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Bond-cleavage mode of *O*-acyl anthracene-9-methanol derivatives in the singlet excited state and their abilities to initiate radical and cationic photopolymerizations

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Abstract

Substituent effects on the bond-cleavage mode in the singlet excited state as well as on the initiation ability for photopolymerization were investigated on the title anthracenemethanol derivatives (**1**). Analysis of substituent effects on the excited-state reactivity and product distribution revealed that intramolecular electron transfer in **1** having the aroyl group is responsible for its excited-state deactivation while the heterolytic and selective CH_2–O bond cleavage is induced on forming a singlet exciplex with some charge-transfer character. It was suggested that substituted benzoate ion-bridged anthrylmethylcarbonium ion is a key intermediate in the photodecomposition process of aroyl-substituted derivatives. On the other hand, less electron-withdrawing acetyl-substituted derivative undergoes the heterolytic CH_2–O bond and homolytic CH_2O–C(=O) bond cleavages to form geminate anthrylmethyl carbonium-acetate ion pair and anthrylmethyloxyl-acetyl radical pair, respectively. An examination of the ability of **1** to initiate radical and cationic photopolymerizations allowed us to propose that *O*-anisoyl anthracene-9-methanol is a likely candidate for novel hybrid-type photoinitiator.
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Keywords: *O*-acyl anthracene-9-methanol derivatives; Bond-cleavage mode; Substituent effects; Photoinitiators; Photopolymerization

1. Introduction

Photochemistry has continued to contribute to the development of efficient and selective transformation of organic compounds into functional materials. Recently, photochemical control of homolytic versus heterolytic bond-cleavage modes has been the subject of extensive research efforts because of its potential application to developing hybrid-type photoinitiators enabling the simultaneous progress of radical and cationic polymerizations [1–9]. Through comprehensive mechanistic studies on the photolysis of arylmethyl esters in nucleophilic solvents, Pincock and his co-workers have shown that the dominant primary step is homolytic C–O bond cleavage from the singlet excited state and the subsequent electron transfer in a radical pair intermediate eventually gives an ion-derived product along with a radical-derived one [4–7]. In contrast, Zimmerman proposed based on the ab initio computation results regarding total energies of methoxy-substituted benzyl acetate-derived ion and radical pairs that the heterolytic and homolytic CH_2–O bond cleavages take place competitively and the former cleavage is preferred in the singlet excited state [10–12]. There are still many controversies concerning this bond-cleavage mode in the excited state.

On the other hand, there has been no study on the possibility of heterolytic bond cleavage induced by the formation of an intramolecular exciplex with some charge-transfer

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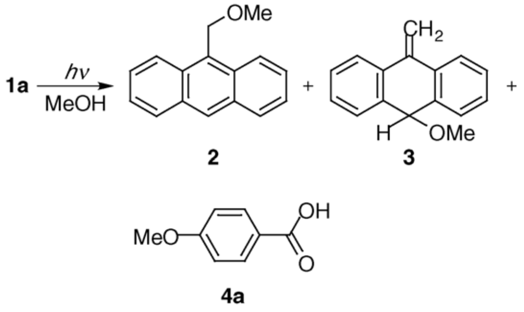
character. Taking into account this fact, we embarked on a systematic study toward the characterization of excited-state reactivities of bichromophoric hydroxamic acid derivatives. It was found that 1-benzyloxy-2-pyridone in the singlet excited state undergoes homolytic N–O bond cleavage exclusively giving benzaldehyde and 2-pyridone as major products along with a minor amount of benzyl alcohol [13]. Very recently, we succeeded in controlling two bond-cleavage modes in bichromophoric 1-(9-anthrylmethyloxy)-2-pyridone through the formation of a non-emissive intramolecular singlet exciplex [14]. An important finding in the previous study is that a strong charge-transfer interaction between the two chromophores in the singlet exciplex causes polarization of the CH_2–O bond, which is responsible for the heterolytic cleavage of this bond. In addition, the pyridone derivative examined was found to initiate radical photopolymerization of styrene but did not function as a photoinitiator for the cationic polymerization of oxetane [9]. The problem encountered is that no cationic species is generated in this non-polar monomer, owing to the exclusive homolysis of the N–O bond. Because the N–O bond has low bond-dissociation energy and is susceptible to homolytic cleavage in the singlet excited state [13], the replacement of the 2-pyridone-1-yl group in 1-(9-anthrylmethyloxy)-2-pyridone by the electron-withdrawing acyl group allows us to expect that the heterolysis of the CH_2–O bond occurs to some extent even in non-polar monomers. In order to clarify a major factor controlling homolytic versus heterolytic bond-cleavage modes and to estimate the ability with which radical and cationic photopolymerizations proceed, we synthesized *O*-acyl anthracene-9-methanol derivatives (**1a**–**g**) and investigated substituent effects on the bond-cleavage mode in protic polar solvents as well as on the photopolymerization efficiency of styrene (St) and 1,2-epoxycyclohexane (EpC) in the presence of **1**.

2. Results and discussion

2.1. Substituent and solvent viscosity effects on the photoreactivity and bond-cleavage mode

On irradiation of a nitrogen-saturated methanol solution of **1a** (2.5×10^{-4} mol dm^{-3}) with 366 nm light (from a 450 W high-pressure Hg lamp) at room temperature, there appeared three new high-performance liquid chromatography (HPLC) signals in addition to that of **1a**. The two of these three products were identified as 9-(methoxymethyl)anthracene (**2**) and 4-methoxybenzoic acid (**4a**) by comparing their HPLC behavior with that of the corresponding authentic samples. Since the unexpected product was observed, we attempted to isolate this product by HPLC over ODS and succeeded in obtaining 9-methoxy-10-methylene-9,10-dihydroanthracene (**3**), the stability of which was not so high (Scheme 1). Control experiment showed that **3** is not formed by the irradiation of **2** under the same conditions and, hence, is a primary photoproduct. In addition, HPLC signals attributable to anthracene-9-methanol and anthracene-9-carbaldehyde were not detected on the chromatogram. We previously found that the photolysis of 1-(9-anthrylmethyloxy)-2-pyridone in methanol gives the heterolytic CH_2–O bond-cleavage products: 1-hydroxy-2-pyridone and 9-(methoxymethyl)anthracene, along with 2-pyridone, anthracene-9-methanol and anthracene-9-carbaldehyde derived from the N–O bond homolysis [14]. This finding led us to conclude that 9-anthrylmethyl carbonium ion and 9-anthrylmethyloxyl radical intermediates are the precursors of heterolytic and homolytic bond-cleavage products, respectively. Therefore, the product distribution obtained substantiates the occurrence of exclusive heterolysis of the CH_2–O bond in excited-state **1a**.



Scheme 1. Product distribution obtained by the photolysis of **1a** in methanol.

In order to discuss substituent effects on the excited-state reactivity of **1**, quantum yields for appearance of **2**–**4** were repeatedly determined at less than 15% conversions of **1** using a potassium tris(oxalato)ferrate(III) actinometer [15] and collected in Table 1. The finding that $\Phi_{\mathbf{4}}$ is nearly equal to the sum of $\Phi_{\mathbf{2}}$ and $\Phi_{\mathbf{3}}$ substantiates negligible decomposition of the products (**2** and **3**) during irradiation. Because the sum of $\Phi_{\mathbf{2}}$ and $\Phi_{\mathbf{3}}$ reflects the excited-state reactivity of **1**, analysis of substituent effects on the quantum yields demonstrates that the introduction of a substituent (such as CF_3 or CN group) having the great ability to attract electron into the benzoyl benzene ring substantially lowers the excited-state reactivity. This observation suggests the involvement of electron-transfer interaction between the anthryl and aroyl chromophores as one of the deactivation pathways of excited-state **1**, as exemplified by the intramolecular charge-transfer deactivation of excited-state

Table 1
Substituent effects on the quantum yields (Φ) for appearance of **2**–**4a**–**f** in nitrogen-saturated methanol at room temperature[a]

Compound	$\Phi_{\mathbf{2}}$	$\Phi_{\mathbf{3}}$	$\Phi_{\mathbf{4a–f}}$
1a	0.008	0.006	0.013
1b	0.008	0.006	0.014
1c	0.008	0.007	0.016
1d	0.009	0.007	0.016
1e	0.001	0.001	0.002
1f	<0.001	<0.001	<0.001

[a] Experimental errors inherent in the quantum-yield determination are of the order of 5–10%.

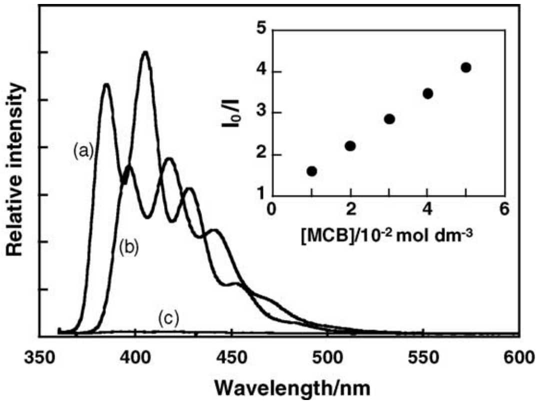


Fig. 1. Fluorescence spectra of anthracene (curve a, 1.0×10^{-5} mol dm^{-3}), **1a** (curve b, 1.0×10^{-5} mol dm^{-3}) and **1f** (curve c, 1.0×10^{-5} mol dm^{-3}) in nitrogen-saturated methanol at room temperature. Inset: Stern–Volmer plot for the fluorescence quenching of anthracene (1.0×10^{-4} mol dm^{-3}) by MCB in nitrogen-saturated methanol at room temperature. Both excitation wavelengths are 366 nm.

ω-(9-anthryl)acetophenone [16] and 1-naphthylmethyl benzoate derivatives in polar solvents [17]. As typically shown in Fig. 1, the anthracene fluorescence was highly quenched in **1f** and moderately in **1a**. Additionally, the intermolecular fluorescence quenching of anthracene (singlet excitation energy, $E_S = 319$ kJ mol^{-1}; oxidation potential, $E_{ox} = 1.16$ V versus SCE [18]; fluorescence lifetime, $\tau_s = 4.2$ ns [14]) by methyl 4-cyanobenzoate (MCB; $E_S > 400$ kJ mol^{-1}; reduction potential, $E_{red} \approx -1.9$ V versus SCE [19]) was observed (inset of Fig. 1). From the slope (63 dm^3 mol^{-1}) of the linear Stern–Volmer plot, the florescence-quenching rate constant was estimated to be 1.5×10^{10} dm^3 mol^{-1} s^{-1} at room temperature. These quenching results, therefore, provide evidence in support of the above suggestion. Based on the simplified Weller equation: ΔG (kJ mol^{-1}) = $96.5(E_{ox} - E_{red}) - E_S$ [20,21], we estimated approximate free energy changes (ΔG) for intramolecular electron transfer from the anthracene to benzoyl (**1c**, E_{red} for methyl benzoate = −2.3 V versus SCE [19]) and 4-cyanobenzoyl moieties (**1f**) as 15 and −24 kJ mol^{-1}, respectively. This thermodynamic consideration allows us to propose that emission quenching in **1e** and **1f** takes place predominantly by an electron-transfer mechanism giving the ion radical pair (**I**) that deactivates excited-state **1**, whereas the quenching in **1a**–**d** proceeds through the non-emissive singlet exciplex (**II**) which may be in equilibrium with **I**, as shown in Fig. 2. As previously suggested [14], in this exciplex there must be a charge-transfer interaction between the 2p orbital of the ester carbonyl carbon and the 2p orbital of the anthracene-ring carbon at the 9-position to cause polarization of the CH_2–O bond.

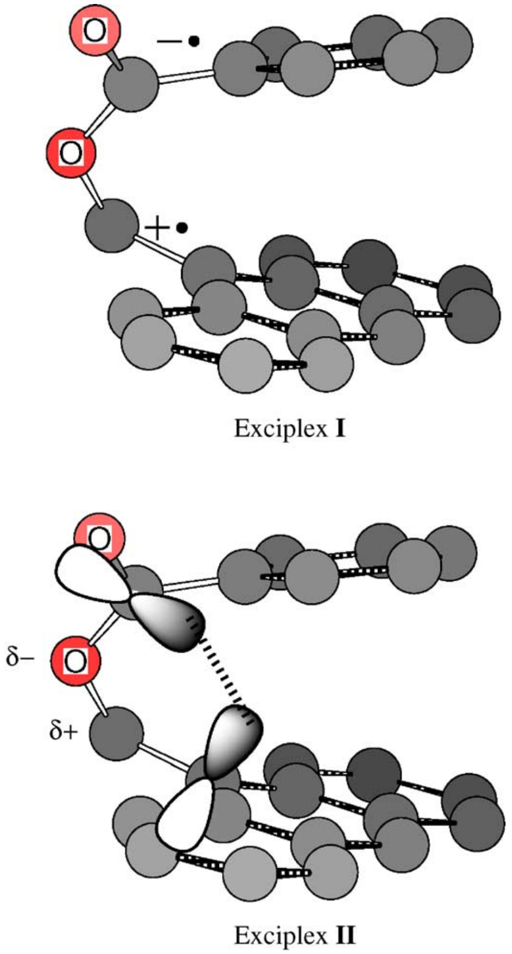
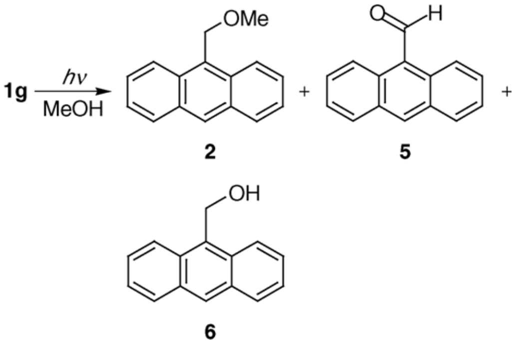


Fig. 2. Schematic illustration for the singlet exciplex intermediates **I** and **II** derived from **1c**.

Interestingly, when a nitrogen-saturated methanol solution of *O*-acetyl anthracene-9-methanol (**1 g**, 2.5×10^{-4} mol dm^{-3}) was irradiated with 366 nm light, we were able to detect HPLC signals attributable to anthracene-9-carbaldehyde (**5**) and anthracene-9-methanol (**6**) along with that of **2** but no signal of **3** was observed on the chromatogram (Scheme 2). The appearance of **5** and **6** indicates the existence of the 9-anthrylmethyloxyl radical as their precursor, thus confirming that homolytic CH_2O–C(=O) bond cleavage occurs in competition with the heterolysis of the CH_2–O bond in the excited state [no attempts to detect acetate ion- and acetyl radical-derived products were made]. In addition, a comparison of Φ_2 (0.005) with Φ_5 (0.002) and Φ_6 (0.001) shows that the latter bond cleavage



Scheme 2. Product distribution obtained by the photolysis of **1g** in methanol.

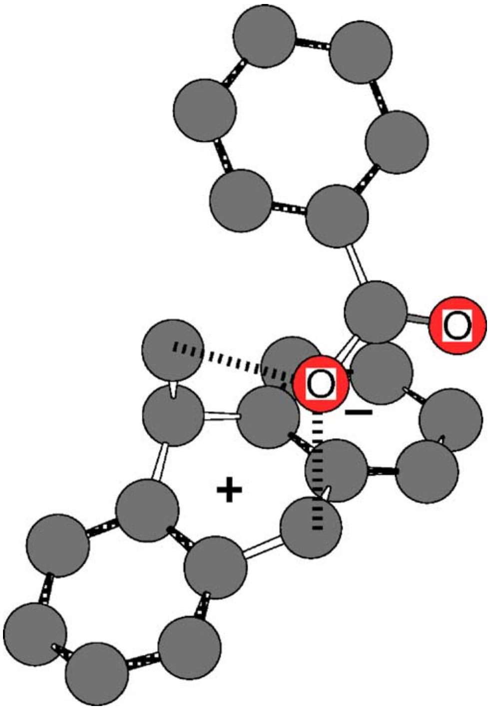
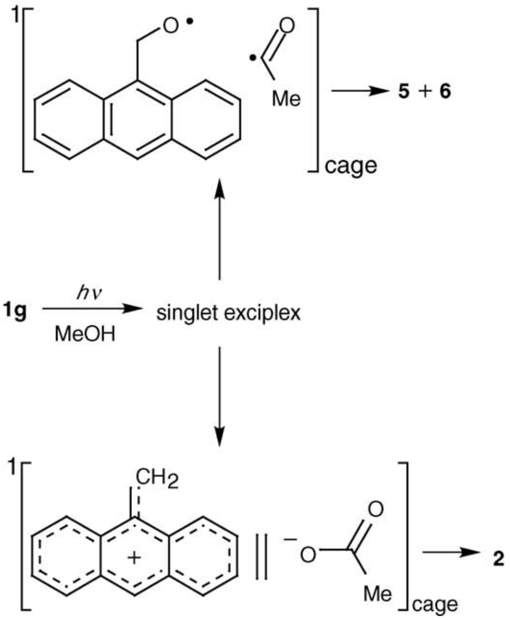


Fig. 3. Schematic illustration for the benzoate ion-bridged 9-anthrylmethyl carbonium ion intermediate **III**.

occurs in preference to the former. As compared with the acetyl group, the benzoyl group has the greater ability to stabilize the negative charge developing on the ester oxygen in the singlet exciplex (**II**, Fig. 2). It is, thus, reasonable to conclude that the bond cleavage in excited-state **1a**–**f** takes place exclusively from **II** to form the substituted benzoate ion-bridged 9-anthrylmethylcarbonium ion intermediate (**III**, Fig. 3). The competitive nucleophilic attack of a solvent molecule on the anthrylmethyl carbon and the anthracene-ring carbon at the 10-position eventually produces **2** and **3** in comparable quantum yields. On the other hand, a much weaker charge-transfer-type interaction in the **1g**-derived exciplex renders the generation of **III** difficult and may lead to geminate ion and radical pairs (Scheme 3).

Based on the previous findings [13,14], we predict that **2** and **5** are derived from the ‘in-cage’ reactions of anthrylmethyl carbonium ion and anthrylmethyloxyl radical, respectively, whereas **6** is obtained by the ‘out-of-cage’ reaction of this radical. Solvent viscosity effect on a given reaction has been a useful tool for differentiating between the ‘in-cage’ and ‘out-of-cage’ products [22,23]. In our study solvent viscosity was adjusted by using methanol and glycerol of comparable polarity [24] and its effect on the quantum yields for the photolysis of **1a** and **1g** was examined (Table 2). The finding that solvent viscosity exerts its effect on Φ_6 but not on $\Phi_{2\text{–}5}$ establishes that **2**–**5** and **6** arise from the ‘in-cage’ and ‘out-of-cage’ reactions, respectively, being consistent with our prediction. Therefore, a solvent-separated ion pair intermediate should be involved as the precursor of **1g**-derived 9-(methoxymethyl)anthracene (**2**) (Scheme 3).



Scheme 3. Reaction mechanism proposed for the photolysis of **1g** in methanol.

2.2. Substituent effects on the ability to initiate radical and cationic photopolymerizations

Any photoinitiator that generates both reactive radical and cation may be used for the two polymerization modes: radical and cationic polymerizations. As demonstrated in the preceding section, on irradiation at 366 nm aroyl-substituted 9-anthracenemethanols afford the corresponding anthrylmethyl carbonium and substituted benzoate ions selectively, though their formation efficiencies are low. It is, thus, possible that both radical and cationic species are generated through the photodecomposition of these anthracenemethanol derivatives in monomer of low polarity. In order to estimate the ability of **1** to initiate the two types of photopolymerizations described above, we chose **1a**, **1b** and **1f** and investigated radical photopolymerization of St and cationic ring-opening photopolymerization of EpC.

As shown in Table 3, the 6 h irradiation of **1a** (0.2 mol.%) dissolved in St with light of wavelengths longer than 340 nm gave polystyrene (PSt) having a number-average molecular weight (M_n) of 2.4×10^4 in 2.5% yield. The 24 h irradiation under the same conditions increased not only the polymer yield but also the M_n value and if there was no **1a**, PSt was obtained only in less than 0.5% yield by this 24 h irradiation. Almost the same polymerization behavior was observed by the use of **1b** as a photoinitiator. The much lower photoreactivity of **1f** as compared to that of **1a** and **1b**, which was already described, is clearly reflected in nearly negligible polymer yields at any irradiation times. On the other hand, the irradiation ($\lambda > 320$ nm) of **1a** (1.0×10^{-2} mol dm^{-3}) in toluene being used instead of St afforded 4-methoxybenzaldehyde (14%, HPLC yield; conversion of **1a**, 20%) as the only identifiable product. The absence of anthrylmethyloxyl radical-

Table 2
Solvent viscosity effects on the quantum yields (Φ) for appearance of **2**, **3**, **4**, **5** and **6** in the photolysis of **1a** and **1g** in methanol–glycerol at room temperature

Compound	Solvent (viscosity η, mPa s)[a]	Φ_2	Φ_3	Φ_4	Φ_5	Φ_6
1a	MeOH–glycerol (100:0 v/v, $\eta = 0.57$)	0.008	0.006	0.013	0	0
	MeOH–glycerol (85:15 v/v, $\eta = 1.32$)	0.008	0.007	0.015	0	0
	MeOH–glycerol (70:30 v/v, $\eta = 3.19$)	0.009	0.008	0.015	0	0
	MeOH–glycerol (55:45 v/v, $\eta = 10.4$)	0.009	0.007	0.016	0	0
1g	MeOH–glycerol (100:0 v/v, $\eta = 0.57$)	0.006	0	–[b]	0.002	0.001
	MeOH–glycerol (85:15 v/v, $\eta = 1.32$)	0.007	0	–[b]	0.002	<0.001
	MeOH–glycerol (70:30 v/v, $\eta = 3.19$)	0.008	0	–[b]	0.002	0
	MeOH–glycerol (55:45 v/v, $\eta = 10.4$)	0.007	0	–[b]	0.002	0

[a] Solvent viscosities were determined using a Ubbelohde viscometer at 25 °C.
[b] Not determined.

Table 3
Yield number-average molecular weight (M_n) and polydispersity (M_w/M_n) of PSt and PEpC obtained by the photopolymerization of St and EpC containing **1a**, **1b** or **1f** (0.2 mol.% for St and 0.5 mol.% for EpC) at room temperature, respectively

Monomer	Initiator	Time (h)	Yield (%)	M_n ($\times 10^{-4}$)	M_w/M_n
St	**1a**	6	2.5	2.4	2.1
		24	8.3	5.5	2.2
	1b	6	2.5	3.9	2.2
		24	8.1	4.8	2.3
	1f	6	0.3	–	–
		24	0.7	4.2	2.3
EpC	**1a**	6	2.1	2.2	1.5
	1b	6	<0.3	–	–
	1f	6	0.0	–	–

derived products **5** and **6** in the reaction mixture suggests that this radical formed by the homolytic $CH_2O–C(=O)$ bond cleavage is captured by a toluene molecule prior to its hydrogen abstraction. The finding that PSt isolated exhibits the characteristic fluorescence of the anthracene chromophore is consistent with the generation of anthrylmethyloxyl radicals in St, as depicted in Fig. 4 in which the fluorescence spectrum of **1a** is given for comparison. It is, thus, very likely that anthrylmethyloxyl and 4-methoxybenzoyl radicals are involved in the polymerization of St and then the anthrylmethyloxy group is one of the polymer end groups. If so, the M_n value of PSt is predicted to increase with an increase in polymer yield, as already confirmed experimentally in the previous study [9]. The data given in Table 3 substantiates this prediction.

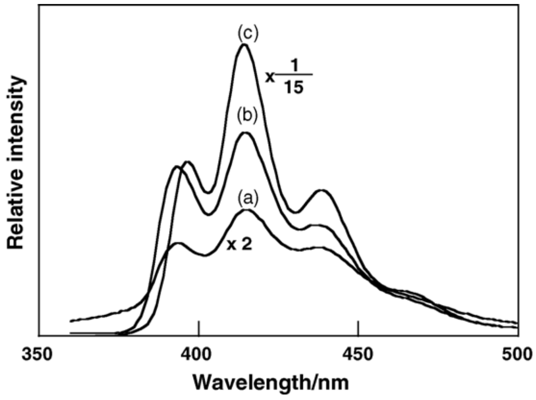


Fig. 4. Fluorescence spectra of PSt (curve a, 5.0×10^{3} g mL^{-1}), PEpC (curve b, 5.0×10^{-4} g mL^{-1}) and **1a** (curve c, 2.0×10^{-4} mol dm^{-3}) in chloroform at room temperature. Excitation wavelength is 340 nm.

Inspection of the results collected in Table 3 revealed that **1a** (0.5 mol.%) initiates the cationic ring-opening photopolymerization of EpC to give the polymer in 2.1% yield but negligible amounts of polymers are obtained on using **1b** and **1f** as photoinitiators. Because the EpC-derived polymer (PEpC) obtained shows the characteristic fluorescence of the anthracene chromophore (Fig. 4), it is suggested that the anthrylmethyl carbonium ion is responsible for the initiation of the cationic polymerization of EpC. A piece of evidence for this suggestion comes from the observation that the irradiation ($\lambda > 320$ nm) of a 1,2-dimethoxyethane solution of **1a** (1.0×10^{-2} mol dm^{-3}) gives **4a** (1%, HPLC yield; conversion of **1a**, 20%) and **6** (<0.1%) in addition to 4-methoxybenzaldehyde (3%) and **5** (1%) as identifiable products. The negligible formation of **6** implies that the anthrylmethyl carbonium ion generated is trapped by a dimethoxyethane molecule to give many unidentifiable products. If we take into account that substituted benzoate ion-bridged 9-anthrylmethylcarbonium ions may be key intermediates in the photolysis of **1a**–**f**, it can be assumed that the 4-methoxybenzoate ion-bridged carbonium ion has the much higher ability to initiate the cationic photopolymerization, as compared to the other carbonium ions.

Based on the above considerations, it is reasonable to conclude that *O*-(4-anisoyl) anthracene-9-methanol (**1a**) is a likely candidate for novel hybrid-type photoinitiator.

3. Experimental

3.1. Measurements

Ultraviolet (UV) absorption and fluorescence spectra were recorded on a Hitachi U-3300 spectrophotometer and a Hitachi F-4500 spectrofluorimeter, respectively. Nuclear magnetic resonance (NMR) spectra were taken with a JEOL JNM-ECA600 spectrometer. Chemical shifts (in ppm) were determined using tetramethylsilane as an internal standard. Infrared (IR) spectra were taken with a Shimadzu IRPrestige-21 infrared spectrophotometer. Elemental analyses were performed on a Perkin-Elmer 2400 series II CHNS/O analyzer. Mass spectra were recorded on a Shimadzu/Kratos MALDI IV spectrometer. High-performance liquid chromatography (HPLC) analysis was carried out on a Shimadzu LC-10AT HPLC system equipped with a 4.6 mm × 250 mm ODS (Zorbax) column and a Shimadzu SPD-10A UV detector [detection wavelength = 240 nm; mobile phase, MeCN–H_2O (60:40 v/v)]. The viscosities of methanol and methanol containing glycerol were determined using an Ubbelohde viscometer at 25 °C.

A potassium tris(oxalato)ferrate(III) actinometer was employed to determine the quantum yields for appearance of the products (**2**–**6**) at less than 15% conversions of the starting anthracene-9-methanol derivatives (**1a**–**g**) [15]. A 450 W high-pressure Hg lamp was used as the light source from which 366 nm light was selected with Corning 0–52, Corning 7–60 and Toshiba IRA-25S glass filters. All of the quantum yields are an average of more than five determinations. Linear calibration curves for **2**–**6**, made under the same analytical conditions, were utilized to quantify the formation of these products.

A prescribed amount of **1** was dissolved in St or EpC (2.0 g) placed in a glass tube where air was replaced by argon. The glass tube was irradiated at room temperature with light of wavelengths longer than 340 nm, (which was selected with Corning 0–52 and Toshiba IRA-25S glass filters,) from a 500 W high-pressure Hg lamp. Reaction mixtures were poured into aqueous methanol and then the precipitated polymer was filtered and dried in vacuo at 40 °C. The polymer yield was estimated gravimetrically as an average of more than two determinations. The molecular weight distribution of the polymer was obtained with a Tosoh 8000 series gel permeation chromatography (GPC) system equipped with a TSKgel MultiporeH_{XL}-M×2 at 40 °C. A calibration curve from 500 to 1.11×10^6 was obtained using standard PSt.

3.2. Materials and solvents

O-acyl anthracene-9-methanol derivatives (**1a**–**g**) were prepared according to the following procedure. Acyl chloride (35 mmol) dissolved in chloroform (25 mL) was slowly added to a chloroform solution (250 mL) containing anthracene-9-methanol (6.3 g, 30 mmol) and triethylamine (3.6 g, 35 mmol) with stirring at 0 °C. After 2 h, the reaction mixture was warmed to room temperature and then stirring was continued for additional 2 h. After the mixture was washed with three 100 mL portions of water and dried over anhydrous $MgSO_4$, it was concentrated to dryness in vacuo to afford the solid residue which was subjected to column chromatography over silica gel (70–230 mesh, Merck) using chloroform as an eluent. Prepurified anthracene-9-methanol derivatives were recrystallized from ethyl acetate or ethyl acetate–hexane to afford analytical grade **1a**–**g** in 40–50% yields. The reaction of sodium methoxide with 9-(chloromethyl)anthracene in methanol allowed us to obtain crude 9-(methoxymethyl)anthracene (**2**) which was subjected to column chromatography over silica gel (70–230 mesh, Merck) using chloroform-hexane as an eluent. Physical and spectroscopic data of **1a**–**g** and **2** are as follows.

*3.2.1. O-(4-Anisoyl) anthracene-9-methanol (**1a**)*

mp 148.0–149.0 °C. IR (KBr) ν: 1260, 1710 cm^{-1}. ^{1}H NMR (600 MHz, DMSO-d$_6$) δ: 3.77 (3H, s), 6.37 (2H, s), 6.97 (2H, d, $J = 9.2$ Hz), 7.57 (2H, dd, $J = 6.7$, 8.5 Hz), 7.65 (2H, dd, $J = 6.7$, 8.5 Hz), 7.83 (2H, d, $J = 9.2$ Hz), 8.16 (2H, d, $J = 8.5$ Hz), 8.49 (2H, d, $J = 8.5$ Hz), 8.73 (1H, s). ^{13}C NMR (150 MHz, DMSO-d$_6$) δ: 55.4, 58.6, 114.0 (2C), 121.6 (2C), 124.0 (2C), 125.2 (2C), 126.6, 126.7 (2C), 128.9 (2C), 130.5, 130.9 (2C), 131.2 (2C), 135.3, 163.1, 165.3. Analysis: calculated for $C_{23}H_{18}O_3$: C, 80.76%; H, 5.30%; found: C, 80.68%; H, 5.30%.

*3.2.2. O-(4-Toluoyl) anthracene-9-methanol (**1b**)*

mp 116.0–117.0 °C. IR (KBr) ν: 1274, 1713 cm^{-1}. ^{1}H NMR (600 MHz, DMSO-d$_6$) δ: 2.31 (3H, s), 6.38 (2H, s), 7.25 (2H, d, $J = 8.5$ Hz), 7.57 (2H, dd, $J = 6.7$, 8.5 Hz), 7.64 (2H, dd, $J = 6.7$, 8.6 Hz), 7.77 (2H, d, $J = 8.5$ Hz), 8.16 (2H, d, $J = 8.5$ Hz), 8.49 (2H, d, $J = 8.6$ Hz), 8.74 (1H, s). ^{13}C NMR (150 MHz, DMSO-d$_6$) δ: 21.1, 58.9, 124.0 (2C), 125.3 (2C), 126.5, 126.78, 126.82 (2C), 129.0 (2C), 129.18 (2C), 129.24 (3C), 130.5 (2C), 130.9 (2C), 143.7, 165.7. Analysis: calculated for $C_{23}H_{18}O_2$: C, 84.64%; H, 5.56%; found: C, 84.78%; H, 5.37%.

*3.2.3. O-Benzoyl anthracene-9-methanol (**1c**)*

mp 81.5–82.5 °C. IR (KBr) ν: 1272, 1713 cm^{-1}. ^{1}H NMR (600 MHz, DMSO-d$_6$) δ: 6.41 (2H, s), 7.45 (2H, dd, $J = 7.3$, 7.9 Hz), 7.57 (2H, dd, $J = 7.9$, 8.5 Hz), 7.60 (1H, dd, $J = 7.3$, 7.3 Hz), 7.66 (2H, dd, $J = 7.9$, 8.5 Hz), 7.86 (2H, d, $J = 7.9$ Hz), 8.17 (2H, d, $J = 8.5$ Hz), 8.50 (2H, d, $J = 8.5$ Hz), 8.74 (1H, s). ^{13}C NMR (150 MHz, DMSO-d$_6$) δ: 59.0, 124.0 (2C), 125.2 (2C), 126.1 (2C), 126.3, 128.9 (2C), 129.07 (2C), 129.14 (3C), 129.4. 130.5, 130.9 (2C), 133.3 (2C), 165.6. Analysis: calculated for $C_{22}H_{16}O_2$: C, 84.59%; H, 5.16%; found: C, 84.51%; H, 4.81%.

*3.2.4. O-(4-Chlorobenzoyl) anthracene-9-methanol (**1d**)*

mp 143.0–144.0 °C. IR (KBr) ν: 1266, 1719 cm^{-1}. ^{1}H NMR (600 MHz, DMSO-d$_6$) δ: 6.41 (2H, s), 7.52 (2H, d, $J = 8.5$ Hz), 7.58 (2H, dd, $J = 7.3$, 7.9 Hz), 7.65 (2H, dd, $J = 7.3$, 7.9 Hz), 7.87 (2H, d, $J = 8.5$ Hz), 8.16 (2H, d, $J = 7.9$ Hz), 8.49 (2H, d, $J = 7.9$ Hz), 8.74 (1H, s). ^{13}C NMR (150 MHz, DMSO-d$_6$) δ: 58.3, 123.9 (2C), 125.2 (2C), 126.1, 126.8 (2C), 128.2, 128.9 (2C), 129.0 (2C), 130.5 (2C), 130.87 (2C), 130.92 (2C), 138.2 (2C), 164.8. Analysis: calculated for $C_{22}H_{15}ClO_3$: C, 75.88%; H, 4.45%; found: C, 76.19%; H, 4.36%.

*3.2.5. O-(4-Trifluoromethylbenzoyl) anthracene-9-methanol (**1e**)*

mp 118.0–119.0 °C. IR (KBr) ν: 1272, 1719 cm^{-1}. ^{1}H NMR (600 MHz, DMSO-d$_6$) δ: 6.45 (2H, s), 7.58 (2H, dd,

J = 7.9, 7.9 Hz), 7.66 (2H, dd, J = 7.9, 8.5 Hz), 7.82 (2H, d, J = 7.9 Hz), 8.07 (2H, d, J = 7.9 Hz), 8.17 (2H, d, J = 7.9 Hz), 8.51 (2H, d, J = 8.5 Hz), 8.75 (1H, s). ^{13}C NMR (150 MHz, DMSO-d_6) δ: 59.7, 123.6 (1C, q, J = 273 Hz), 124.0 (2C), 125.3 (2C), 125.8 (2C, q, J = 4 Hz), 126.0, 126.9 (2C), 129.2 (2C), 129.99 (2C), 130.03 (2C), 130.6 (2C), 130.9, 132.8 (1C, q, J = 31 Hz), 133.2, 164.7. Analysis: calculated for $C_{23}H_{15}F_3O_2$: C, 72.33%; H, 3.96%; found: C, 72.63%; H, 3.97%.

3.2.6. *O-(4-Cyanobenzoyl) anthracene-9-methanol (**1f**)*

mp 180.5–181.5 °C. IR (KBr) ν: 1272, 1719, 2230 cm^{-1}. ^{1}H NMR (600 MHz, DMSO-d_6) δ: 6.44 (2H, s), 7.58 (2H, dd, J = 6.7, 7.9 Hz), 7.65 (2H, dd, J = 6.7, 8.5 Hz), 7.92 (2H, d, J = 8.5 Hz), 8.01 (2H, d, J = 8.5 Hz), 8.16 (2H, d, J = 7.9 Hz), 8.50 (2H, d, J = 8.5 Hz), 8.75 (1H, s). ^{13}C NMR (150 MHz, DMSO-d_6) δ: 59.7, 115.4, 117.9, 123.9 (2C), 125.2 (2C), 125.8, 126.9 (2C), 128.9 (2C), 129.1 (2C), 129.8 (2C), 130.5, 130.9 (2C), 132.7 (2C), 133.3, 164.4. Analysis: calculated for $C_{23}H_{15}NO_2$: C, 81.88%; H, 4.48%; N, 4.13%; found: C, 81.59%; H, 4.56%; N, 4.13%.

3.2.7. *O-Acetyl anthracene-9-methanol (**1g**)*

mp 110.0–110.5 °C. IR (KBr) ν: 1249, 1726 cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 2.08 (3H, s), 6.15 (2H, s), 7.49 (2H, dd, J = 6.9, 8.0 Hz), 7.57 (2H, dd, J = 6.9, 8.6 Hz), 8.03 (2H, d, J = 8.0 Hz), 8.33 (2H, d, J = 8.6 Hz), 8.51 (1H, s). ^{13}C NMR (150 MHz, DMSO-d_6) δ: 21.0, 58.8, 123.9 (2C), 125.1 (2C), 126.2, 126.7 (2C), 129.1 (2C), 129.2, 131.1 (2C), 131.4 (2C), 171.3. Analysis: calculated for $C_{17}H_{14}O_2$: C, 81.58%; H, 5.64%; found: C, 81.29%; H, 5.48%.

3.2.8. *9-(Methoxymethyl)anthracene (**2**)*

mp 88.0–89.0 °C. IR (KBr) ν: 1192 cm^{-1}. ^{1}H NMR (600 MHz, DMSO-d_6) δ: 3.56 (3H, s), 5.43 (2H,s), 7.47 (2H, dd, J = 6.4, 8.5 Hz), 7.55 (2H, dd, J = 6.4, 8.5 Hz), 8.03 (2H, d, J = 8.5 Hz), 8.40 (2H, d, J = 8.5 Hz), 8.48 (1H, s). ^{13}C NMR (150 MHz, DMSO-d_6) δ: 58.4, 66.5, 124.3 (2C), 125.1 (2C), 126.2 (2C), 128.5, 129.0 (2C), 131.0 (2C), 131.5 (2C), 134.0. Analysis: calculated for $C_{16}H_{14}O$: C, 86.45%; H, 6.35%; found: C, 86.34%; H, 6.23%.

Anthracene-9-carbaldehyde (**5**) and anthracene-9-methanol (**6**) were purified by recrystallization from ethyl acetate–hexane. 4-Substituted benzoic acids **(4a–f)** were recrystallized from ethanol–water. Glycerol and toluene were of spectroscopic grade and used without further purification. Methanol and 1,2-dimethoxyethane were purified according to the standard methods [24]. All other chemicals employed were obtained from commercial sources and were of the highest grade available.

3.3. *Photolysis and product analysis*

In order to isolate the photoproduct (**3**) and determine its structure, a nitrogen-saturated methanol solution of **1a** (5.0×10^{-3} mol dm^{-3}, 100 mL) was irradiated with light of wavelengths longer than 340 nm (which was selected with Corning 0–52 and Toshiba IRA-25S glass filters) from a 450 W high-pressure Hg lamp for 10 h at room temperature (conversion of **1a**, 45%; HPLC analysis). The irradiated solution was concentrated to dryness in vacuo and the resulting residue was subjected to HPLC over ODS (20 mm × 250 mm column) using MeCN–H_2O (60:40 v/v) as a mobile phase. Fractions containing only **3** were combined and concentrated to one-half its initial volume and the product was extracted with three 50 mL portions of chloroform. After the chloroform solution was dried over anhydrous $MgSO_4$, it was concentrated to dryness in vacuo to give the solid residue which was subjected to NMR and mass spectral analyses. Because the isolated product had not so high stability, it was contaminated with small amounts of **3**-derived decomposition products (HPLC analysis). NMR and mass spectroscopic data of **3** are as follows.

3.3.1. *9-Methoxy-10-methylene-9,10-dihydroanthracene (**3**)*

^{1}H NMR (600 MHz, $CDCl_3$) δ: 3.19 (3H, s), 5.28 (1H, s), 5.38 (2H, s), 7.36–7.38 (4H, m), 7.50–7.52 (2H, m), 7.75–7.77 (2H, m). ^{13}C NMR (150 MHz, CDCl3) δ: 56.2, 78.4, 110.0, 124.6 (2C), 127.8 (2C), 128.4 (2C), 128.9 (2C), 133.9 (2C), 136.3 (2C), 140.6. MALDI TOF *m/z:* 245.292 $(M + Na)^+$; calculated for $C_{16}H_{14}ONa$: 245.290.

A toluene or a 1,2-dimethoxyethane solution of **1a** (1.0×10^{-2} mol dm^{-3}, 10 mL) was placed in a Pyrex glass tube, degassed by bubbling nitrogen through it for 10 min and sealed. Deaerated solutions were irradiated in parallel for a given period of time on a merry-go-round apparatus with light of wavelengths longer than 320 nm from a 400 W high-pressure Hg lamp. This irradiation light was selected with a Pyrex-glass cylinder (pathlength, 1 cm) containing an aqueous solution of copper(II) sulfate (1.0 mol dm^{-3}). The irradiated solution was subjected to HPLC analysis [mobile phase, MeCN–H_2O (60:40 v/v); detection wavelength, 240 nm].

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