it was poured into ice water and the crystalline solid that precipitated was extracted with ethyl acetate. The ethyl acetate solution was washed with water several times and dried over anhydrous $MgSO_4$. The residual solid obtained by removing the solvent under reduced pressure was recrystallized from ethyl acetate to afford analytical-grade **1a–d** in 78–93% yields. The physical and spectroscopic data of **1a–d** are as follows.

1-(4-Methoxybenzyloxy)-9,10-anthraquinone (**1a**), mp 186.0–186.5 °C; IR (KBr, cm^{-1}): 1672, 1260; ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.83 (3H, s), 5.28 (2H, s), 6.96 (2H, d, $J = 8.6$ Hz), 7.38 (1H, d, $J = 8.6$ Hz), 7.53 (2H, d, $J = 8.6$ Hz), 7.67 (1H, dd, $J = 7.4$, 8.6 Hz), 7.74 (1H, dd, $J = 7.4$, 7.4 Hz), 7.78 (1H, dd, $J = 7.4$, 7.4 Hz), 7.97 (1H, d, $J = 7.4$ Hz), 8.24 (1H, d, $J = 7.4$ Hz), 8.30 (1H, d, $J = 7.4$ Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 55.7, 71.0, 114.1 (2C), 120.0, 120.1, 122.1, 126.5, 127.2, 128.2, 128.5 (2C), 132.5, 133.2, 134.2, 134.8, 135.0, 135.7, 159.3, 159.4, 182.2, 183.5. (Found: C, 76.64; H, 4.74%. Calcd for $C_{22}H_{16}O_4$: C, 76.73; H, 4.68%).

1-(2-Methoxybenzyloxy)-9,10-anthraquinone (**1b**), mp 191.0–191.5 °C; IR (KBr, cm^{-1}): 1672, 1265; ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.90 (3H, s), 5.38 (2H, s), 6.91 (1H, d, $J = 8.0$ Hz), 7.08 (1H, dd, $J = 7.4$, 8.6 Hz), 7.31 (1H, dd, $J = 7.4$, 8.6 Hz), 7.41 (1H, d, $J = 8.6$ Hz), 7.68 (1H, dd, $J = 7.4$, 7.4 Hz), 7.74 (1H, dd, $J = 7.4$, 7.4 Hz), 7.79 (1H, dd, $J = 7.4$, 8.0 Hz), 7.91 (1H, d, $J = 7.4$ Hz), 7.96 (1H, d, $J = 7.4$ Hz), 8.23 (1H, d, $J = 7.4$ Hz), 8.31 (1H, d, $J = 8.0$ Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 54.8, 65.8, 109.4, 119.2, 119.4, 120.6, 124.2, 126.1, 126.8, 127.4, 128.2, 128.5, 132.0, 132.6, 133.7, 134.4, 134.6, 135.2, 155.6, 159.0, 181.8, 183.1. (Found: C, 76.85; H, 4.63%. Calcd for $C_{22}H_{16}O_4$: C, 76.73; H, 4.68%).

1-(4-Methoxynaphthalen-1-ylmethyloxy)-9,10-anthraquinone (**1c**), mp 178.5–179.0 °C; IR (KBr, cm^{-1}): 1666, 1266; ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.01 (3H, s), 5.70 (2H, s), 6.84 (1H, d, $J = 8.0$ Hz), 7.26 (1H, d, $J = 8.0$ Hz), 7.51 (1H, dd, $J = 6.9$, 8.0 Hz), 7.59 (1H, dd, $J = 6.9$, 8.0 Hz), 7.67 (1H, dd, $J = 7.4$, 8.6 Hz), 7.71–7.79 (3H, m), 7.97 (1H, d, $J = 7.4$ Hz), 8.12 (1H, d, $J = 8.6$ Hz), 8.23 (1H, d, $J = 7.4$ Hz), 8.27 (1H, d, $J = 8.0$ Hz), 8.33 (1H, d, $J = 8.0$ Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 55.5, 69.9, 103.2, 120.2, 120.4, 122.7, 123.2, 123.4, 125.3, 125.9, 126.6 (2C), 127.0, 127.3, 129.0, 131.9, 132.5, 133.1, 134.2, 134.7, 135.1, 135.8, 155.9, 159.4, 182.2, 183.5. (Found: C, 79.04; H, 4.64%. Calcd for $C_{26}H_{18}O_4$: C, 79.17; H, 4.60%).

1-(2-Methoxynaphthalen-1-ylmethyloxy)-9,10-anthraquinone (**1d**), mp 199.5–200.0 °C; IR (KBr, cm^{-1}): 1670, 1266; ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.03 (3H, s), 5.87 (2H, s), 7.28 (1H, d, $J = 9.2$ Hz), 7.35 (1H, dd, $J = 6.9$, 8.0 Hz), 7.56 (1H, dd, $J = 6.9$, 8.0 Hz), 7.61 (1H, dd, $J = 7.4$, 8.6 Hz), 7.66–7.71 (2H, m), 7.73–7.77 (2H, m), 7.85 (1H, d, $J = 9.2$ Hz), 7.89 (1H, d, $J = 8.0$ Hz), 8.19 (1H, d, $J = 8.0$ Hz), 8.24 (1H, d, $J = 7.4$ Hz), 8.48 (1H, d, $J = 8.6$ Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 56.7, 62.7, 112.9, 116.3, 119.9, 121.0, 124.0, 124.5, 125.3, 126.5, 127.2, 127.3, 128.2 (2C), 129.0, 129.2, 131.3, 133.0, 133.7, 134.1, 134.6, 135.7, 155.2, 159.4, 182.1, 183.7. (Found: C, 79.20; H, 4.66%. Calcd for $C_{26}H_{18}O_4$: C, 79.17; H, 4.60%).

The St and CHO monomers were purified by vacuum distillation before use. All other chemicals were obtained from commercial sources and were of the highest grade available.

Measurements

UV absorption spectral changes of **1a–d** (2.0×10^{-4} mol dm^{-3}) were obtained at room temperature in nitrogen-saturated toluene or 1,2-dimethoxyethane (25 mL) by irradiation at wavelengths longer than 340 nm (Corning 0-52 and Toshiba IRA-25S glass filters) from a 500 W high-pressure Hg lamp. Irradiation intensity was 170 mW cm^{-2}.

For analysis of photoproducts derived from **1a–d** (1.0×10^{-3} mol dm^{-3}), nitrogen-saturated toluene or 1,2-dimethoxyethane solutions (25 mL) in Pyrex vessels were irradiated at wavelengths longer than 340 nm (Corning 0-52 and Toshiba IRA-25S glass filters) from a 500 W high-pressure Hg lamp. The irradiated solution was subjected to HPLC analysis

[mobile phase, MeCN-H$_2$O (60:40 v/v); detection wavelength, 240 nm]. Structures of the photoproducts were determined by comparing HPLC data (retention times and shapes of HPLC signals) of products with those of commercially available authentic samples.

A prescribed amount of **1** was dissolved in St or CHO in a glass tube and the resulting solution was degassed through three freeze-pump-thaw cycles. The sealed glass tube, maintained at a given temperature, was irradiated at wavelengths longer than 340 nm (Corning 0-52 and Toshiba IRA-25S glass filters) from a 500 W high-pressure Hg lamp. Irradiation intensity was 170 mW cm^{-2}. The reaction mixture, irradiated for a given period of time, was poured into aqueous methanol, and the precipitated polymer was filtered and dried *in vacuo* at 40 °C. The polymer yield was estimated gravimetrically using an average of more than two measurements.

IR spectra were taken with a Shimadzu Prestige-21 IR spectrophotometer. The ^{1}H and ^{13}C NMR spectra were recorded on a JEOL JNM-A500 spectrometer at 500 and 125 MHz, respectively, in CDCl$_3$ with tetramethylsilane as an internal standard. Elemental analysis was performed on a Perkin-Elmer 2400 series II CHNS/O analyzer. Irradiation intensity was measured with a UV-M03 intensity meter (ORC, Tokyo, Japan) equipped with a UV-SN35-M10 photodetector. UV absorption and fluorescence spectra were obtained with a Hitachi U-3300 spectrophotometer and a Hitachi F-4500 spectrofluorimeter, respectively. HPLC analysis was conducted on a Shimadzu LC-10AT$_{VP}$ HPLC system equipped with a 4.6 × 250-mm ODS (Zorbax) column and a Shimadzu SPD-10A$_{VP}$ UV detector. The molecular weight distribution of a polymer was estimated by gel permeation chromatography (GPC) with the use of a Tosoh model HLC-8020 GPC unit equipped with a refractive index detector using two TSK-gel columns (Multipore H$_{XL}$-M × 2) and tetrahydrofuran as an eluent. A calibration curve for molecular weights in the range of 500–1.11 × 10^6 was made under the same conditions with standard polystyrene.

RESULTS AND DISCUSSION

Photoreactivity of 1a–d

To determine the photoreactivity of the 9,10-anthraquinonyl-substituted initiators, toluene and 1,2-dimethoxyethane solutions of **1a–d** were irradiated under a nitrogen atmosphere at wavelengths longer than 340 nm at room temperature. Typical results are shown in Figure 1. Upon irradiation in toluene, the UV absorption of the starting **1c** at 375 nm decreased with appearance of an absorption band at 320 nm. Similar spectral changes were observed for the other derivatives, although some differences were found in rates at which the absorption bands of **1a–d** disappeared. Because the intense absorption observed near 320 nm is similar to that of 9,10-anthraquinone, the anthraquinone-type photoinitiator **1** is considered to preferentially undergo homolytic Ar–OCH$_2$ bond cleavage in its excited state. In contrast, irradiation of **1c** in nitrogen-saturated 1,2-dimethoxyethane under the same conditions as those for
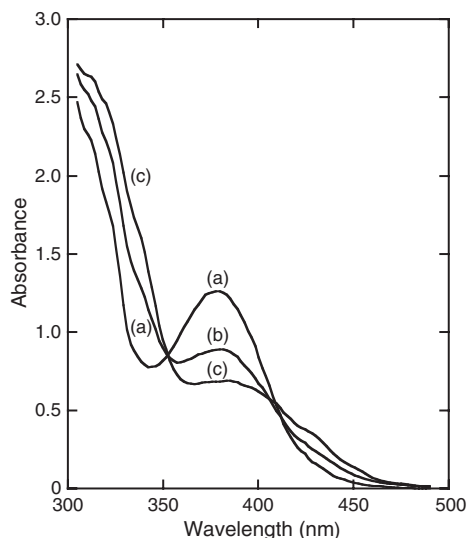

Figure 1. UV absorption spectral changes caused by irradiation ($\lambda >$ 340 nm) of **1c** (2.0 × 10^{-4} mol dm^{-3}) in nitrogen-saturated toluene at room temperature. Irradiation times are 0 (curve a), 5 min (curve b), and 10 min (curve c).
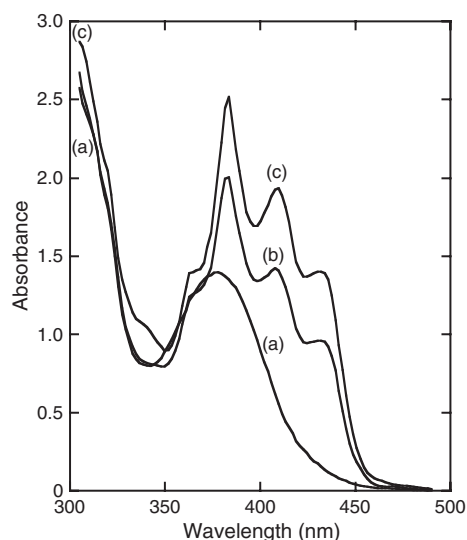

Figure 2. UV absorption spectral changes caused by irradiation ($\lambda >$ 340 nm) of **1c** (2.0 × 10^{-4} mol dm^{-3}) in nitrogen-saturated 1,2-dimethoxyethane at room temperature. Irradiation times are 0 (curve a), 3 min (curve b), and 10 min (curve c).

1c in toluene caused UV absorption spectral changes different from those shown in Figure 1 (Figure 2). Upon photolysis in 1,2-dimethoxyethane, an intense absorption band with structures appeared at 380 nm, but prolonged irradiation slowly decreased the absorption of the 380 nm band. Similar absorption spectral changes were obtained for the other derivatives in 1,2-dimethoxyethane. In addition, a resemblance existed between the UV absorption bands displayed by the **1**-derived photoproducts and those of 1-hydroxy-9,10-anthraquinone in the wavelength region of 350–450 nm. Thus, it is likely that in 1,2-dimethoxyethane photoinitiator **1** undergoes partial heterolytic ArO–CH$_2$ bond cleavage in its excited state.
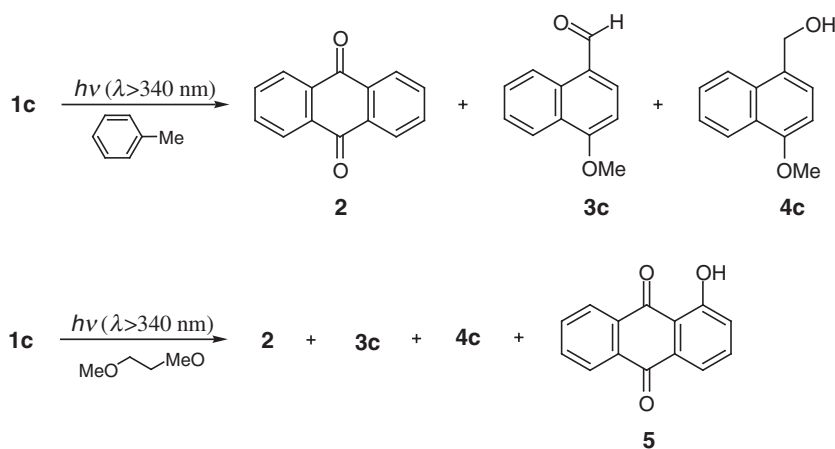
Scheme 2.

A previous study showed that photolysis of 1-(2-methoxy-naphthalen-1-ylmethyloxy)anthracene in 1,2-dimethoxyethane affords 1-hydroxyanthracene as the heterolytic ArO–CH$_2$ bond cleavage product, while only the homolytic Ar–OCH$_2$ bond cleavage products—anthracene, 1-formyl-2-methoxynaphthalene, and 1-hydroxymethyl-2-methoxynaphthalene—are detected upon irradiation in toluene.[18] Thus, product distribution analysis can provide a reliable criterion for the bond cleavage mode of this type of bichromophoric photoinitiator. Taking into account that no large difference in photoreactivity was observed among **1a–d** in any solvent, **1c** and **1d** were chosen as model initiators and the **1**-derived product distribution was examined by comparing HPLC data of the photoproducts with those of authentic samples. As shown in Scheme 2, irradiation of a nitrogen-saturated toluene solution of **1c** (1.0 × 10^{-3} mol dm^{-3}) at wavelengths longer than 340 nm gave 9,10-anthraquinone (**2**, 15.4% HPLC yield), 1-formyl-4-methoxynaphthalene (**3c**, 4.5%), and 1-hydroxymethyl-4-methoxynaphthalene (**4c**, 3.6%) at *ca.* 45% conversion. A similar product distribution was obtained when a nitrogen-saturated toluene solution of **1d** was irradiated under the same conditions: 9,10-anthraquinone (**2**, 12.6%), 1-formyl-2-methoxynaphthalene (**3d**, 3.8%), and 1-hydroxymethyl-2-methoxy-naphthalene (**4d**, 2.0%) were detected at *ca.* 45% conversion. Furthermore, negligible formation of 1-hydroxy-9,10-anthraquinone (**5**) occurred. These observations strongly suggest that homolysis of the Ar–OCH$_2$ bond takes place exclusively in the aprotic nonpolar solvent toluene. Homolytic cleavage of this bond should form 9,10-anthraquinon-1-yl and arylmethyloxyl radicals as precursors of **2**, **3c,d**, and **4c,d**. Hydrogen abstraction of these radicals from the solvent gives **2**, **4c**, and **4d**, while **3c** and **3d** must be derived (along with **2**) from hydrogen abstraction of the former radical from the latter one in a given solvent cage. In contrast, in addition to these products (**2**: 3.2% for **1c** and 2.9% for **1d**; **3c,d**: 7.9% for **1c** and 7.8% for **1d**; **4c,d**: 8.5% for **1c** and 8.3% for **1d**), **5** (12.5% for **1c** and 10.5% for **1d**) and **2**-derived byproducts were formed upon irradiation in nitrogen-saturated 1,2-dimethoxy-ethane (*ca.* 45% conversion) under the same conditions (Scheme 2). 1-Hydroxy-9,10-anthraquinone (**5**) and part of the hydroxymethyl-substituted methoxynaphthalenes (**4c,d**) arise from hydrolytic reaction of 9,10-anthraquinon-1-yloxy anion and arylmethyl carbocation in 1,2-dimethoxyethane contaminated with water. Thus, photodecomposition of **1** in this solvent must proceed *via* homolytic Ar–OCH$_2$ bond cleavage and heterolytic ArO–CH$_2$ bond cleavage modes. Product analysis indicated that 1-(arylmethyloxy)-9,10-anthra-quinone derivatives afford the arylmethyloxyl radical and arylmethyl carbocation through photolyses, allowing function as hybrid-type photoinitiators in the polymerization of St and CHO.

Photopolymerization with 1a–d

Tables I and II summarize the yields, number-average molecular weights (M_n), and polydispersities (M_w/M_n, M_w: weight-average molecular weights) of poly(styrene) (PSt) and poly(cyclohexene oxide) (PCHO) obtained by the bulk photopolymerization of St and CHO in the presence of **1a–d**. Control experiments demonstrated that irradiation of St and CHO without an initiator for 8 h at 60 °C produced the corresponding polymers in minor (5%) and negligible yields, respectively. In addition, the presence of 2,2,6,6-tetramethylpiperidinyl-1-oxy (0.2 mol %) completely inhibited polymerization of St but had no influence on CHO polymerization, confirming the requirement of a radical mechanism in the former polymerization.

Because polymer yield reflects the excited-state reactivity of a given initiator,[18] the yields of PSt obtained using different photoinitiators should not vary much based on the substituent effect on the photoreactivity of **1a–d**. The data given in Table I clearly show that PSt is obtained in similar yield from photopolymerization of St containing **1a**, **1b**, or **1c** (0.1 mol %), consistent with expectations. It is likely only a minor difference exists in the ability of arylmethyloxyl and related radicals (generated by the photolysis of **1**) to initiate radical polymerization. The data also show that number-average molecular weight (M_n) tends to increase with the yields of **1**-derived PSt. A previous report interpreted this tendency in terms of the photodissociation of the polymer end group(s)

Table I. Photopolymerization of St with **1a–d** as initiators

Initiator	Time (h)	Temperature (°C)	Yield (%)	$M_n \times 10^{-4}$	M_w/M_n
1a[a]	8	RT	16.1	1.9	1.9
	8	60	22.1	2.2	1.9
	12	60	41.7	4.3	1.6
1b[a]	8	RT	11.3	1.4	1.8
	8	60	22.4	1.9	1.9
	12	60	46.1	3.3	1.7
1c[a]	8	RT	17.5	2.3	2.2
	8	60	23.1	2.7	2.3
	12	60	47.7	4.1	2.1
1d[b]	8	RT	11.8	2.1	1.8
	8	60	26.0	2.7	2.0
	12	60	55.8	5.5	1.8

[a][Initiator]/[St] = 0.1 mol % and the initiator was irradiated with $\lambda > 340$ nm.
[b][Initiator]/[St] = 0.05 mol % and the initiator was irradiated with $\lambda > 340$ nm.

Table II. Photopolymerization of CHO with **1a–d** as initiators

Initiator	Time (h)	Temperature (°C)	Yield (%)	$M_n \times 10^{-4}$	M_w/M_n
1a[a]	8	RT	3.1	1.3	1.7
	8	60	19.0	1.0	1.6
	16	60	24.7	1.3	1.6
1b[a]	8	RT	1.3	1.1	1.7
	8	60	6.4	1.5	1.7
	16	60	9.4	0.7	1.6
1c[a]	8	RT	4.9	0.8	1.7
	8	60	29.4	2.0	1.6
	16	60	40.0	0.8	1.6
1d[b]	8	RT	5.8	1.4	1.6
	8	60	8.1	1.3	1.6
	16	60	19.3	0.6	1.6

[a][Initiator]/[CHO] = 0.1 mol % and the initiator was irradiated with $\lambda > 340$ nm.
[b][Initiator]/[CHO] = 0.05 mol % and the initiator was irradiated with $\lambda > 340$ nm.

and subsequent repolymerization by propagating radical(s) formed.[18] Interestingly, PSt could be isolated in a comparable or higher yield even in the presence of 0.05 mol % **1d**. Additionally, the 8 h irradiation of St containing 0.05 mol % **1c** at 60 °C enhanced polymer yield by 10% (23.1 to 33.2%).

As shown in Table II, PCHO was obtained in a reasonable yield when CHO containing **1c** was irradiated for 16 h at 60 °C, and its yield was greater for **1c** and **1a** than for **1d** and **1b**. The latter observation suggests that photoinitiator **1**, bearing substituents that exert greater steric effects on photoreactivity, has a lower ability to initiate cationic polymerization of CHO. In addition, methoxynaphthyl-substituted photoinitiators **1c** and **1d** displayed much greater abilities to initiate cationic polymerization of CHO as compared to the corresponding methoxyphenyl-substituted photoinitiators **1a** and **1b**. Since the anthraquinone chromophore may almost completely absorb the incident light of wavelengths longer than 340 nm, the greater initiation abilities of **1c** and **1d** can be explained by the increased stability of methoxy-substituted 1-naphthylmethyl carbocations compared to the corresponding benzyl carbocations. The results of these analyses of substituent effects on initiation ability of **1** are consistent with the involvement of the methoxy-substituted arylmethyl carbocation in the initiation step of the photopolymerization. In contrast, a relation between the magnitude of M_n for PCHO and the yield of PCHO suggests a contribution of chain transfer reaction to the cationic polymerization of CHO. However, if the GPC elution curve for this polymer is unimodal, estimating the extent of the contribution of chain transfer reaction induced by an adduct formed between the **1**-derived arylmethyl carbocation and CHO monomer is very difficult.

As described above, **1c** gave reasonable results in all polymerization modes tested and is a candidate for a new hybrid photoinitiator (containing no halogen or metal) that can function at fairly low concentrations. For this reason **1c** was chosen as the hybrid photoinitiator and an equimolar mixture of St and CHO was chosen as a model monomer; and the ability

of **1c** to initiate the photopolymerization of the model monomer mixture was examined. The St-CHO mixture was irradiated at wavelengths longer than 340 nm for 12 h at 60 °C in the presence of 0.1 mol % **1c**. The usual workup afforded a polymer in a 16.3% yield; its ^{1}H NMR spectrum indicated this polymer contained the St and CHO units in a mole ratio of 5:1, respectively. If the polymer formed is a mixture of PSt and PCHO, with PSt as the major component, the reprecipitation of the polymer mixture from methanol-hexane is expected to increase the relative amount of CHO units. In contrast, if this mixture includes a copolymer composed of St and CHO units as the chief component, the reprecipitation procedure is expected to exert only a small effect on the relative composition of the units. Thus, the great increase in relative composition of the CHO units upon repeated reprecipitation confirms that the major product obtained is a mixture of PSt and PCHO and also the copolymerization of St and CHO contributes to only a minor extent. Unfortunately, in addition to the pronounced overlap between GPC elution curves for PSt and PCHO, the preferential formation of the PSt polymer made it very difficult to determine the M_n and M_w/M_n values of each polymer. For this reason these values were estimated to be 1.4×10^4 (M_n) and 2.2 (M_w/M_n) using the single GPC curve. A decrease in solvent polarity should enhance the contribution of the homolytic bond cleavage process during photolysis of **1** and, hence, is responsible for the preferential formation of PSt. In contrast, it is likely that CHO is a good hydrogen donor for the initiating radical during polymerization of St, the C=C double bonds of which also possess some reactivity toward the **1c**-derived initiating cation. Thus, the mixture of St and CHO may lower the reactivity of the two initiating radical and cation species to cause a decrease in polymer yield.

To analyze the polymer end groups, ^{1}H NMR and fluorescence spectra were obtained for PSt and PCHO produced by photopolymerization with **1c**. Although the relative intensities of the proton signals of any polymer end groups were too weak to be detected by NMR, the fluorescence spectra allowed the
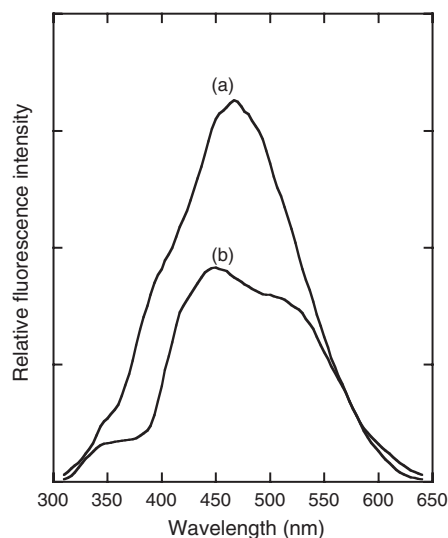
Figure 3. Fluorescence spectra of PSt (curve a, 0.50 g dm⁻³) and PCHO (curve b, 0.50 g dm⁻³), obtained by irradiation ($\lambda > 340$ nm) of St and CHO, respectively, in the presence of 0.1 mol % **1c** at 60 °C in nitrogen-saturated chloroform at room temperature. Excitation wavelength was 283 nm.

analysis of the structure of the end groups. As shown in Figure 3, a broad fluorescence band having shoulders near 350 and 400 nm was observed at about 470 nm upon excitation of **1c**-derived PSt, while PCHO gave the 450 nm emission band with shoulders near 350 nm and 510 nm. Taking into account the possible existence of 4-methoxynaphthalen-1-ylmethyloxy and 9,10-anthraquinon-1-yl chromophores (for PSt) and 4-methoxynaphthalen-1-ylmethyl and 9,10-anthraquinon-1-yloxy chromophores (for PCHO) at the polymer-chain ends, fluorescence spectra of **4c**, **2**, and **5** were obtained under the same conditions. The finding that **4c** produces emission bands at 360 nm, **2** at 465 nm, and **5** at 570 nm supports the conclusion that the emissions observed near 350 nm and 450 nm are due to the methoxynaphthylmethyl- and 9,10-anthraquinonyl-type chromophores, respectively. This suggests it is very likely that these two chromophores occupy some polymer ends, which is consistent with involvement of the arylmethyloxyl radical and arylmethyl carbocation in the polymerization of St and CHO, respectively. However, clarifying the structure of the end groups with fluorescence shoulders appearing near 400 nm (PSt) and 510 nm (PCHO) was difficult. The low material balance in photolysis of **1c** in toluene (<40%) and 1,2-dimethoxyethane (<40%) indicates the participation of reactive species other than the above-mentioned arylmethyl- and anthraquinonyl-type intermediates in the initiation and termination steps of the observed photopolymerization reactions.

CONCLUSIONS

A newly-designed 1-(4-methoxynaphthalen-1-ylmethyloxy)-9,10-anthraquinone photoinitiator (**1c**) successfully in-

duced both radical polymerization of St and cationic polymerization of CHO to afford the corresponding polymers in reasonable yields. Analyses of the concentration and substituent effects on the polymer yields confirmed that, while the initiators tested could initiate photopolymerizations even at fairly small quantities, the hybrid initiator **1c** produced the best results among the photoinitiators examined. In addition, **1c** induced hybrid photopolymerization of an equimolar mixture of St and CHO to yield PSt and PCHO in a mole ratio of 5:1, respectively. The participation of the arylmethyloxyl radical and arylmethyl carbocation species in the initiation steps of the photopolymerization reactions for St and CHO was supported by HPLC analysis of the product distribution derived from photolysis of **1** as well as fluorescence analysis of the polymer end groups.

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