Photochromism of Spiropyrans in Organized Molecular Assemblies. Formation of *J- and* H-Aggregates of Photomerocyanines in Bilayers–Clay Matrices

Hideo Tomioka* and Toshio Itoh

Chemistry Department for Materials, Faculty of Engineering, Mie University, Tsu, Mie 514, Japan

Photochromism of a series of 1′-alkyl-3′,3′-dimethyl-6-nitro-8-alkanoyloxymethylspiro(2*H*-1-benzopyran-2,2′-indoline) derivatives (SPs) having different lengths of their alkyl chains has been investigated in didodecyldimethylammonium chloride–clay matrices; stable H (parallel type) and J (head-to-tail type) aggregates of photo-merocyanines are formed when SPs containing an appropriate length of alkyl chains are irradiated.

Many studies have been reported[1] on the photochromism of spiropyrans (SPs) reversibly forming photomerocyanines (PMCs) probably because of their potential usefulness as photoresponsive materials. *e.g.* reversible light filters, ornaments and reversible optical recording media. In order to obtain a spiropyran having the photochromic properties required for applications systems, one of the most frequently employed approaches has been to modify its structure. On the other hand, as it has become clear that the photochromic properties of spiropyrans are greatly improved by changing the surrounding matrices, studies have increasingly concentrated on this aspect. Thus, the photochromic behaviour of spiropyrans in polymer films,[2] monolayer[3] and bilayer membranes,[4,5] Langmuir–Blodgett multilayers,[6] liquid crystals[7] and micelles[8] have been studied and useful information concerning the factors which stabilize photomerocyanines in these molecular assembles is now available. As a part of our studies[9] on the photochromic behaviour of spiropyrans, we studied their photochromism in bilayer–clay matrices.

Spiropyrans which we employed in this study were 1′-alkyl(R^1)-3′,3′-dimethyl-6-nitro-8-alkanoyloxymethyl(R^2)-spiro(2*H*-1-benzopyran-2,2′-indoline) derivatives[3,6] having different lengths of alkyl chains and are roughly classified into four groups (SP*xy*00, SP*xy*12, SP*xy*22 and SP*xy*30) according to the chain length of R^2. A cast film consisting of the SP incorporated into a bilayer intercalated into a clay was prepared on a glass plate by slowly evaporating a solution of the SP and compounds[10] resulting from intercalation of didodecyldimethylammonium chloride (DDAC) into montmorillonite (Mont) in $CHCl_3$. The film became strongly coloured probably owing to formation of the PMC immediately upon exposure to UV light from a 500 W high-pressure Hg lamp at room temperature, and the colour faded upon heating in the dark to reform the SP. The photochromic properties were conveniently studied in the usual way using UV spectroscopy; the thermal isomerization of PMC to SP in the films exhibited first-order kinetics. Computer-generated correlations of plots of ln $(A_t - A_\infty)$ *vs.* time were linear over at least two half-lives with correlation coefficients $r>0.99$.

In Table 1, we summarize λ_{max} values and the thermal decoloration rates (k) of PMC. For comparison, λ_{max} observed in EtOH and n-hexane are also listed. The results show that the length of the alkyl chains in the R^1 and R^2 substituents affected the λ_{max} of the PMC and its thermal stability. Thus, in the SPxy00 series, the λ_{max} of the PMC shifted to longer wavelengths in going from SP0100 to SP1800, with a corresponding decrease in thermal stability. This can be interpreted as indicating that SPs having longer alkyl chains tend to be immobilized in a less polar site of DDAC bilayers presumably as a result of hydrophobic interactions between the long alkyl chains in SP and DDAC.[5] Essentially similar trends were observed with the three other series of SPs, but new trends also emerged in these longer alkyl chain systems. Thus, in the SP*xy*12 series, λ_{max} shifted to longer wavelength in going from SP0112 to SP1012, but a new, rather sharp absorption appeared at a shorter wavelength when longer R^1 alkyl chains were introduced. Thus, PMC1612 exhibited a new absorption at 493 nm with a half-width ($\Delta_{1/2}$) of 40 nm in addition to the absorption at 570 nm due to the monomeric PMC. Similarly, SP1812 showed a new absorption at 497 nm ($\Delta_{1/2}$ 46 nm). On the other hand, a new absorption appeared at a longer wavelength in SPs bearing much longer alkyl chains. Thus, SP1822 as well as SP1830 exhibited new sharp absorption bands at 615 ($\Delta_{1/2}$ 29 nm) and 617 nm ($\Delta_{1/2}$ 35 nm), respectively, when exposed to UV light. The properties of these new coloured forms exhibiting new absorption bands were quite different from those of monomeric PMC. Thus, they were not photobleached: the colour did not fade even

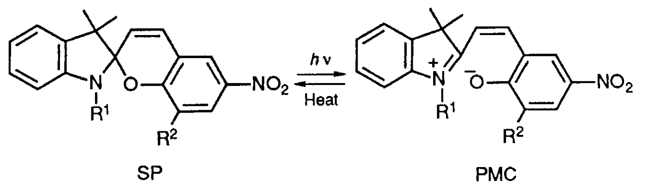

Table 1 Photochromism of spiropyrans (SP) in DDAC–Mont cast film[a]

			DDAC–Mont film			λ_{max}/nm[b]	
SP	R^1	R^2	λ_{max}/nm[b]	10^4k/s^{-1} [c]	T/°C	EtOH	n-C_6H_{14}
0100	Me	H	552	1.21	37	540	580
1800	$(CH_2)_{17}Me$	H	574	19.3	37	542	576
0112	Me	$CH_2OCOC_{11}H_{23}$	550	2.90	37	542	620
1012	$(CH_2)_9Me$	$CH_2OCOC_{11}H_{23}$	580	11.2	37	547	576
1612	$(CH_2)_{15}Me$	$CH_2OCOC_{11}H_{23}$	493(H),570	17.5,25.9	60	547	577
1812	$(CH_2)_{17}Me$	$CH_2OCOC_{11}H_{23}$	497(H),570	16.7,25.0	65	549	580
0822	$(CH_2)_7Me$	$CH_2OCOC_{21}H_{43}$	578	12.7	37	546	578
1822	$(CH_2)_{17}Me$	$CH_2OCOC_{21}H_{43}$	615(J),566	16.0,16.5	70	553	579
0130	Me	$CH_2OCOC_{29}H_{59}$	565	1.50	37	543	576
1230	$(CH_2)_{11}Me$	$CH_2OCOC_{29}H_{59}$	576	4.58	37	548	577
1830	$(CH_2)_{17}Me$	$CH_2OCOC_{29}H_{59}$	617(J),566	5.35,2.35	70	548	578

[a] The SP/DDAC–Mont molar ratio is 1/2. [b] Absorption maximum of PMC. [c] The first-order rate constants for the thermal isomerization of PMC to SP at the indicated temperature.

Table 2 Arrhenius parameters for the thermal decoloration reaction in DDAC–Mont cast film

SP	PMC	E_a/kJ mol^{-1}	S/J mol^{-1} K^{-1}
0100	Monomer	58.2	−141.0
1812	H-aggregate	298.0	+573.4
1822	J-aggregate	406.0	+1247

upon prolonged irradiation with visible light corresponding to their absorption maximum. Moreover, they did not fade appreciably at 37 °C, at which temperature the other monomeric PMCs faded at reasonable rates, but they did undergo decoloration at measurable rates when heated at >60 °C to reproduce the SP, which regenerated the new coloured forms upon UV irradiation.

The observations strongly suggest that these new absorptions are ascribable to aggregates of PMCs which are reported to be formed[5,6] occasionally in organized molecular assemblies and we assign the absorption around 500 nm to H (parallel type) aggregates and that around 610 nm to J (head-to-tail type) aggregates of PMC. Activation parameters of the thermal process were determined in the usual way and are summarized in Table 2; there is a large difference between monomeric and aggregated PMCs. A noticeably high activation energy and highly positive activation entropy for J and H PMCs are in good agreement with those obtained[5,6] in other molecular assemblies which are known[11] to be characteristic features for the thermal entropy-driven decoloration process of aggregates. Owing to this large difference in E_a, the rate difference between the monomeric and aggregated PMCs becomes more pronounced at lower temperatures. At 37 °C the decoloration of H-PMC1812, for instance, was calculated to be 1.2×10^5 times slower than that of the monomeric form, and that of J-PMC1822 was 1.07×10^7 times slower.

In conclusion, we have found that bilayer membranes immobilized in clays provide convenient matrices in which PMCs can aggregate to give J and H PMCs depending on the length of the alkyl chains. Very sharp new UV–VIS absorption bands and the high thermal stability of these aggregates should make them attractive materials for recording media.

This work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture, Japan and by the Mazuda Foundation.

Received, 5th December 1990; Com. 0/05482H

References

1 For a pertinent review, see: R. C. Bertelson, in *Photochromism*, ed. by G. H. Brown, Wiley-Interscience, New York, 1971, ch. III.
2 K. Horie and I. Mita, *Kobunshi*, 1985, **34**, 448; G. Smetz, *Adv. Polym. Sci.*, 1983, **50**, 17.
3 D. A. Holder, H. Ringsdorf, V. Deblauwe and G. Smetz, *J. Phys. Chem.*, 1984, **88**, 716.
4 B. Nadolski, P. Uznanski and M. Kryszewski, *Macromol. Chem., Rapid Commun.*, 1984, **5**, 327.
5 T. Seki and K. Ichimura, *J. Chem. Soc., Chem. Commun.*, 1987, 1186; T. Seki and K. Ichimura, *Macromolecules*, 1987, **20**, 2958; T. Seki and K. Ichimura, *J. Photopolym. Sci. Technol.*, 1988, **1**, 254; 1989, **2**, 147; T. Seki, K. Ichimura and E. Ando, *Langmuir*, 1988, **4**, 1068; T. Seki and K. Ichimura, *Macromolecules*, 1990, **23**, 31; T. Seki and K. Ichimura, *J. Phys. Chem.*, 1990, **94**, 3769.
6 E. Ando, J. Miyazaki, K. Morimoto, H. Nakahara and K. Fukuda, *Thin Solid Films*, 1985, **133**, 21.
7 V. Ramesh and M. M. Labes, *J. Am. Chem. Soc.*, 1987, **109**, 3228.
8 J. Sunamoto, K. Iwamoto, M. Akutagawa, M. Nagase and H. Kondo, *J. Am. Chem. Soc.*, 1982, **104**, 4904.
9 H. Tomioka and T. Itoh, *Nippon Kagaku Kaishi*, 1988, 1031; H. Tomioka, S. Murata and F. Inagaki, *J. Photopolym. Sci. Technol.*, 1989, **2**, 143; H. Tomioka and F. Inagaki, *J. Photopolym. Sci. Technol.*, 1989, **2**, 83.
10 T. Kunitake, A. Tsuge and N. Nakashima, *Chem. Lett.*, 1984, 1783.
11 M. A. Lauffer, *Entropy-Driven Processes in Biology*, Springer-Verlag, Berlin, 1975, ch. 9.