1-(Arylmethyloxy)anthracenes: Novel Photoinitiators for Radical and Cationic Polymerizations

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Introduction. Photochemistry has continued to contribute to the development of various types of functional initiators.[1] Recently, much attention is being denoted to novel photoinitiators which enable the initiation of both radical and cationic polymerizations,[2−8] owing to the potential that a combination between these two types of polymerizations will produce a hybrid polymer composed of radical- and cation-derived polymer units. For instance, interpenetrating network polymers[9−11] that combine the properties of given polymers are an attractive research subject from a practical point of view.

Previously, we investigated into the reactivity and initiation ability of 9-anthrylmethyl-substituted bichromophoric molecules in radical and cationic photopolymerizations[7,12] and found that strong charge transfer-type interaction in these molecules assists competitive heterolytic and homolytic cleavages of specific σ-bonds to generate radicals and cations of some initiation abilities.[13] Thus, these bichromophoric initiators are good candidates for the hybrid-type photoinitiator (which means the initiator undergoing two different bond cleavages in the excited state to give radical and ionic species that enable the initiation of both radical and ion polymerizations), containing no halogen and/or metal. While they functioned as effective photoinitiators for the radical polymerization of styrene (St), the cationic polymerization of cyclohexene oxide (CHO) was induced to only a minor extent in the presence of these photoinitiators. On the basis of these findings, it was suggested that the much lower polarity of CHO compared to that of methanol renders the heterolytic cleavage of a given bond very inefficient. In order to enhance this bond cleavage efficiency in monomers of low polarity, our attention was directed to a dramatic increase in the acidity of phenol and naphthol in their singlet excited states[14] and allowed to design a new type of photoinitiator, 6-cyano-2-arylmethyloxynaphthalene derivative. While we succeeded in generating an arylmethyl carbonium ion intermediate in less polar solvent such as 1,2-dimethoxyethane, the ability of this derivative to initiate the cationic photopolymerization of CHO was still low mainly because of its weak absorption in long wavelength region.[15] The great possibility that the oxyanthracene chromophore exhibits strong absorption in this wavelength region led us to improve the previous initiator design and to synthesize 1-arylmethyloxyanthracene derivatives **1a**−**d** as more refined hybrid-type photoinitiators (Chart 1). In this Communication we present results that demonstrate that methoxynaphthyl-substituted 1-anthracene derivative **1d** is a good candidate for the practical hybrid-type photoinitiator consisting of only carbon, hydrogen, and oxygen atoms.

Results and Discussion. Unirradiated 1-arylmethyloxyanthracene derivative **1d** (2.0×10^{-3} mol dm^{-3}) exhibited anthracene ring-derived vibrational bands near 340 (molar absorption coefficient, $\epsilon = 4380$ dm^3 mol^{-1} cm^{-1}), 350 (3680), 370 (4770), and 390 nm (3680) in both 1,2-dimethoxyethane and toluene. The large relative absorbance at about 340 nm is due to the presence of the 2-methoxynaphthyl chromophore giving the first absorption band at 323 nm ($\epsilon = 2410$ dm^3 mol^{-1} cm^{-1}) and 336 nm (2690 dm^3 mol^{-1} cm^{-1}). On irradiating the 1-anthryloxy chromophore preferentially with light [of wavelengths longer than 340 nm ($\lambda > 340$ nm)] from a 500 W high-pressure Hg lamp in N_2-saturated 1,2-dimethoxyethane, absorption bands originating from the anthracene ring were decreased with the appearance of new absorption bands in the 300−330 nm region. Similar absorption spectral changes were observed also in the less polar solvent, toluene. The extent to which absorbance at 390 nm is decreased per second was found to be lowered in order of **1d** (1.4×10^{-2}) > **1c** (1.1×10^{-2}) > **1b** (3.9×10^{-3}) > **1a** (2.3×10^{-3}), suggesting some contribution of a charge-transfer-type interaction between the two aromatic chromophores in the excited state to the overall photoreactivity of **1**. Since the electron-donating ability of the aryl group is decreased in this order, the group is considered to act as an electron donor.

The excited-state bichromophoric interaction is very likely to be directly reflected in the emission behavior of a given molecule,[13] so that we measured the fluorescence spectra of **1a**−**d**. While there was a clear tendency of the fluorescence maximum wavelength to slightly shift to the longer wavelength side with an increase in the electron-donating ability of the aryl group in 1,2-dimethoxyethane (**1a**, 427 nm; **1d**, 430 nm), the emission intensity (I_f) was also enhanced with this ability [I_f(**1d**)/I_f(**1a**) = 1.9]. These findings are consistent with the participation of a charge-transfer-type interaction in the excited state described above. In the less polar solvent, toluene, the aryl substituent exerted only a very minor effect on both the emission maximum and the emission intensity, providing a piece of evidence for this interaction. In addition, the pK_a values of 1-hydroxyanthracene in the singlet ground (9.6) and excited (4.2) states, estimated through the pH dependence of its UV absorption and fluorescence spectra in N_2-saturated H_2O containing 0.1 mol dm^{-3} KCl, revealed the establishment of a charge-separated state during the excited-state lifetime to greatly enhance the acidity of this derivative as in the cases of phenol and naphthol.[14] These considerations allows us to predict that both heterolytic CH_2−O bond and homolytic CH_2O−Ar bond cleavages in **1d** take place in 1,2-dimethoxyethane, whereas toluene induces the homolysis of the latter bond in preference to the heterolysis of the former bond.

Our previous study showed that the photodecomposition of 6-cyano-2-(9-anthrylmethyloxy)naphthalene in 1,2-dimethoxyethane affords 6-cyano-2-hydroxynaphthalene and anthracene-9-methanol as the heterolytic CH_2−O bond cleavage products and also only the homolytic CH_2O−Ar bond cleavage products; namely, 6-cyanonaphthalene, anthracene-9-carbaldehyde, and anthracene-9-methanol are detected on irradiation in toluene.[15]

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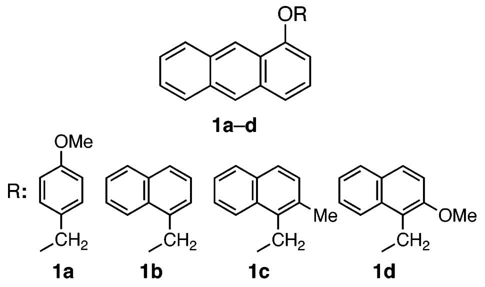
Chart 1



Scheme 1

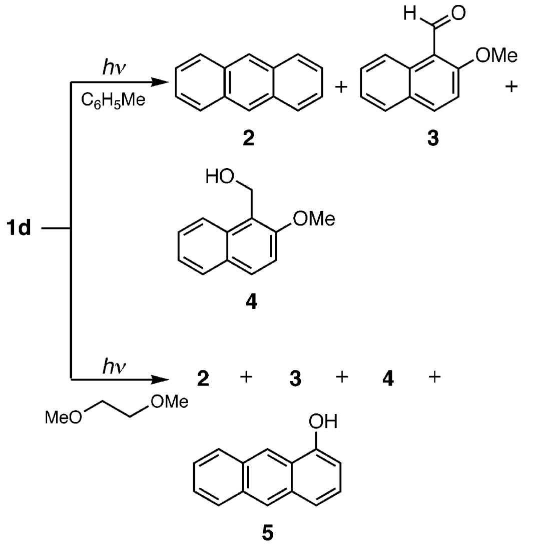


Table 1. Bulk Photopolymerization of Styrene (St) and Cyclohexene Oxide (CHO) Containing 0.2 mol % 1a−d[a]

initiator	monomer	irradiation time (h)	temp (°C)	yield (%)	mol wt ($M_n \times 10^{-4}$, GPC)[b]	polydispersity (M_w/M_n,GPC)[b]
1a	St	8	rt	9.9	2.8	2.2
		8	60	15.5	9.9	2.9
		12	60	23.8	9.5	2.8
1b	St	8	rt	15.7	2.0	3.2
		8	60	31.5	3.2	2.8
		12	60	44.9	5.6	2.9
1c	St	8	rt	19.7	2.1	2.4
		8	60	36.7	3.1	2.9
		12	60	64.2	5.7	3.1
1d	St	8	rt	24.3	2.1	2.4
		8	60	57.8	3.2	3.0
		12	60	76.5	5.9	3.2
1a	CHO	8	rt	<0.1		
		8	60	2.5	0.60	1.6
		16	60	8.6	0.91	1.1
1b	CHO	8	rt	<0.1		
		8	60	5.8	0.62	1.5
		16	60	15.4	0.54	1.5
1c	CHO	8	rt	13.8	0.68	1.4
		8	60	34.9	0.66	1.6
		16	60	52.1	1.4	1.8
1d	CHO	8	rt	22.3	0.69	1.7
		8	60	50.4	1.9	1.8
		16	60	62.7	1.6	1.7

[a] Polymerization mixture in a glass tube sealed under vacuum was irradiated with light of $\lambda > 340$ nm with stirring at room temperature (rt) or 60 °C. After the irradiation, the mixture was poured into methanol in order to obtain the corresponding polymer as a precipitate. The polymer was purified by reprecipitation from methanol and dried in vacuo at 40 °C. [b] M_n, M_w, and GPC represent number-average molecular weight, weight-average molecular weight, and gel permeation chromatography, respectively. M_n and M_w were estimated at rt by GPC using tetrahydrofuran and poly(styrene) (500−1.11 × 10^6) as an eluent and a molecular weight standard, respectively.

This product distribution is, thus, a reliable criterion for the bond cleavage mode of this type of bichromophoric molecule. As shown in Scheme 1, the irradiation of an N_2-saturated toluene solution of **1d** (2.0×10^{-3} mol dm^{-3}) with Pyrex-filtered light of $\lambda > 280$ nm gave anthracene (**2**, 18.1% HPLC yield), 1-formyl-2-methoxynaphthalene (**3**, 6.4%), and 1-hydroxymethyl-2-methoxynaphthalene (**4**, 5.9%) at ca. 35% conversion. On the basis of the above criterion, we confirmed the exclusive homolysis of the CH_2O-Ar bond. Interestingly, in addition to these products (**2**, 2.3%; **3**, 4.2%; **4**, 11.0%), 1-hydroxyanthracene (**5**, 13.3%) and hydroxyanthracene-derived byproducts were formed on irradiation in 1,2-dimethoxyethane (ca. 35% conversion) under the same conditions. This finding substantiates that the photodecomposition proceeds in homolytic and heterolytic bond cleavage modes and, hence, consistent with our prediction.

Analysis of the **1d**-derived product distribution indicates that the arylmethyloxyl radical and the arylmethyl carbonium ion are initiating species for the radical and cationic polymerization reactions of given monomers, respectively. Table 1 summarizes the data obtained by the bulk photopolymerization of St and CHO in the presence of **1a**−**d** irradiated with light of $\lambda > 340$ nm. Because poly(styrene) (PSt) and poly(cyclohexene oxide) (PCHO) were only obtained in negligible yields without either photoirradiation or a photoinitiator, the data reveal that both of these two polymer yields increase with polymerization temperature, irradiation time, and also the electron-donating ability of the aryl group. These control experiments were performed under the same conditions as those given in Table 1. While the enhanced reaction time and temperature have a propensity to render number-average molecular weight (M_n) and polydispersity (M_w/M_n) for PSt larger slightly, these M_n and M_w/M_n values for PCHO were not affected. Because previous results substantiate the participation of a radical mechanism in the photopolymerization of St,[7,15] it is possible to interpret the observation (that M_n shows a tendency to increase with increasing the yield of **1b**−**d**-derived PSt) in terms of the photodissociation of the substituted naphthylmethyloxy end group and the subsequent repolymerization by propagating radical formed, as already suggested.[7] Substituent effects on the polymer yields imply that the aryl group exerts a great effect not only on the excited-state reactivity of **1** but also on the ability to initiate a given polymerization. Interestingly, methoxynaphthyl-substituted anthracene derivative **1d**, one of the non-salt-type initiators consisting of carbon, oxygen, and hydrogen atoms, functions as a hybrid-type photoinitiator to give high-molecular-weight PSt and PCHO in good yields.

In order to explore the end groups of these two polymers, we synthesized PSt (M_n = 8800) and PCHO (6900) having lower M_n in the presence of **1d** (0.2 mol %, $\lambda > 340$ nm) at room temperature and analyzed their ^{1}H NMR and fluorescence spectra. Although the strong overlap of NMR signals for aromatic protons made a polymer end-group analysis very difficult, the independent appearance of methoxynaphthyl- and anthryl-derived fluorescences enabled qualitative estimation of the polymer end-group composition. As depicted in Figure 1, PSt exhibited intense fluorescence at 365 nm and very weak one near 450 nm, whereas both the 365 and 450 nm emission bands were observed with nearly equal intensities on excitation of PCHO. Because 1-hydroxymethyl-2-methoxynaphthalene and 1-hydroxyanthracene gave their fluorescences at 365 and 448 nm under the same analytical conditions, respectively, the former

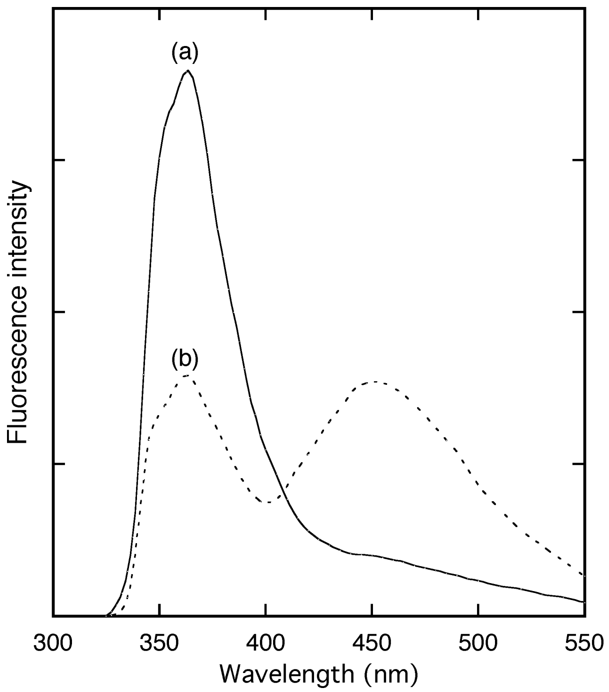


Figure 1. Fluorescence spectra of polystyrene (curve a, 0.50 g dm^{-3}) and poly(cyclohexene oxide) (curve b, 0.50 g dm^{-3}), obtained by the irradiation ($\lambda > 340$ nm) of styrene and cyclohexene oxide in the presence of 0.2 mol % **1d** at room temperature (rt), respectively, in N$_2$-saturated chloroform at rt. Excitation wavelength is 283 nm.

finding revealed that the methoxynaphthylmethyloxy chromophore is the major end group of PSt and the anthryl end group plays only a minor role. In addition, the latter finding substantiates the existence of both methoxynaphthylmethyloxy and 1-anthryloxy chromophores as major end groups for PCHO. Thus, we were led to conclude that the arylmethyloxyl radical and the arylmethyl carbonium ion are involved as reactive intermediates to initiate the polymerization of St and CHO, respectively.

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