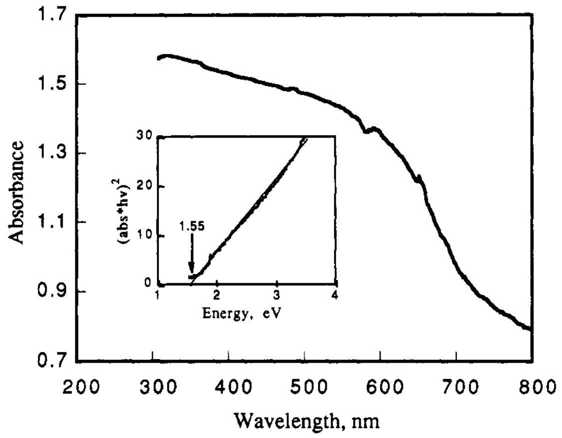


Figure 9. Absorption spectrum of CdSe film as deposited on Ti and removed with Scotch tape. The inset shows a plot of (absorbance × $h\nu$)^2 vs $h\nu$ for the same sample.

band edge was not as obvious in all films analyzed, indicating that the electronic properties of this material vary somewhat from sample to sample. Presumably this arises from the very fine grain structure in these films. Deviations from the expected bulk properties of CdSe films have previously been attributed to quantum confinement effects arising from the very small crystallite size obtained with electrodeposited films.[14,17,18] Hot-probe measurement of the as-deposited CdSe films indicated that the material in n-type.

Conclusions

The cyclic electrodeposition technique used in the present study produces homogeneous films of CdSe that are close to 1:1 atomic ratio of Cd to Se. The scan parameters are designed to lay down sequential monolayers of CdSe in order to avoid the accumulation of excess Se in the material. For the purpose of producing stoichiometric semiconductor films, this is an improvement over previous potentiostatic or galvanostatic electrochemical techniques, which tend to produce films containing excess Se. The key feature in this process appears to be the continuous deposition and stripping of excess Cd, which is proposed to react with any excess Se that may deposit. The material produced by sequential monolayer electrodeposition contains 3-4% by weight Cl as the major impurity when CdCl$_2$ is used as the Cd source. The films produced using the present technique consist of a dense layer underneath scattered dendrites, similar to CdSe films electrodeposited by other routes. In addition, the optical properties of these films are similar to those of previously studied films. Thus, although the present technique provides an improvement in the stoichiometry of electrodeposited films, in other respects the films do not significantly differ from those made by previous routes. Current work is directed at elucidating the mechanism of CdSe growth, characterizing the electronic properties of these films, and extending the procedure to other semiconductor systems.

Acknowledgment. We thank Jan Talbot for helpful discussions. A.M.K. thanks the U.S. Department of Education for a graduate fellowship.

Registry No. CdSe, 1306-24-7; Ti, 7440-32-6; Ni, 7440-02-0; CdCl$_2$, 10108-64-2; CdSO$_4$, 10124-36-4; SeO$_2$, 7446-08-4; H$_2$SeO$_3$, 7783-00-8.

Redox Photochromism in Films of Viologens and Related Compounds Bearing Long-Chain Alkyl Groups

Hiroyoshi Kamogawa* and Toshihiko Ono

Department of Applied Chemistry, Yamanashi University, Takeda 4, Kofu 400, Japan

Received April 15, 1991. Revised Manuscript Received September 11, 1991

1,1′-Bis(benzyl or *p*-methylbenzyl)-4,4′-bipyridinium and *trans*-4,4′-vinylenebis(1-benzylpyridinium) bis-(*p*-alkylbenzenesulfonate)s bearing long-chain alkyl groups (viologen Ia,b), prepared from their respective dichlorides by the anion-exchange reaction, were sandwiched between two glass plates by melting to afford thin transparent and mainly isotropic films. These almost colorless or pale yellow films developed intense visible colors by near-UV irradiation, which bleached upon heating (photochromism). This behavior is considered to be due to reversible redox reactions consisting of the one-electron transfer to viologen Ia,b dication from the counteranion by the photon mode (color development) and vice versa by the heat mode (bleaching).

Introduction

It has been widely known that some 1,1′-disubstituted bipyridinium, i.e., viologens, and related salts reversibly develop intense colors with visible lifetimes when exposed to radiation of the solar level in solutions in the presence of reductants,[1] in activating matrix polymer films,[2] and in the crystalline state.[3]

We report here reversible photoreductions accompanied by visible color developments (photochromism), which have been found for thin isotropic films made of the viologens bearing long-chain alkyl groups without any

---

(1) (a) Koizumi, M.; Obata, H. *Bull. Chem. Soc. Jpn.* **1958**, *31*, 823. (b) Bruin, F.; Heineken, F. W.; Bruin, M.; Zahlen, M. *J. Chem. Phys.* **1962**, *36*, 2783. (c) Johnson, C. S.; Gutowsky, H. S. *Ibid.* **1963**, *39*, 58-62. (d) Ledwith, A.; Russel, P. J.; Sutcliffe, L. H. *Chem. Commun.* **1971**, 964-965. (e) Ledwith, A. *Acc. Chem. Res.* **1972**, *2*, 1768-1772. (f) Evans, A. G.; Dodson, N. K.; Raes, N. H. *J. Chem. Soc., Perkin Trans. 2* **1976**, 859-863. (g) Takuma, K.; Kajiwara, M.; Matsuo, T. *Chem. Lett.* **1977**, 1199-1202. (h) Brown, N. M. D.; Cowley, D. J.; Hashmi, M. *Ibid.* **1978**, 462-468. (i) Jones, II, G.; Zisk, M. B. *J. Org. Chem.* **1986**, *51*, 947-950.

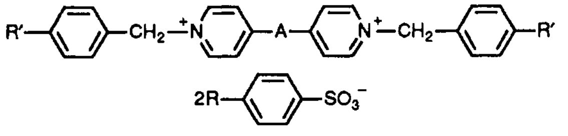
(2) (a) Kamogawa, H.; Masui, T.; Nanasawa, M. *Chem. Lett.* **1980**, 1145-1148. (b) Kamogawa, H.; Masui, T.; Amemiya, S. *J. Polym. Sci., Polym. Chem. Ed.* **1984**, *22*, 383-390. (c) Kamogawa, H.; Sugiyama, M. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 2443-2444. (d) Kamogawa, H.; Amemiya, S. *J. Polym. Sci., Polym. Chem. Ed.* **1985**, *23*, 2143-2423. (e) Kamogawa, H.; Satoh, S. *Ibid.* **1988**, *26*, 653-656. (f) Kamogawa, H.; Nanasawa, M. *Chem. Lett.* **1988**, 373-376. (g) Kamogawa, H.; Kikushima, K. *J. Polym. Sci., A: Polym. Chem.* **1989**, *27*, 393-396.

(3) (a) Kamogawa, H.; Suzuki, T. *J. Chem. Soc., Chem. Commun.* **1985**, 525-526. (b) Kamogawa, H.; Suzuki, T. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 794-796. (c) Kamogawa, H.; Satoh, S. *Ibid.* **1991**, *64*, 1066-1068.

0897-4756/91/2803-1020$02.50/0 © 1991 American Chemical Society

additives. This has made possible for the first time the color development by light of transparent films based on a redox mechanism consisting of the photon mode color development and the heat mode bleaching.

The compounds prepared and investigated in this study, which are hereafter referred to as "viologens", are shown in Ia,b, where R represents alkyl groups with C_6–C_{15}.



Ia,b: A = none (Ia) or –CH═CH– (Ib); R′ = H or CH_3

Experimental Section

Materials. All reagents employed were of the highest purity and used as received, unless otherwise noted. The alkyl groups (R) of *p*-alkylbenzenes were identified by means of mass spectrometry and gas chromatography.

Instrumentation. Infrared (IR), ^{1}NMR, mass, and EPR spectra were recorded on a Hitachi 215 spectrophotometer, a JNM-PMX 60 spectrometer, a Hitachi M808MS spectrometer, and a JES-FE1 XG spectrometer, respectively, under standard conditions. Elemental analyses were made with a Perkin-Elmer 240 instrument. Visible absorption spectra were obtained with a Shimazu UV-160 spectrophotometer. Gas chromatography was carried out with a Hitachi 164 gas chromatograph fitted with a SE-30 column under a helium stream (30 mL min^{-1}).

1,1′-Dibenzyl-4,4′-bipyridinium Bis(*p*-alkylbenzenesulfonate) (Ia, R′ = H). 1,1′-Dibenzyl-4,4′-bipyridinium dichloride (0.10 g, 0.24 mmol), prepared by refluxing 4,4′-bipyridine with benzyl chloride for 24 h, was dissolved in hot ethanol (50 mL). To the resulting solution was added an anion-exchange resin (Amberlite IRA-900, capacity, 1 mg equiv/mL; 10 mL), loaded with *p*-alkylbenzenesulfonate anion by exchanging the OH^- type with *p*-alkylbenzenesulfonic acid, which had been synthesized by the sulfonation of *p*-alkylbenzene with 30% fuming sulfuric acid, followed by stirring at 30 °C overnight. The resin was filtered off, and the filtrate was concentrated on a rotary evaporator and precipitated into ether (200 mL) to provide crude product, which was purified by recrystallization from ethanol-ether.

Anal. Calcd for $C_{48}H_{56}N_2S_2O_6$ (R = *n*-C_6H_{13}): C, 70.24; H, 6.83; N, 3.41%. Found: C, 70.12; H, 6.90; N, 3.31%. Calcd for $C_{52}H_{64}N_2S_2O_6$ (R = *n*-C_8H_{17}): C, 71.24; H, 7.76; N, 3.19%. Found: C, 71.25; H, 7.83; N, 3.22%. Calcd for $C_{54}H_{68}N_2S_2O_6$ (R = *n*-C_9H_{19}): C, 71.69; H, 7.52; N, 3.10%. Found: C, 71.60; H, 7.48; N, 3.09%. Calcd for $C_{56}H_{72}N_2S_2O_6$ (R = *n*-$C_{10}H_{21}$): C, 72.11; H, 7.72; N, 3.00%. Found: C, 72.48; H, 7.75; N, 2.86%. Calcd for $C_{58}H_{76}N_2S_2O_6$ (R = *n*-$C_{11}H_{23}$): C, 72.50; H, 7.92; N, 2.92%. Found: C, 72.64; H, 7.97; N, 2.90%. Calcd for $C_{60}H_{80}N_2S_2O_6$ (R = *n*-$C_{12}H_{25}$): C, 72.87; H, 8.10; N, 2.83%. Found: (R = *n*-$C_{12}H_{25}$): C, 72.58; H, 8.13; N, 2.90%. (Film no. 11 in Table III): C, 72.84; H, 8.14; N, 2.88%. Calcd for $C_{62}H_{84}N_2S_2O_6$ (R = *n*-$C_{13}H_{27}$): C, 73.23; H, 8.27; N, 2.76%. Found: C, 73.20; H, 8.23; N, 2.76%. Calcd for $C_{64}H_{88}N_2S_2O_6$ (R = *n*-$C_{14}H_{29}$): C, 73.57; H, 8.42; N, 2.68%. Found: C, 73.30; H, 8.37; N, 2.66%. Calcd for $C_{66}H_{92}N_2S_2O_6$ (R = *n*-$C_{15}H_{31}$): C, 73.88; H, 8.58; N, 2.61%. Found: C, 73.45; H, 8.51: N, 2.63%.

IR (KBr) 1190, 1030 (–SO_3^-) cm^{-1}. ^{1}H NMR (DMSO-d_6) δ 0.5–2.0 (m, alkyl), 2.5 (t, 4 H, $2CH_2$), 6.0 (s, 4 H, $2CH_2$), 6.9–8.0 (m, 18 H, ArH), 8.8 (d, 4 H, pyridinium), 9.4 (d, 4 H, pyridinium).

1,1′-Bis(*p*-methylbenzyl)-4,4′-bipyridinium Bis(*p*-dodecylbenzenesulfonate) (Ia, Film No. 12 in Table III). The same reaction procedure as that for Ia (R′ = H) was applied to 1,1′-bis(*p*-methylbenzyl)-4,4′-bipyridinium dichloride to provide a colorless crystalline powder. Anal. Calcd for $C_{62}H_{84}N_2S_2O_6$: C, 73.23; H, 8.27; N, 2.76%. Found: C, 73.17; H, 8.30; N, 2.66%. IR (KBr) 1200, 1040 (–SO_3^-) cm^{-1}. ^{1}H NMR (DMSO-d_6) δ 0.5–2.0 (m, 46 H, $2C_{11}H_{23}$), 2.3 (s, 6 H, $2CH_3$), 2.5 (t, 4 H, $2CH_2$), 5.9 (4 H, $2CH_2$), 6.9–7.8 (m, 16 H, ArH), 8.8 (d, 4 H, pyridinium), 9.5 (d, 4 H, pyridinium).

***trans*-4,4′-Vinylenebis(1-benzylpyridinium) Bis(*p*-dodecylbenzenesulfonate) (Ib, Film No. 13 in Table III).** This colorless compound was synthesized in the same manner as for Ia (R′ = H), starting with *trans*-4,4′-vinylenebis(1-benzylpyridinium) dichloride, also prepared using *trans*-1,2-bis(4-pyridyl)ethylene instead of 4,4′-bipyridine. Anal. Calcd for $C_{62}H_{82}N_2S_2O_6$: C, 73.37; H, 8.09; N, 2.76%. Found: C, 73.25; H, 8.12; N, 2.71%. IR (KBr) 1180, 1040 (–SO_3^-) cm^{-1}. ^{1}H NMR (DMSO-d_6) δ 0.5–0.2 (m, 46 H, $2C_{11}H_{23}$), 2.5 (t, 4 H, $2CH_2$), 5.9 (s, 4 H, $2CH_2$), 7.0–7.9 (m, 18 H, ArH), 8.2 (s, 2 H, —CH═CH—), 8.5 (d, 4 H, pyridinium), 9.3 (d, 4 H, pyridinium).

Preparation of the Glass-Sandwiched Film. Finely divided crystals of viologen Ia,b were spread on a glass plate and melted quickly (above 140 °C), followed by the immediate tight covering with another glass plate and cooling to room temperature to afford an almost air-tight glass-sandwiched film ranging in thickness from 0.008 to 0.012 mm. All these operations were carried out in a glovebox filled with purified nitrogen.

The film thus prepared was transparent and almost colorless or pale yellow. The isotropic property of the film was checked with crossed polarizers.

Light Sources for Photochromic Measurements. The glass-sandwiched films were subjected to the 10-min irradiation by 366-nm UV light, obtained by passing the light from a 75-W high-pressure mercury lamp (Toshiba SHL-100UV) through a JASCO CT-10S monochromator. A 150-W xenon lamp, fitted with a Toshiba O-59 filter cutting the light below 590 nm, was employed for the visible irradiation on the film, which had been irradiated with the near-UV light and had developed color.

Since the viologens and related compounds described above belong to the same compound group as a herbicide Paraquat,[4] handling in an appropriate manner so as to avoid exposure is recommended.

Results and Discussion

Viologens Ia,b were synthesized starting with 1,1′-bis(benzyl or *p*-methylbenzyl)-4,4′-bipyridinium dichloride or *trans*-4,4′-vinylenebis(1-benzylpyridinium) dichloride by the anion-exchange reaction using an anion-exchange resin.

Fine powders of the viologens thus synthesized were heated just to their melting points (>140 °C) under nitrogen and then sandwiched between two glass plates to provide air-tight thin films free of oxygen. The glass-sandwiched films thus prepared, which were transparent and mainly isotropic, were subjected to near-UV irradiation (366 nm) from a 75-W high-pressure mercury lamp for 10 min, and the resulting absorbance increases in the visible region were recorded.

With the irradiation, initially colorless or pale yellow films gradually developed visible colors with almost linear increases of absorbances.

Figure 1 indicates typical absorption spectra obtained when the irradiation was stopped after 10 min.

It is recognized in this figure that absorption spectra based on the transmission of light, the measurements of which had been impossible for viologen crystals,[3] could be determined satisfactorily.

The shape and position of absorption maximum (ca. 600 nm, blue coloration) of curve 1 are quite similar to those of the radical cations derived from the conventional viologens in solutions[5] and viologen crystals,[3] and those of curve 2 are also consistent with the characteristics of the absorption spectra including a lot of the associated radical cations.[6] Moreover, EPR spectra exemplified in Figure 2 correspond exactly to the absorption change, so that it is confirmed that the radical cation was produced by the one-electron transfer from the counteranion to viologen dication, as demonstrated in the case of viologen crystals.[3] However, no appreciable differences in the IR

---

(4) Budavari, S., Ed. *The Merck Index*, 11th ed.; Merck & Co.: 1989; p 6984.

(5) Bockman, T. M.; Kochi, J. K. *J. Org. Chem.* **1990**, *55*, 4127–4135.

(6) Yamana, M.; Kawada, R. *Nippon Kagaku Kaishi* **1977**, *7*, 941–946.

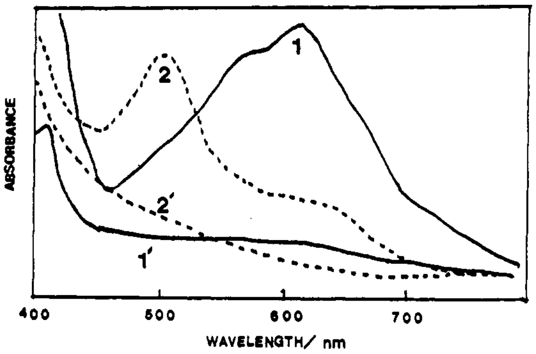


Figure 1. Typical visible absorption spectra for the glass-sandwiched viologen Ia,b films subjected to near-UV irradiation. Curves 1 and 1′ indicate the spectrum immediately after irradiation and that before irradiation or upon a 10 min standing at 70 °C after irradiation, respectively, in the case of R = 70% *n*- + 30% highly branched $C_{12}H_{25}$ and R′ = H (Ia); curves 2 and 2′ are those in R = *n*-$C_{14}H_{29}$. The measure of absorbance is arbitrary only to show the shapes of absorption spectra.

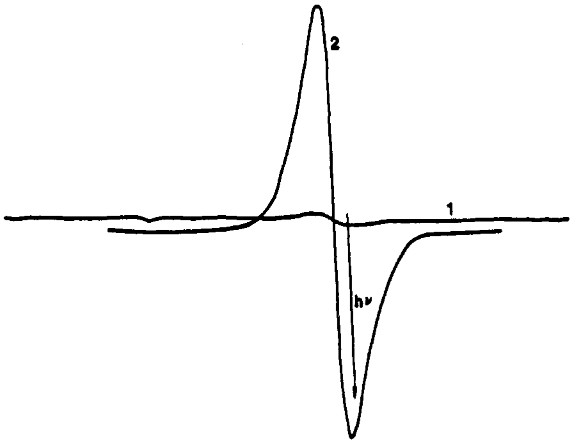
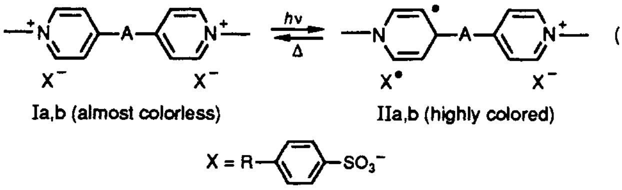


Figure 2. Typical EPR spectra for the glass-sandwiched viologen Ia,b films subjected to near-UV irradiation. Spectra 1 and 2 correspond to 1′ and 1 in Figure 1, respectively. Measurement conditions: field, 3290 G + 250 G; modulation 100 kHz; amplitude, 1.25 × 10; response, 0.01.

spectrum were recognized between before and after irradiation, presumably because the change in concentration is so small as to not be detectable.

Figure 1 also indicates that these increases in visible absorption induced by light can be recovered to the original states 1′ and 2′ upon 10 min of standing at 70 °C.

Such being the case, the reversible relation given in eq 1 may exist between the original viologen Ia,b and the



(1)

Ia,b (almost colorless)

IIa,b (highly colored)

X = R–C₆H₄–SO₃⁻

radical ion pair IIa,b produced as a result of irradiation. Namely, as for viologens Ia,b bearing long alkyl chains, reversible photoredox reactions, i.e., intense color development by the photon mode and bleaching of the developed color by the heat mode (redox photochromism), may take place in the absence of oxygen.

A typical example indicating the effect of temperature on bleaching of the color developed by light is given in Table I. It is recognized in this table that the initial bleaching rate (A/A_0) at λ_{max} increased rapidly with temperature, and in this case bleaching was almost complete at 70 °C in 1 min (expt no. 5). Irradiation of visible light above 590 nm on the colored film, however, provided little changes (expt no. 10), thereby suggesting that the back reaction was of the heat mode nature. It can be also seen in Table I that the presence of excess *p*-dodecylbenzenesulfonic acid in the film enhanced the bleaching rate significantly (expt no. 8), presumably due at least partly to a plasticizing effect; lack of $RPhSO_3^-$ caused the reverse effect (expt no. 9), as expected.

Table I. Effect of Temperature on Bleaching of the Color Developed in a Typical Viologen Film[a] by Near-UV Light

expt. no.	temp, °C	init bleaching rate[b] A/A_0 (613 nm), min^{-1}
1	30	0.03
2	40	0.24
3	50	0.66
4	60	0.72
5	70	0.99
6	80	1.00
7	90	1.48
8	70	2.10[c]
9	70	0.12[d]
10	Xe lamp[e]	0.01

[a] Viologen corresponding to curves 1 and 1′ in Figure 1 [R = 70% *n*- + 30% highly branched $C_{12}H_{25}$; R′ = H (Ia)]. [b] A_0: absorbance increase at 613.0 nm induced by light. A: Initial decrease of absorbance reduced to 1 min. [c] In the presence of a half-molar excess of *p*-dodecylbenzenesulfonic acid. [d] Viologen anions are composed of $RPhSO_3^-$–Cl^- in 3:1 molar ratio. [e] 150 W, >590 nm, 5 cm × 1 h.

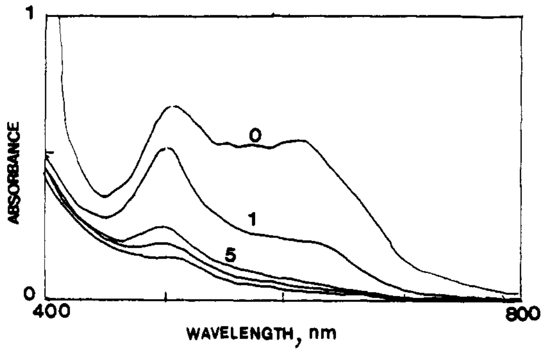


Figure 3. Typical change of the visible absorption spectra developed for viologen Ia,b films by light with heating at 70 °C. Absorption spectra are those for viologen Ia with R = 70% *n*- + 30% highly branched $C_{12}H_{25}$ and R′ = CH_3. Figures in the diagram denote standing times at 70 °C in minutes after irradiation.

It is also recognized in Figure 3 that the absorbance peak around 600 nm attributable to the monomeric radical cation, as mentioned above, decreases more rapidly by heating than the peak around 500 nm attributable to the associated ones does, indicating that the former is less stable thermally than the latter. This is a general tendency in the present study.

Effects of the kind of viologen Ia,b on the visible absorption changes induced by light, i.e., photochromic behavior by redox mechanism, as determined by transmittance, are summarized in Tables II and III.

It is known from Table II that both isotropic properties and photoredox behavior of the film are affected significantly by the chain length of R. Thus, as for Ia with R composed of an *n*-alkyl group alone, the values of the absorbance increase induced by UV irradiation were reduced to those for the 0.01-mm film thickness in order to prevent errors caused by slight deviations from 0.01-mm thickness. The corrected absorbance increase, i.e., photosensitivity, at λ_{max} around 500 nm appears to first become larger with an increase in carbon number to reach

Table II. Effect of Chain Length of R on Photochromic Behavior of Viologen Ia (R′ = H) Films[a]

film no.	R	abs increase[b] induced by light ca. 500 nm	abs increase[b] induced by light 610 nm	A/A_0,[c] min^{-1}	isotropic[d] property of film
1	n-C_6H_{13}	0.362 (504)[e]	0.190	0.36	transparent but a little anisotropic
2	n-C_8H_{17}	0.625 (505)[e]	0.318	0.45	transparent but a little anisotropic
3	n-C_9H_{19}	0.788 (506)[e]	0.421	0.48	transparent and isotropic
4	n-$C_{10}H_{21}$	0.787 (506)[e]	0.451	0.52	transparent and isotropic
5	n-$C_{11}H_{23}$	0.783 (507)[e]	0.441	0.46	transparent and isotropic
6	n-$C_{12}H_{25}$	0.690 (506)[e] 0.686 (506)[f]	0.379	0.43	transparent and isotropic
7	n-$C_{13}H_{27}$	0.571 (505)[e]	0.279	0.41	transparent and isotropic
8	n-$C_{14}H_{29}$	0.469 (505)[e]	0.200	0.41	transparent but a little anisotropic
9	n-$C_{15}H_{31}$	0.360 (505)[e]	0.179	0.37	transparent but a little anisotropic

[a] See Experimental Section. [b] Reduced to 0.01-mm film thickness. [c] See Table I. Values at λ_{max} around 500 nm. [d] Determined with crossed polarizers. [e] Values at λ_{max} indicated in parentheses. [f] Values after 50 cycles of irradiation and subsequent thermal bleaching (70 °C × 10 min).

Table III. Effect of R, R′, and A in Viologens Ia,b on Color Development by Light[a]

film no.	R	R′	A	abs increase[b] induced by light ca. 500 nm	abs increase[b] induced by light 610 nm	isotropic[c] property of film
10	mixture[e]	H	none	0.612 (507)[d]	0.522[f]	transparent and isotropic
11	$C_{12}H_{25}$[g]	H	none	0.242 (500)	0.793 (613)[d] 0.791 (613)[h]	transparent and isotropic
12	$C_{12}H_{25}$[g]	CH_3	none	0.672 (509)[d]	0.549 (612)[d]	transparent and isotropic
13	$C_{12}H_{25}$[g]	H	—CH=CH—	0.322 (535)[d]	0.107[f]	transparent and isotropic

[a] See Experimental Section. [b–d] See Table II. [e] Mixture of viologens with R = n-C_8H_{17}, n-$C_{10}H_{21}$, n-$C_{12}H_{25}$, and n-$C_{14}H_{29}$ in an equimolar quantity. [f] Shoulder. [g] 70% n- + 30% highly branched. [h] Values after 50 cycles of irradiation and subsequent thermal bleaching (70 °C × 10 min).

a maximum at C_{9-11} and then become gradually smaller with a further increase in carbon number. The value of the λ_{max} and the isotropic property of the film determined with crossed polarizers, which is considered to stand for amorphous character, varied corresponding to the photosensitivity change.

It can be concluded from these results that, within the scope of the present experimental conditions, the isotropic property of film Ia is gradually improved with an increase in carbon number to reach the best amorphous character at C_{9-11}, causing the highest photosensitivity. The amorphous character becomes worse, however, with a further increase in carbon number, presumably due to the crystallization effect of the long alkyl chains among each other.

It is also known from Table II that better isotropic films may afford larger values of A/A_0, consisting with the results in Table I.

The results summarized in Tables II and III differ from those obtained for viologen crystals, previously reported,[3a,b] particularly in that this kind of photochromism was observed for all viologen films investigated and associations of radical cations were much more marked especially in the case of R = n-C_nH_{2n+1} (Table II), indicating that the dicationic and counteranionic parts of the viologen molecule are situated next to each other at the sites permitting the general occurrence of the light-induced reaction shown in eq 1 and that the dications tend to lie at the sites, where the association of the radical cations produced therefrom could take place.

Mixing anions bearing varied R, which may also cause a plasticizing effects, is favorable in that it affords an isotropic film, in which the monomeric radical cation (λ_{max}, ca. 600 nm) may exist in a high content, and that a high photosensitivity is obtained (see curve 1 in Figure 1 and film nos. 10–12 in Table III).

Viologen Ib bearing the conjugated —CH=CH— group provided similar results. A typical example is given also in Table III (film no. 13).

In this case, however, the absorption peak around 400 nm found for the radical cation from Ia, as seen in Figures 1 and 3, appears to be red-shifted to 535 nm (red coloration) through extended conjugation.

As can be supposed from Tables II and III (expt nos. 6 and 11), viologen films of the present study could be subjected to at least 50 photochromic redox cycles, one of which was composed of the irradiation as described in the Experimental Section and subsequent 10 min standing at 70 °C.

Registry No. **1a** (R′ = H)(R = n-C_6H_{13}), 136893-34-0; **1a** (R′ = H)(R = n-C_8H_{17}), 136893-35-1; **1a** (R′ = H)(R = n-C_9H_{19}), 136893-36-2; **1a** (R′ = H)(R = n-$C_{10}H_{21}$), 136893-37-3; **1a** (R′ = H)(R = n-$C_{11}H_{21}$), 136893-38-4; **1a** (R′ = H) (R = n-$C_{13}H_{27}$), 136893-40-8; **1a** (R′ = H) (R = n-$C_{14}H_{29}$), 136893-42-0; **1a** (R′ = H)(R = n-$C_{15}H_{31}$), 136893-44-2; **1a** (R′ = Me)(R = n-$C_{12}H_{25}$), 136893-45-3; (E)-**1b** (R′ = H)(R = n-$C_{12}H_{25}$), 136893-47-5.