Simultaneous Photoinduced Color Formation and Photoinitiated Polymerization

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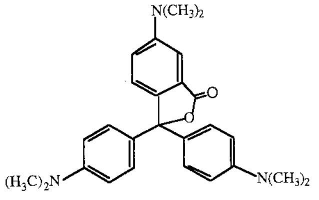
Crystal violet lactone (CVL, **1**, 3,3-bis[4-(dimethylamino)phenyl]-6-(dimethylamino)-1(3*H*)-isobenzofuranone) and other lactone dye precursors **2**−**5** form colored triphenylmethyl cations when irradiated with UV light in the presence or absence of [4-(octyloxy)phenyl]phenyliodonium hexafluoroantimonate (OPPI). In selected monomers in the presence of iodonium salt, color formation and polymerization occur simultaneously. The excited singlet state lifetimes of **1**−**5** estimated from quantum yields for the disappearance of CVL in the presence of OPPI are similar to those observed for fluorescence quenching and occur mainly by electron transfer. On the basis of the transient absorption spectra, it can be concluded that triarylmethane cations are generated from the lactone precursors in the presence of OPPI in acetonitrile with a pseudo first order rate constant of 10^4 s^{-1}. Color formation in the absence of OPPI is suggested to occur from the excited singlet states of the lactone via a biradical formed by photoinduced *β*-bond cleavage.

Introduction

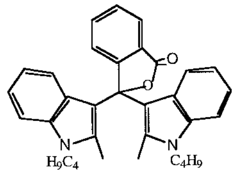
Crystal violet lactone (CVL, **1**) is one of a series of important commercial materials that form the basis of the "carbonless" carbon paper response by turning from "colorless" to "colored" in the presence of acid. In the paper industry, **1** is dissolved in a nonpolar solvent and encapsulated in microcapsules and the latter adhered to a paper support. A second paper, generally coated with a low molecular weight Novolak resin, is laminated to the first. Rupturing the microcapsule of the first sheet onto the acidic surface of the second sheet causes a deep blue color to form at the point of rupture. Other lactones producing other colors by the same reaction are shown in Figure 1. It is the purpose of this work to report the processes by which dye precursors **1**−**5** form color in the presence, as well as the absence, of photoreactive iodonium salts such as diphenyliodonium hexafluoroantimonate.

Background

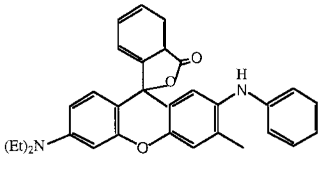
CVL has been reported to form cationic triarylmethane dyes in the presence of acetic acid in acetonitrile,[2] while diphenyliodonium salts are known to decompose to form an acid upon electron transfer in a reaction that may take place from the triplet or singlet state of a sensitizer[3] as well as by chemical sensitization.[4] Moreover, diphenyliodonium cation (Ph_2I^+) decomposition, either from electron transfer or by direct means,[5] is both an important pathway to phenyl radicals and a photochemical route to the acid.[6] The reaction can be sensitized by triplet sensitizers,[3g] like ketocoumarins,[3e,f] where a transient absorption assigned to the ketocoumarin radical cation is detected in the presence of iodonium salts in methanol. Diffusion controlled electron transfer photosensitization of diphenyliodonium salts by anthracene (AN) or 9,10-diethoxyanthracene (DEAN) has also been observed and inferred to be a singlet state reaction in acetonitrile.[3a] The transient absorption resulting from picosecond laser flash photolysis was shown to be the anthracene radical cation formed from the quenching of anthracene singlet by Ph_2I^+, though neither the phenyl radical nor the diphenyliodonium radical could be detected on this time scale.



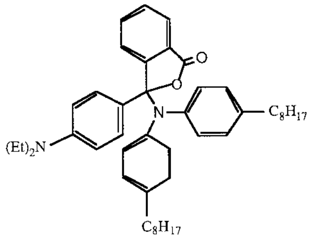
1: CVL; 3,3-bis[4-(dimethylamino)phenyl]-6-(dimethylamino)-1(3H)isobenzofuranone



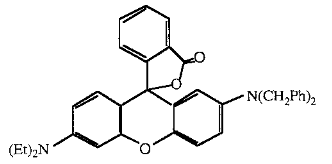
4: 3,3-bis[1-(butyl)-2-(methyl)indolinyl]-1(3H) isobenzofuran-3-one: *magenta dye precursor*



2: 3-(diethylamino)-6-(methyl)-7-(aminophenyl) [isobenzofuran-1(3H), 9'-[9H]-xanthen]-3-one *black dye precursor*



5: 3-[4-(diethylamino)phenyl]-3-{bis[4-(octyl) phenyl]amino}-1(3H)isobenzofuran-3-one: *orange dye precursor*



3: 3-(diethylamino)-7-(dibenzylamino) [isobenzofuran-1(3H), 9'[9H]-xanthen]-3-one *green dye precursor*

Figure 1. Structures of dye precursors.

Linden and Neckers prepared onium salts of Rose Bengal.[7] The excited singlet states of Rose Bengal disodium or monosodium salts were found effectively quenched by Ph_2I^+, with a bimolecular rate constant ($k_q = (1.26-2.30) \times 10^{10}$ M^{-1} s^{-1}) in methanol, though it seems clear that in this solvent the compounds exist as solvent separated ion pairs.[8]

Systems comprised of onium salts, reducing agents, and sensitizers, for example, ketone/amine/onium salts[9] or dye/amine/onium salts,[10] are excellent photoinitiators for the polymerization of acrylates. Irradiation of benzoin ethers[4b] or

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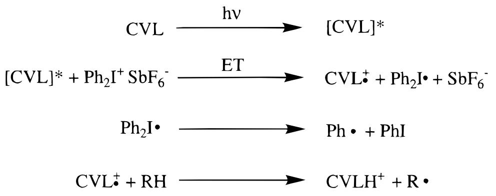
SCHEME 1

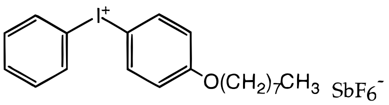


benzophenones in the presence of onium salts results in efficient decomposition. Chemical sensitization can result from hydrogen abstraction from ethers or alcohols by ketone triplets,[3b,f] yielding radicals which in turn reduce diphenyliodonium salts. Esters and amines undergo a similar chain process also leading to diphenyliodonium salt decomposition.

Color Formation by Electron Transfer

The first electron transfer color-forming reaction postulated as such we believe was the photoinduced reaction of diphenylamine with carbon tetrabromide, which forms blue colors.[11] Maclachlan has shown that color formation from leuco aminotriarylmethane dyes (e.g., leuco crystal violet) also takes place in the presence of electron acceptors such as CBr_4, CCl_4, and quinones. He measured the quenching rate constants of the excited singlet states of the leuco dye and the quantum yield for color formation with or without oxygen using both steady state and transient spectroscopy. He also determined if singlet or triplet quenching processes were responsible for color formation.[12]

Recently, Ren et al. have reported a unique system involving colorless lactone dye precursors, such as those found in Figure 1, and [4-(octyloxy)phenyl]phenyliodonium hexafluoroantimonate (OPPI)



that simultaneously photoinduced color formation and caused polymerization of appropriate monomer mixtures.[2b] These reactions have substantial potential in many lithographic, stereolithographic, and other processes requiring color for purposes of differentiation and identification. A mixture of crystal violet lactone (i.e., a blue color precursor) and OPPI was demonstrated to be an efficient photoinitiator for radical polymerization. They also proposed that diaryliodonium radical generates iodobenzene and a phenyl radical after electron transfer from the excited state of CVL. The more stable $CVLH^+$ seems to result from abstraction of a hydrogen atom from solvent by crystal violet cation radical, $CVL^{•+}$ (Scheme 1).

The mechanism of simultaneous photoinduced color formation and free radicals generating from lactone dye precursors with OPPI and the systems's use as an initiator for polymerization based on Scheme 1 have been investigated.[2b] Transient absorption and fluorescent spectroscopies were used to follow the intermediates formed and to outline the mechanism of the reactions.

Experimental Section

Materials. Crystal violet lactone (CVL, **1**;[13] Figure 1) was obtained from Aldrich. Dye precursors **2**−**5** (Figure 1) were obtained from Hilton Davis, Int., and Mead Corp. [4-(Octyloxy)phenyl]phenyliodonium hexafluoroantimonate (OPPI) was a gift from GE Silicones. All of the materials were recrystallized twice from acetone. Solvents were spectrophotometric grade and obtained from Aldrich.

Absorption and Fluorescence Spectra. Absorption spectra were recorded using a Hewlett Packard 8452A diode array UV−visible spectrophotometer at concentrations ≈ 10^{-5} mol/L in acetonitrile, benzene, hexane, or 2-propanol. Fluorescence spectra ($\lambda_{ex} = 365$ nm) were recorded using a SPEX Fluorolog spectrophotometer at concentrations of ≈ 10^{-3}−10^{-2} mol/L in acetonitrile, both in the presence and the absence of OPPI. No reabsorption of fluorescence was observed at this concentration since the Stokes shift is very large. Fluorescence quantum yields in acetonitrile were measured after 20 min of argon bubbling using rhodamine B as the actinometer.

Laser Flash Photolysis. Nanosecond laser flash photolysis was carried out using the apparatus described previously.[14] The third harmonic (355 nm) of a Q-switched Nd:YAG laser (full width at half-maximum (fwhm), 8 ns) was used for excitation. During the flash experiment sample solutions in 1 cm quartz cuvettes were continuously purged with argon. Before the experiment, a 20 min argon purge was carried out.

Quantum Yield of Color Formation. Quantum yields of the formation of dye precursor cations were measured using laser flash photolysis techniques.[15] The transient absorption ($\Delta OD°_T$) at some monitoring wavelength λ, immediately after laser, is given by eq 1, where ϵ_T and ϵ_G are the extinction

$$\Delta OD°_{T\lambda} = 2.303E_0A_{0\lambda}(\epsilon_T - \epsilon_G)_\lambda \Phi_T l' \qquad (1)$$

coefficients of the excited state and ground state at λ', l' is the length of the flashed volume traversed by the measuring beam, A_0 is the ground state absorbance at the excitation wavelength, Φ_T is the quantum yield of formation of the transient species, and E_0 is the incident flash excitation energy. As both E_0 and A_0 decrease, $\Delta OD°_T$ becomes proportional to the transient species. In this situation, the ratio R is as follows:

$$R = 1/A_0[d(\Delta OD_T)/dE_0] = 2.303(\epsilon_T - \epsilon_G)\Phi_T l' \qquad (2)$$

For measurements on two solutions a 1.2×10^{-3} M benzophenone/benzene solution was used as the reference, and the dye precursor solution in acetonitrile was used as the sample

$$R/R' = [(\epsilon_T - \epsilon_G)\Phi_T]/[(\epsilon_{T'} - \epsilon_{G'})\Phi_{T'}] \qquad (3)$$

Once one has the product $(\Delta\epsilon)'\Phi_{T'}$ for the reference solution, determination of R/R' and $\epsilon_T - \epsilon_G$ then gives the quantum yield Φ_T of the cationic triarylmethane dye. $\epsilon_{T'}$ and $\epsilon_{G'}$ used for benzophenone were 7220 and 0 M^{-1} cm^{-1} at 530 nm, respectively. The quantum yields for color formation were determined for the values of R for the benzophenone triplet and the products. The values of transient absorbance ($\Delta OD°_T$) obtained after 1 ms correspond to the absorption from colored species formed after laser irradiation, and the average of several measurements was used.

Cyclic Voltammetry. The oxidation potential of each dye precursor was measured by cyclic voltammetry using a BAS 100A electrochemical analyzer controlled with the commercial BAS 100W (version 1.0) software package. Measurements were done in acetonitrile containing 0.1 M tetrabutylammonium perchlorate (TBAP) as a supporting electrolyte. Electrochemical measurements were carried out in 10 mM acetonitrile solutions with 0.1 M TBAP. A platinum sphere working electrode, a Ag/Ag^+ nonaqueous reference electrode, and a platinum wire

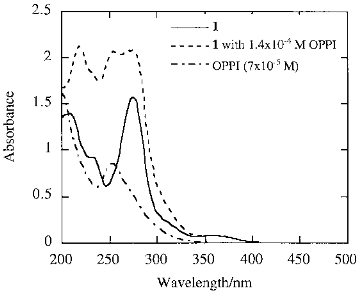


Figure 2. Absorption spectra of **1**, **1** + 1.4×10^{-4} M OPPI, and OPPI in acetonitrile.

TABLE 1: Summary of Absorption of 1−5 with or without Acetic Acid in Acetonitrile

	CH_3COOH	color	λ_{max}/nm	$\epsilon/M^{-1}\ cm^{-1}$
1	0	colorless	274	3.9×10^4
			358	2.3×10^3
	90%	blue	605	2.8×10^4 [2a]
2	0	colorless	222	4.3×10^4
			280	3.4×10^4
			448	1.8×10^4
	30%	dark green	586	2.0×10^4
3	0	colorless	276	3.6×10^4
			316	8.8×10^3
			462, 436	1.3×10^4, 1.4×10^4
	30%	green	604	1.3×10^4
4	0	colorless	228	6.9×10^4
			286	1.9×10^4
			380	7.0×10^3
	30%	pink	534	3.3×10^4
5	0	colorless	254	3.2×10^4
			288	2.0×10^4
	30%	yellow	466	2.5×10^4

as a counter electrode were employed in all experiments. The data were calibrated against SCE using ferrocene as the standard.

Results

Absorption Spectra of CVL and the Other Dye Precursors. The steady state absorption spectrum of **1** in acetonitrile (6.4×10^{-5} M) has two clear peaks at 274 and 358 nm, and a shoulder at 234 nm, Figure 2. The absorption also has a tail at 320−400 nm. The spectrum of **1** is similar in 2-propanol but differs significantly in cyclohexane, where the spectrum is blue-shifted compared to the spectrum in acetonitrile or in 2-propanol. This means that the lower excited singlet state of **1** corresponds to a $\pi\pi^*$ state.

The spectra obtained for an OPPI solution, that for **1** and an OPPI/**1**/acetonitrile solution overlapped, and no evidence for the formation of a ground state complex was found.

The absorption maxima and molar absorption coefficients of the other lactone dye precursors, **2**−**5**, in acetonitrile are shown in Table 1. In each case the lower excited states were assigned to the $\pi\pi^*$ state in acetonitrile.

When acetic acid was added to solutions of **1**−**5** in acetonitrile, new absorptions appeared and the color of the solutions changed, Table 1. This indicates that cationic triarylmethane structures were formed in the presence of the acid.

Fluorescence Spectra. The fluorescence spectrum of **1** in acetonitrile (8.3×10^{-4} M), upon excitation at 365 nm in the presence of OPPI, is shown in Figure 3. The fluorescence intensity at its peak (541 nm) decreased with an increase in the concentration of OPPI. The $k_q\tau_s$ of **1** with OPPI as the quencher was 35.8 M^{-1} measured from the slope of the Stern−Volmer plot.

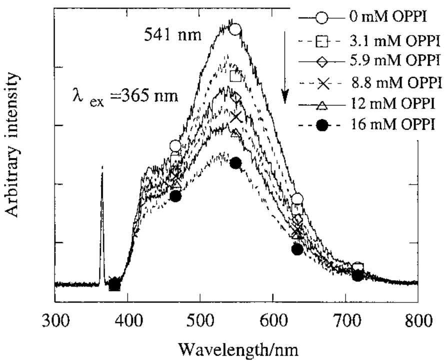


Figure 3. Fluorescence spectra of **1** with several concentrations of OPPI acetonitrile.

TABLE 2: Fluorescence Characteristics of 1−5 in Acetonitrile upon Excitation at 365 nm

	λ_{max}/nm	Φ_f	$k_q\tau_s{}^a/M^{-1}$	$\tau_s{}^b$/ns
1	541	1.3×10^{-3}	35.8	1.8
2	532	1.4×10^{-3}	30.6	1.5
3	537	3.5×10^{-4}	31.6	1.6
4	491	2.9×10^{-2}	62.2	3.1
5	550	2.3×10^{-3}	32.2	1.6

[a] For quenching by OPPI. [b] Assuming $k_q = 2 \times 10^{10}\ M^{-1}\ s^{-1}$.

$$I_0/I = 1 + k_q\tau_s[\mathrm{OPPI}] \tag{4}$$

The fluorescence intensities of the other lactone dye precursors in acetonitrile (6.1×10^{-3} M for **2**, 3.0×10^{-3} M for **3**, 1.0×10^{-2} M for **4**, and 6.0×10^{-3} M for **5**) also decreased with an increase in the concentration of OPPI. Quantum yields and $k_q\tau_s$ for fluorescence quenching by OPPI, obtained from the slope of the Stern−Volmer plot, are reported in Table 2. In our case, the interaction between CVL and OPPI in the ground state, as in the formation of a charge transfer complex, is not observed from the absorption spectra, Figure 2. Therefore, the reaction should be intermolecular and controlled by the diffusion rate in the solvent which is $2 \times 10^{10}\ M^{-1}\ s^{-1}$ in acetonitrile. The $k_q\tau_s$ and fluorescence quantum yield for **4** was larger than those of the other dye precursors.

The lifetimes for the excited singlet state of the lactone dye precursors were estimated from $k_q\tau_s$, as shown in Table 2. Assuming electron transfer takes place at the rate of diffusion, the lifetimes are of the order of a few nanoseconds.

Laser Flash Photolysis of CVL. Figure 4A shows the time resolved transient absorption spectra of **1** in acetonitrile (2.0×10^{-4} M) after excitation with 355 nm laser pulses. Maximum transient absorptions were observed at 350 and 470 nm immediately after laser irradiation. The decay of the absorption at 470 nm suggests two components (Figure 5A). The lifetime of one component, assigned to the triplet state of **1** (^{3}CVL*), was determined to be about 14.9 μs in acetonitrile. For comparison, the lifetime of ^{3}CVL* in benzene was determined to be 17.9 μs. The other component had a lifetime based on a second order rate constant ($k/\epsilon = 1.5 \times 10^6\ s^{-1}$).

A new absorption, assigned to CVLH$^\bullet$, was observed at 400 nm in 2-propanol. It was observed as the rising process which had a rate constant $k_{RH} = 4.2 \times 10^4\ s^{-1}$. The absorption spectrum of CVLH$^\bullet$, which has a half-life of 21 ms in 2-propanol as measured by flash photolysis, has already been reported[2a] to have a broad maximum at 380 nm and a very weak

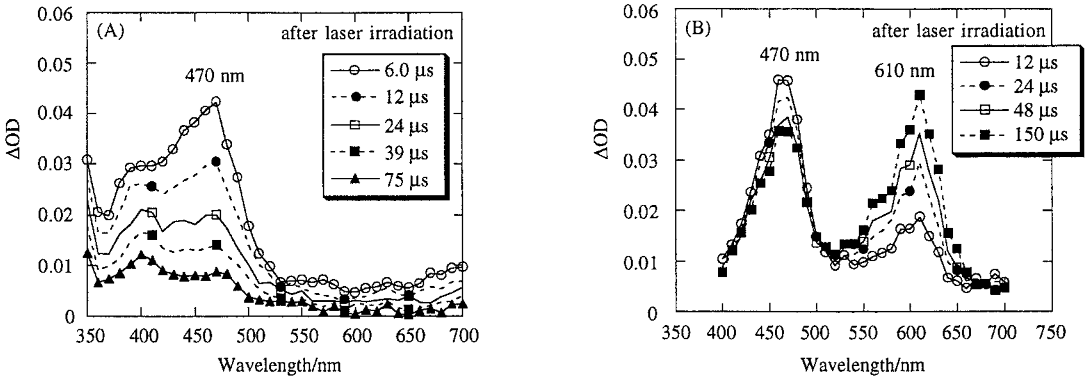


Figure 4. Time resolved transient absorption spectra of **1** without (A) and with (B) OPPI in acetonitrile on excitation at 355 nm laser pulses.

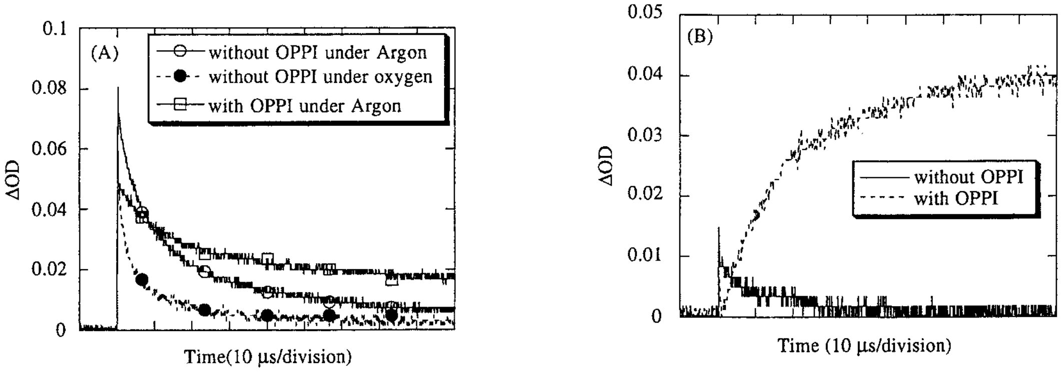


Figure 5. (A) Decay of transient absorption of **1** under various conditions in acetonitrile at 470 nm. (B) The decay profiles of **1** at 610 nm.

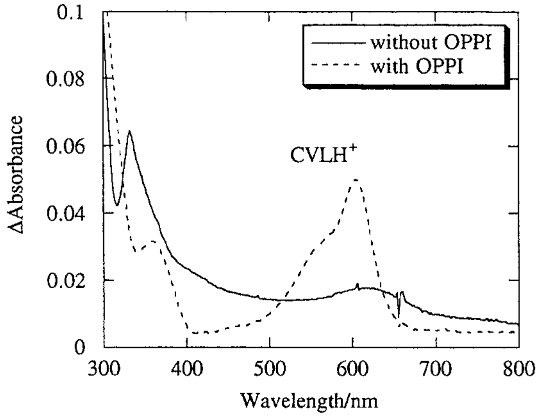
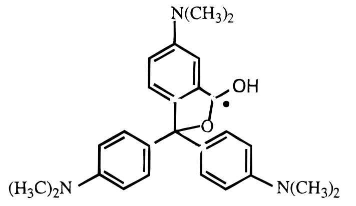


Figure 6. Steady state different absorption spectra of **1** before and after laser irradiation in acetonitrile in the absence and presence of OPPI.

absorption at 610 nm. No rising absorption was observed at 400 nm in acetonitrile.



CVLH•

The steady state UV spectrum of **1** in acetonitrile (Figure 6) was distinctly different before and after laser irradiation and agreed with the absorption of CVLH$^+$.[1a] As shown in Figure 4B, a new absorption band with a maximum at 610 nm was also observed at longer times in the transient spectrum when OPPI was added to a **1**/acetonitrile solution. The transient absorbance of the slow component in the decay curve, observed at 470 nm, increased in the presence of OPPI (Figure 5A). However the lifetime of the CVL triplet was not changed by the addition of OPPI. The rate constant for the rising of the new absorption with its maximum, around 610 nm, was calculated for a pseudo first order reaction to be 2.3×10^4 s^{-1} (Figure 5B). After the laser pulse, the colorless solution changed to a blue solution. The rising of absorption, which could not be observed in the absence of OPPI, suggests that the cationic colored form (CVLH$^+$) which is reported to have λ_{max} at 610 nm was generated by abstraction of a hydrogen atom from the solvent by the crystal violet lactone radical cation (CVL$^{\bullet+}$), likely generated upon electron transfer between the excited singlet state of **1** and OPPI. No color formation was observed from **1** in the presence of OPPI in dimethyl sulfoxide, a solvent from which hydrogen abstraction is apparently more difficult. The increase of absorption, which corresponds to CVLH$^+$, was also observed in the presence of triphenylsulfonium hexafluoroarsenate ($Ph_3S^+AsF_6^-$) in acetonitrile. The generation of CVLH$^+$ in the presence of OPPI in 2-propanol, which has the rate constant of 6.2×10^2 s^{-1}, was observed at 610 nm, while the rising process for CVLH$^\bullet$, which has the rate constant of 4.4×10^4 s^{-1}, was derived at 400 nm.

Laser Flash Photolysis of the Other Dye Precursors. Transient absorption spectra of the other lactone dye precursors in acetonitrile were measured after excitation at 355 nm by nanosecond laser flash photolysis. The transient absorption spectrum of **2** (7.4×10^{-4} M) without OPPI has two peaks at 420 and 580 nm. The decay curve at 420 nm also suggested two components, as in the case of CVL. The lifetime of the first component was determined to be about 134 μs and assigned to the $\pi\pi^*$ triplet state. The slow component had a lifetime of more than 1 ms. An increase in absorption of the product with a rate constant of 2.38×10^5 s^{-1} was observed at 460 nm and

TABLE 3: Summary of Data for Transient Absorption of Dye Precursors

	solvent	λ_{max}/nm	$\tau_T/\mu s$	k_{RH}/s^{-1}
CVL (blue dye precursor)	CH_3CN	470	14.9	2.26×10^{4} [a]
	C_6H_6	380, 450	17.9	
	cyclohexane		11.3	
	2-propanol	400, 450	60.0	6.20×10^{2} [a]
	2-propanol			4.40×10^{4} [b]
	2-propanol			4.20×10^{4} [c]
black dye precursor	CH_3CN	420, 580	134	7.34×10^{4} [a]
	C_6H_6	350, 420, 470	0.114	
green dye precursor	CH_3CN	430	26.9	
	C_6H_6	430	14.1	
magenta dye precursor	CH_3CN	350	12.5	1.06×10^{4} [a]
	C_6H_6	370, 460	0.209	
orange dye precursor	CH_3CN	420	69.0	1.72×10^{4} [a]
	C_6H_6	420	111	

[a] In the presence of OPPI. [b] In the presence of OPPI at 400 nm. [c] In the absence of OPPI at 400 nm.

around 580 nm without OPPI in acetonitrile. The decay of the triplet excited state of **2** in benzene measured at 430 nm had a lifetime of 114 ns obtained by fitting first order kinetics. Absorbance of the triplet of **2** in benzene was much larger than that in acetonitrile under the same concentration of dye precursor.

When OPPI was added to the **2**/acetonitrile solution, an increase in absorption bands around 450 and 560 nm in the transient spectra was observed. These absorption increases indicate the triarylmethane cation of **2** was formed, because an absorption spectrum at the final time corresponded to the steady state absorption spectrum of **2**. The latter was also formed from **2** with acetic acid in acetonitrile. The rising process observed at 586 nm has a lifetime of 7.34×10^{4} s^{-1} on the basis of the pseudo first order rates.

Table 3 summarizes the data for the transient absorption spectra of **1**−**5**.

Discussion

Mechanism. Solvent effects on the absorption spectra of **1** suggest the lower excited singlet state corresponds to a $\pi\pi^*$ state. However, in acetonitrile the excited singlet seems also to include $n\pi^*$ contributions, because the quantum yield of fluorescence is low. In general, the $n\pi^*$ excited singlet state of a carbonyl group, as in the case of benzophenone, should readily undergo intersystem crossing to the triplet state. It can be seen that the quantum yields of intersystem crossing for **1**−**5** are estimated to be approximately unity ($\Phi_{isc} \approx 1 - \Phi_f$). The fluorescence of **1**−**5** in acetonitrile is quenched by OPPI, suggesting that electron transfer takes place in acetonitrile in competition with the intersystem crossing.

To consider the fate of the radical cation of the dye precursor that is formed after electron transfer, the products formed from transient species after decomposition in the presence of OPPI, and also the transient absorptions obtained in the absence of onium salt, were measured. In the latter case, the observed transients result from the deactivation of the triplets formed from the dye precursors. These transient species decay by second order reactions in the absence of OPPI. Comparison of the results from the transient absorption experiments with the steady state absorption spectra of dye precursors in the absence of OPPI before and after laser irradiation indicates the triarylmethane cation is the most stable compound formed in acetonitrile. The absorption spectrum of **1** under protonating conditions was recognized to be similar to the well-known absorption spectrum of the crystal violet cation. It should be noted that the values of the quantum yields for formation of triarylmethane cations from the dye precursors in acetonitrile were very low in the absence of OPPI, Table 4.

TABLE 4: Quantum Yields of Formation of Triarylmethane Cations of Dye Precursors in Acetonitrile

	[OPPI]/M	Φ_r[a]
1	0	3.4×10^{-4}
	1.38×10^{-4}	1.3×10^{-2}
	1.33×10^{-4} [b]	4.4×10^{-2} [b]
	1.32×10^{-4} [c]	1.1×10^{-2} [c]
2	0	8.7×10^{-3}
	1.38×10^{-4}	2.4×10^{-2}
3	0	4.7×10^{-3}
	1.38×10^{-4}	1.1×10^{-2}
4	0	4.2×10^{-3}
	1.38×10^{-4}	4.4×10^{-2}
5	0	8.4×10^{-3}
	1.38×10^{-4}	3.4×10^{-2}

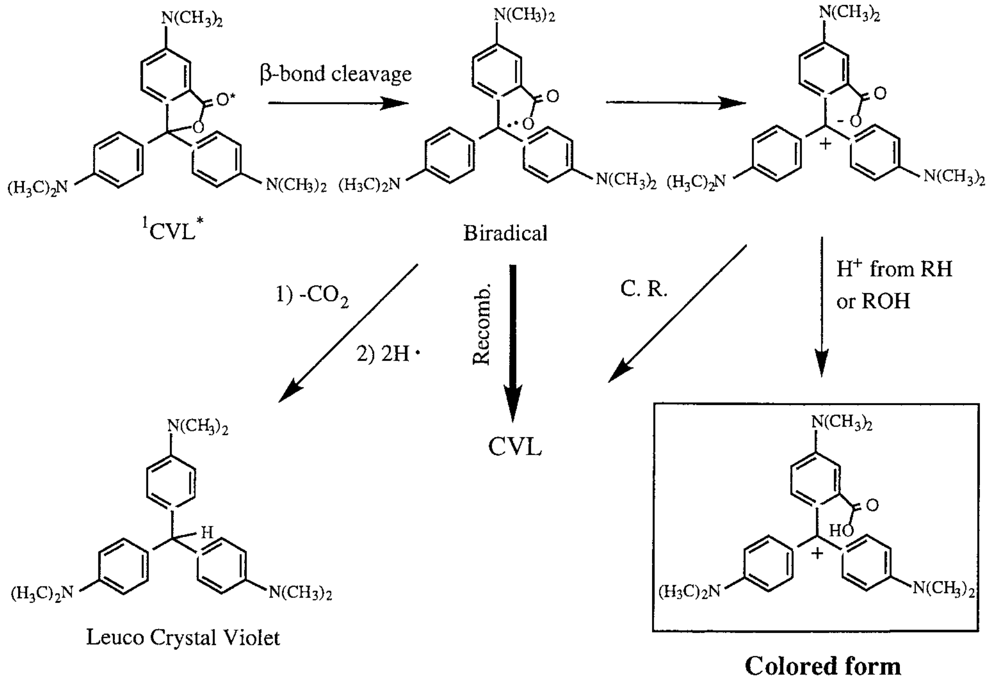
[a] Benzophenone reference. [b] In 2-propanol. [c] In the presence of $Ph_3S^+AsF_6^-$ instead of OPPI.

The lowest excited triplet states of **1**−**5** are likely to be a mixed $\pi\pi^*$ and $n\pi^*$ state in acetonitrile, as was the case for the singlet states. Hydrogen abstraction from 2-propanol by triplet **1** was observed via formation of the free radical from **1** which had an absorption at 400 nm with a rate constant of formation of 4×10^{4} s^{-1}. It would be structurally difficult to explain the mechanism for formation of triarylmethane cation via a dye precursor free radical, in the absence of OPPI, if the $n\pi^*$ excited triplet state of the dye precursor abstracts a hydrogen atom from the solvent. Moreover, it should be difficult for the $n\pi^*$ excited triplet state of the carbonyl group to abstract hydrogen from acetonitrile in view of the situation with other ketones ($k_{RH} < 10^{3}$ s^{-1} for acetone "in acetonitrile").

It is well-known that esters easily generate biradical intermediates as products by a photoinduced β-bond cleavage. These biradicals subsequently either recombine or yield a decarboxylated analogue.[16,17]

1-Naphthyl methyl esters and substituted benzyl acetates have been reported to undergo radical/radical electron transfer after photoinduced bond cleavage.[16] The bond cleavage has been reported for a series of naphthyl methyl and benzylic esters to produce both ionic and radical products. These results suggest excited singlet state homolysis forming a caged radical pair and subsequent electron transfer between the radicals to form an ion pair. At the same time, products resulting from decarboxylation of the biradicals were also observed. However, the quantum yields of product formation for both reactions in methanol were quite low ($\Phi = (0.5-1.7) \times 10^{-2}$ for 1-naphthyl methyl esters). The decarboxylation rate (k_{CO_2}) and electron

SCHEME 2: Formation of Colored Triarylmethane Cation by Electron Transfer in the Absence of OPPI



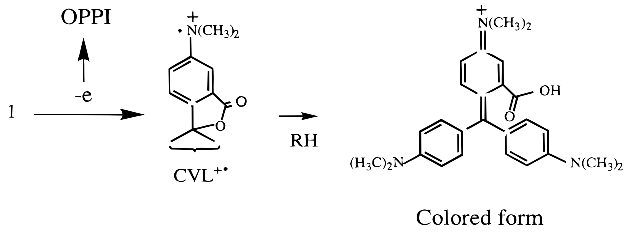
transfer rate (k_{ET}) of the esters were also reported to be respectively 4.6×10^9 s^{-1} and $(1.5-5.8) \times 10^{10}$ M^{-1} s^{-1}. For comparison, the decarboxylation rate of 9-methyl-9-fluorenoyloxy radical is 1.8×10^{10} s^{-1}.[18] The decarboxylation of benzoyloxy radical ($C_6H_5CO_2^{\bullet}$), a radical similar in structure to the biradical formed in Scheme 2, is reported to be directly observed with a rate constant of 5.9×10^6 s^{-1} in acetonitrile.[19]

Assuming that a photoinduced bond cleavage takes place with **1** in the absence of OPPI in acetonitrile, as shown in Scheme 2, the triarylmethane cation would not be formed through an α-bond cleavage. In our case, if the biradical formed by photoinduced bond cleavage from the excited singlet state ($\pi\pi^*$) of **1** in acetonitrile, electron transfer would take place between the radical pair after formation of the biradical in competition with recombination, which re-forms the starting material, and with decarboxlyation of the biradical. It is difficult to observe both decarboxylation and electron transfer directly using nanosecond transient absorption techniques, but it seems that our materials behave similarly to the 1-naphthyl methyl esters.

The decay curves observed in the absence of OPPI overlap the deactivation curves of the triplets of the dye precursors. A bimolecular reaction of a small amount of water in CH_3CN with the ion pair formed from electron transfer during the radical pair is suggested. Except for **2**, the decay curves were successfully fitted to first order kinetics along with a second order component. Only in the case of **2**, where there are multiple components in the decay, is the observation of intramolecular proton transfer, from the linked aromatic amino group to the oxygen of the lactone ring, shown to produce absorptions around 460 and 580 nm with a rate constant of 2.38×10^5 s^{-1}.

The low quantum yield of color formation in the absence of OPPI is suspected to result from the efficient recombination of the biradicals to re-form the starting material. Color formation by **1**−**5** in the absence of OPPI also competes with decarboxylation of the biradical (Scheme 2). If the rate of decarboxylation of the biradical is approximately the same as that of phenyloxyl radical, decarboxylation would not compete with biradical recombination. The quantum yield of triarylmethane cation formation in the case of **1** was the lowest of all the dye precursors.

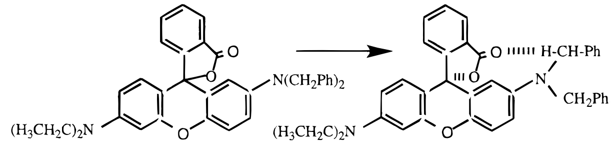
SCHEME 3: Oxidative Ring Opening of CVL



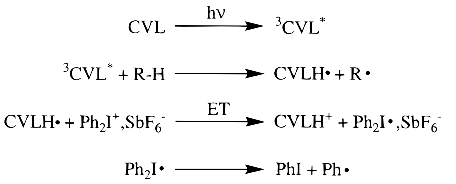
The transient absorption spectra of the dye precursors in the presence of OPPI in acetonitrile, as measured by nanosecond laser flash photolysis, indicated the existence of the more stable colored form when observed on the microsecond time scale. The quantum yield of color formation from **1** in 2-propanol is larger than that in acetonitrile, while no color formation from **1** was observed in dimethyl sulfoxide. This means that the abstraction of hdyrogen from the solvent is very important in that it provides a mechanism for color formation. The rate constants (k_{RH}) for color formation were determined to be of the order of 10^4 s^{-1}, except for **3**. The reason that k_{RH} seems to be slow is because the radical cations of the dye precursors seem to be well-stabilized by resonance structures in acetonitrile. Only when the unpaired electron density resides primarily on the carbonyl group is the triarylmethane cation formed by abstracting hydrogen from the solvent, as shown in Scheme 3. The k_{RH} of **2** seems to be slightly faster than are those of the other dye precursors. Possibly intramolecular hydrogen abstraction takes place from the adjacent amino group. The k_{RH} of **3** is not observed at 604 and 462 nm, although this would correspond to absorption of the triarylmethane cation. This seems to be caused by rapid intramolecular hydrogen transfer. The reaction is thought to proceed via the partial formation of a carbenium ion (Scheme 4) as in the case of 1-arylethyl acetate.[20]

The absorption of CVL$^{\bullet+}$ could not be observed on the nanosecond time scale because the absorptions of both the

SCHEME 4: Intramolecular Interactions in 3



SCHEME 5: Mechanism of Color Formation from Crystal Violet Lactone with OPPI in 2-Propanol



radical and triplet of **1** exist at the same time. Neither the absorption of a diphenyliodonium radical ($Ph_2I^•$) or the phenyl radical ($Ph^•$) was observed between 350 and 700 nm. This is not surprising since it is difficult to find the absorption of $Ph^•$ in the transient absorption spectra at this wavelength range in solution. Phenyl radical in the gas phase, the formation of which is completed within the observed laser pulse width (8 ns), has weak $n\pi^*$ absorption bands around 430−530 nm.[21] Furthermore, $Ph^•$ seems to have a very high reactivity. The existence of $Ph_2I^•$ in the anthracene/diphenyliodonium cation system has not been observed even on the picosecond time scale.[3a]

As shown in Table 4 the quantum yields (Φ_r) of formation of protonated dye precursor cations like $CVLH^+$ with OPPI are found to be high as compared with those without OPPI. Thus, OPPI is critical for the formation of the triarylmethane cations from the dye precursors. The quantum yield for formation of $CVLH^+$ in 2-propanol is significantly higher than it is in acetonitrile at the same concentration of OPPI. This means that the color formation from **1** in 2-propanol takes place not only via the singlet state from **1** but also via electron transfer from CVL free radical ($CVLH^•$) to OPPI after abstraction of hydrogen by the triplet state of **1** (Scheme 5). This is similar to the case of the photodecomposition of diaryliodonium salts sensitized with benzophenone in esters or alcohols.[22]

The oxidation potentials of **1**−**5** in acetonitrile determined as a peak potential were +1.01, +0.87, +0.96, +1.16, and +0.94 (vs SCE) and were irreversible. Free energy changes (ΔG) for electron transfer from the excited singlet states of dye precursors to diphenyliodonium cation ($E^{rd} = -0.70$ V vs SCE)[23] were predicted to be very exothermic ($\Delta G < -1.5$ eV). Bimolecular rate constants (k_q) for electron transfer, from the excited states of the dye precursors with diphenyliodonium cation in acetonitrile, were calculated to be 1.50×10^{10} M^{-1} s^{-1} using Rehm−Weller methodology.[24]

The reciprocal quantum yields of the disappearance of **1** (Φ_d) and the appearance of (Φ_r) $CVLH^+$ as a function of the reciprocal of OPPI concentration were shown to be linear (Figures 7[25] and 8).

Assuming that electron transfer from **1** to OPPI takes place from the excited singlet state of **1**, the mechanism of electron transfer is given in Scheme 6.

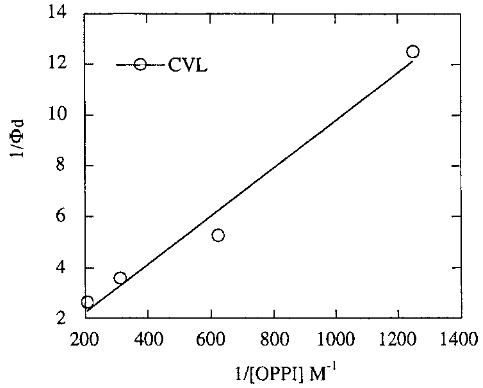


Figure 7. Stern−Volmer plot for the disappearance of **1**.

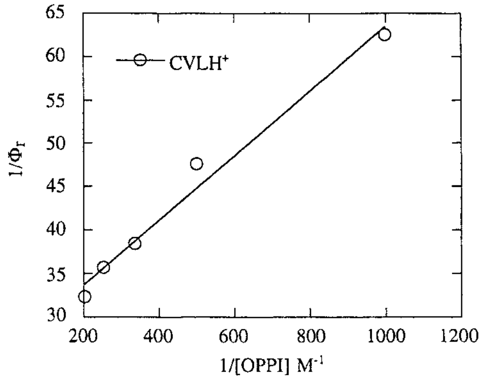
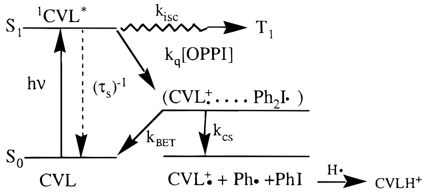


Figure 8. Stern−Volmer plot for the appearance of $CVLH^+$.

SCHEME 6



Electron transfer from the excited singlet state of **1** (S_1) to OPPI forms the radical cation ($CVL^{•+}$) and diphenyliodonium free radical ($Ph_2I^•$) as a contact pair in competition with intersystem crossing to the triplet of **1** (T_1). Subsequently the contact pair is solvent-separated or undergoes back-electron transfer. The equation for the relationship between the quantum yield of the $CVLH^+$ formation and concentration of OPPI was derived from Scheme 6 as follows:

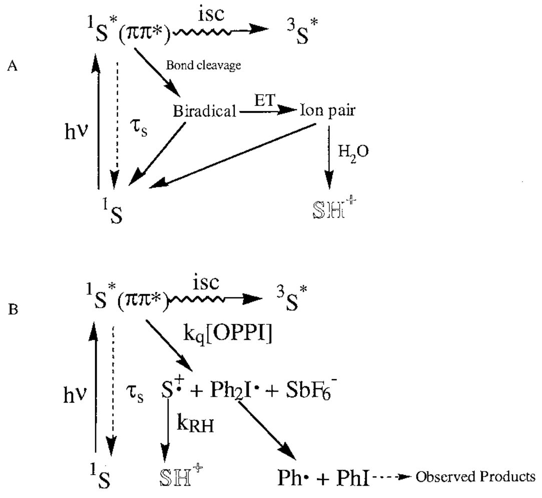
$$\Phi_r = \{k_q[\mathrm{OPPI}]/(1/\tau_s + k_q[\mathrm{OPPI}])\}\{k_{cs}/(k_{BET} + k_{cs})\} \quad (5)$$

where $\tau_s = (k_f + k_d + k_{isc})^{-1}$.

$k_q\tau_s$ was determined to be 36 M^{-1} from the slope and the intercept of the line in Figure 7. If electron transfer from the excited singlet of **1** to OPPI is faster than diffusion controlled (2×10^{10} M^{-1} s^{-1}) in acetonitrile, then τ_s is of the order of 1.8 ns. This is consistent with the τ_s of **1** obtained from $k_q\tau_s$ in the experiment of fluorescence quenching of **1** by OPPI. The quantum yields for formation of $CVLH^+$ (Φ_r) were also found to be in linear relationship in the presence of a high concentration of OPPI (Figure 8). This means that the excited singlet state of **1** is quenched mainly by OPPI because a drastic variation of Φ_r could not be observed up to 1×10^{-3} M OPPI. The limiting Φ_r and k_{bet}/k_{cs} were estimated respectively to be about 3.8×10^{-2} and 25 from the intercept in Figure 8. Assuming the rate constant for cage escape (k_{cs}) to be 5×10^9 s^{-1},[30] the rate constants for charge recombination (k_{bet}) should be 1.25×10^{11} s^{-1}.

Scheme 7 shows the mechanism of formation of the triarylmethane cation from dye precursors with or without OPPI, and the decomposition of the OPPI free radical in acetonitrile after electron transfer. Triarylmethane cation formation from the dye precursor was suggested to take place either in the presence or in the absence of OPPI in acetonitrile.

SCHEME 7: Mechanisms of Color Formation from the Dye Precursor without OPPI (A) or with OPPI (B) in Acetonitrile



In the absence of OPPI, because the biradical formed by photoinduced β-bond cleavage should be unstable, consequent electron transfer between the radicals can be expected to be inefficient. Moreover, even if the ion pair were fortuitously formed, it would be difficult for the ion pair to react readily with a small amount of water in acetonitrile in competition with the rapid charge recombination process. Indeed, the quantum yields for formation of products via electron transfer after homolytic bond cleavage were found to be low in our experiments as was the case of 1-naphthyl methyl esters.

In the presence of OPPI, electron transfer takes place mainly from the excited singlet states in competition with the intersystem crossing process. After electron transfer, the OPPI radical decomposes efficiently to phenyl radical and iodobenzene in competition with the back-electron transfer. The diphenyliodonium radical seems to decompose into PhI and $Ph^\bullet$ with the rate constant of 5×10^9 s^{-1}. These become the initiators for radical polymerization. This is similar to the anthracene/diphenyliodonium cation photosensitized system.

Conclusion

Color formation from dye precursors **1**−**5** with OPPI is proven to take place from the excited singlet states. Abstraction of a hydrogen atom is an important process in forming the more stable triarylmethane cation structure because no color formation occurs in non-proton donor solvents such as dimethyl sulfoxide. The rate constant for color formation is relatively slow due to the formation of a stable radical cation of the dye precursor. The rate constant of **3** is shown to be much faster than that of the other dye precursors because of intramolecular hydrogen atom transfer. We confirmed a minor production of the triarylmethane cations without OPPI in acetonitrile. This process was shown to occur through a biradical formed by photoinduced β-bond cleavage of the lactone group from the excited singlet states. Subsequent electron transfer of the radicals occurs in competition with a rapid recombination of the radicals. A small amount of water included in a solvent was needed as a proton donor in this case.

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References and Notes

(1) Contribution No. 337 from the Center for Photochemical Sciences.

(2) (a) Allen, N. S.; Hughes, N.; Mahon, P. *J. Photochem.* **1987**, *37*, 379. (b) Ren, Y.; Jager, W. F.; Neckers, D. C. *Macromolecules* **1996**, *29*, 3751.

(3) (a) Devoe, R. J.; Sahyun, M. R. V.; Schmid, E.; Serpone, N.; Sharma, D. K.; *Can. J. Chem.* **1988**, *66*, 319. Devoe, R. J.; Sahyun, M. R. V.; Schmid, E.; Sharma, D. K. *Can. J. Chem.* **1990**, *68*, 612. (b) Pappas, S. P.; Pappas, B. C.; Gatechair, L. R. *J. Polym. Sci., Polym. Chem. Ed.* **1984**, *22*, 69. (c) Pappas, S. P.; Gatechair, L. R.; Jilex, J. H. *J. Polym. Sci., Polym. Chem. Ed.* **1984**, *22*, 77. (d) Timpe, H.-J.; Rajendran, A. G. *Makromol. Chem. Rapid Commun.* **1988**, *9*, 399. (e) Timpe, H.-J.; Kronfeld, K.-P.; Lannel, U.; Fouassier, J.-P.; Lougnot, D.-J. *J. Photochem. Photobiol., A. Chem.* **1990**, 52, 111. (f) Timpe, H.-J.; Kronfeld, K.-P.; Mahlow, R. *Eur. Polym. J.* **1991**, *27*, 69. (g) Manivannan, G.; Wu, S.-K.; Fouassier, J. P. *Bull. Soc. Chim. Belg.* **1990**, *99*, 969.

(4) (a) Baumann, H.; Oertel, U.; Timpe, H.-J. *Eur. Polym. J.* **1986**, *22*, 313. (b) Timpe, H.-J.; Rajendran, A. G. *Eur. Polym. J.* **1991**, *27*, 77. (c) Fouassier, J. P.; Burr, D.; Crivello, J. V. *J. Photochem. Photobiol., A: Chem.* **1989**, *49*, 317.

(5) Dektar, J. L.; Hacker, N. P. *J. Org. Chem.* **1990**, *55*, 639. Kampmeier, J. A.; Nalli, T. W. *J. Org. Chem.* **1994**, *59*, 1381. Devoe, R. J. Sahyun, M. R. V.; Serpone, N.; Sharma, K. *Can. J. Chem.* **1987**, *65*, 2342.

(6) Park, Y.-T.; Song, N.-W.; Kim, Y.-H.; Hwang, C.-G.; Kim, S. K.; Kim, D. *J. Am. Chem Soc.* **1996**, *118*, 11399.

(7) Linden, S. M.; Neckers, D. C. *Photochem. Photobiol.* **1988**, *47*, 543.

(8) Linden, S. M.; Neckers, D. C. *J. Am. Chem. Soc.* **1988**, *110*, 1257.

(9) Fouassier, J. P.; Ruhlmann, D.; Takimoto, Y.; Harada, M.; Kawabata, M. *J. Polym. Sci., A: Polym. Chem.* **1993**, *31*, 2245.

(10) Fouassier, J. P.; Chesneau, E. *Makromol. Chem.* **1991**, *192*, 1307. Fouassier, J. P.; Wu, S. K. *J. Appl. Polym. Sci.* **1992**, *44*, 1779. Kawabata, M.; Takimoto, Y. *J. Photopolym. Sci.* **1990**, *2*, 147.

(11) Sprague, R. H.; Fletcher, H. L.; Wainer, E. *Photgr. Sci. Eng.* **1961**, *5*, 98. Steven, D. P.; Coppinger, G. M. *J. Am. Chem. Soc.* **1962**, *84*, 149.

(12) Maclachlan, A. *J. Phys. Chem.* **1967**, *71*, 718.

(13) The IUPAC names for each of the lactones are given underneath their structures, Figure 1.

(14) Hassoon, S.; Neckers, D. C. *J. Phys. Chem.* **1995**, *99*, 9473.

(15) Hurley, J. K.; Sinai, N.; Linschitz, H. *Photochem. Photobiol.* **1983**, *38*, 9.

(16) Barltrop, J. A.; Coyle, J. D. *J. Chem. Soc. B* **1971**, 251.

(17) Decosta, D. P.; Pincock, J. A. *J. Am. Chem. Soc.* **1993**, *115*, 2180. Hilborn, J. W.; Macknight, E.; Picnic, J. A.; Wedge, P. J. *J. Am. Chem. Soc.* **1994**, *116*, 3337.

(18) Fairy, D. E.; Schuster, G. B. *J. Am. Chem. Soc.* **1985**, *107*, 3381.

(19) Wang, J.; Tateno, T.; Sakuragi, H.; Tokumaru, K. *J. Photochem. Photobiol., A: Chem.* **1995**, *92*, 53.

(20) Taylor, R.; Smith, G. G.; Wetzel, W. H. *J. Am. Chem. Soc.* **1962**, *84*, 4817.

(21) Ikeda, N.; Nakashima, N.; Yoshihara, K. *J. Am. Chem. Soc.* **1985**, *107*, 3381.

(22) Pappas, S. P.; Gatechair, L. R.; Jilek, J. H. *J. Polym. Sci., Polym. Chem. Ed.* **1984**, *22*, 77.

(23) Devoe, R. J.; Sahyun, M. R. V.; Schmidt, E.; Sadrai, M.; Serpone, N.; Sharma, D. K. *Can. J. Chem.* **1989**, *67*, 1565.

(24) Rehm, D.; Weller, A. *Israel J. Chem.* **1970**, *8*, 259.

(25) Ren, Y. Unpublished data.