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Thermal Stability of Merocyanine Form in Spiropyran/Silica composite Film

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Abstract

Three types of spiropyran derivatives introduced octadecyl group (SP18), hydroxyl group (SPOH) and carboxyl group (SPCOOH) were synthesized and were dispersed into various matrices such as chloroform solvent, polymethylmetacrylate (PMMA)/acetone solution and poly(perhydrosilazane) (PSz)/*m*-xylene solution. Thermal stability of photomerocyanine isomer (PMC-form) in spiropyran derivatives dispersed in silica composite film was studied. Intensity at λ_{max} of PMC-form in silica composite film keeps at initial values in long time except for SP18. PMC-form of SPOH and SPCOOH forms intermolecular hydrogen bonding between hydroxyl or carboxyl group and oxygen atom in silica matrix. Therefore, PMC-form of SPOH and SPCOOH in silica composite film is stabilized dramatically.

Keywords: Photochromism; Spiropyran; Poly(perhydrosilazane); Optical memory

1. Introduction

Light-induced reversible transformation between two isomers having different absorption spectra is referred to as photochromism [1-4]. Two isomers differ from one another not only in the absorption property but also in refractive indices, dielectric constants, oxidation-reduction potentials, and geometrical structures. Therefore, upon irradiation with an appropriate wavelength of light, these properties can be reversibly switched. One of the most widely studied features of photochromism is the intense absorption of the colored form in the visible region, which is of great importance for practical applications of photochromic compound in optical memory, photooptical switching and display, because photochromic compound can represent two digital codes "0" or "1" as different absorption spectra. Among many types of organic photochromic compounds, the chemistry of spiropyran has been extensively investigated with special

regards to their remarkable properties [5-8]. The photochromism of spiropyrans has a potential usefulness as optical memory and photooptical switching [9-14]. Upon UV irradiation, spirocarbon–oxygen (C–O) bond of the colorless spiro isomer (SP-form) is broken and the subsequent isomerization leads to colored opened isomers called photomerocyanine isomer (PMC-form), as shown in Scheme 1. However, in the last decades, the application of spiropyran in optical memory and optical switches has been hindered by the short half-life time of the colored PMC-form, which reverts thermally to the ring-closed colorless spiropyran. Various methods to stabilize the PMC-form have been developed [15-22].

In this study, three types of spiropyran derivatives introduced octadecyl group (SP18), hydroxyl group (SPOH) and carboxyl group (SPCOOH) were synthesized and were dispersed into various matrices such as chloroform solvent, polymethylmetacrylate (PMMA)/acetone solution and poly(perhydrosilazane) (PSz)/*m*-xylene solution. Thermal stability and thermal bleaching were investigated in the dark after UV irradiation. Especially, this work is focused on PSz/*m*-xylene solution, because PSz converts into colorless transparent silica film under the ambient condition [23,24].

2. Experimental

2.1. General

All reagents for synthesis and PSz/*m*-xylene solution were purchased from Tokyo Kasei Co., and Clariant Japan Co., and used without further purification. The chemical structure of synthesized compounds was characterized by ^1H nuclear magnetic resonance spectrum (^1H -NMR) and fast atom bombardment mass spectrum (FAB-MS). ^1H -NMR spectra were recorded on a Bruker DPX400. FAB-MS were recorded on a JEOL JMS-GC mate IIR. The emission line ($\lambda = 365\text{nm}$) from Hg lamp was used to generate the PMC-form. UV-Vis. absorption spectroscopic study was performed with Shimadzu UV-2200 spectrophotometer.

2.2. Sample preparation

Three types of spiropyran derivatives were dissolved in chloroform, acetone solution with PMMA and *m*-xylene solution with PSz. Concentrations of spiropyran derivatives were 10^{-4} M in chloroform, 4 wt% in PMMA/acetone solution and 2×10^{-2} M in PSz/*m*-xylene solution, respectively. Thin films were prepared by spin-coating (4000 rpm) on a glass substrate. In the case of SP/PSz composite film, it had been carried out through a day at r.t. in order to convert from PSz to silica according to the reaction

equation shown in Scheme 2.

2.3. Synthesis

General procedure for the synthesis of intermediates and spiropyran derivatives is illustrated in Scheme 3. Each spiropyran derivative was prepared by the method in the literatures [25,26].

2.3.1. 1-(2'-Hydroxyethyl)-2,3,3-trimethylindolenium iodide

To a solution of 2,3,3-trimethyl-3H-indole (1.30 g, 8.16 mmol) in 2-butanone 10 ml were added 1-iodoethanol (1.40 g, 8.16 mmol) with stirring. The mixture was heated at reflux for 48 h and cooled to precipitate a solid. The solid was separated by filtration, washed with cold acetone to give a white-red solid (2.43 g, 7.34 mmol) which was used without further purification. Yield 81.0%, mp 145.0-145.5 °C, FAB-MS (M⁺) 331.

2.3.2. 1'-(2''-Hydroxyethyl)-3',3'-dimethyl-6-nitrospiro[2H-1-benzopyran-2,2'-indoline]

To a solution 1-(2'-hydroxyethyl)-2,3,3-trimethylindolenium iodide (1.00 g, 3.02 mmol) in 15 ml methanol were added piperidine (2,3 drops) and then 5-nitrosalicylaldehyde (0.50 g, 3.02 mmol) with stirring. The mixture was heated at reflux for 4 h and cooled. After evaporation of the solvent, the residue was purified by column chromatography (eluent chloroform) to give a white-red crystal (0.37 g, 1.06 mmol). Yield 35.0 %, mp 150.0-150.3 °C, FAB-MS (M⁺) 352, ¹H NMR (400 MHz, CDCl₃) δ=1.15 (s, 3H), 1.24 (s, 3H), 3.34-3.42 (m, 1H), 3.52-3.56 (m, 1H), 3.67-3.72(m, 1H), 3.72-3.76 (m, 1H), 5.82 (d, *J*=10.2 Hz, 1H), 6.65 (d, *J*=7.5 Hz, 1H), 6.86 (d, *J*=10.2 Hz, 1H), 6.87 (t, *J*=7.5 Hz, 1H), 7.10 (d, *J*=7.5 Hz, 1H), 7.17 (t, *J*=7.5 Hz, 1H), 7.62 (d, *J*=2.7 Hz, 1H), 7.69 (d, *J*=2.7 Hz, 1H) ppm.

3. Results and discussion

3.1. Photochromic behavior in solution

Absorption spectra of SP-forms used here were quite similar independent of the kinds of substituent. Main absorption peaks of SP-form appeared around at 260 and 350 nm. These absorption bands were assigned to π - π^* transitions of chlomene and of indoline rings, respectively. Figure 1 shows UV-Vis. absorption spectra of spiropyran derivatives after UV light irradiation with 365 nm in chloroform solution. Upon UV light irradiation, the solution changed from colorless to deeply purple and a broad absorption peak assigned to PMC-form appeared around at 580 nm.

The λ_{max} of PMC-form of spiropyran derivatives in various matrices are shown in Table 1. In the case of silica matrix, the λ_{max} of PMC-form of spiropyran derivatives showed the hypsochromic shift (blue shift) in the visible region. Nadolski et al has pointed out that in PMC-form, the ground state is more polar than the excited state and a polar solvent tends to stabilize the ground state, resulting to hypsochromic shift. In addition, they have also pointed out that the thermal stabilization rate slows down because the potential barrier of the isomerization reaction from PMC-form to SP-form becomes higher [27]. From the experimental results mentioned above, it seems that silica matrix is polar moiety comparing to other matrices. Richardt has introduced the transition energy expressed in kcal/mol in order to explain the solvent effect on λ_{max} of pyridium-*N*-phenoxide betain dye in various solvents. This parameter is referred as the E_T values, which are related with λ_{max} by following equation [28].

$$E_T(\text{kcal/mol}) = 2.859 \times 10^4 / \lambda_{\text{max}}(\text{nm})$$

Figure 2 shows linear plot of λ_{max} of PMC-form versus E_T parameters of various solvent. E_T values of PMMA and silica matrices were estimated to 42 kcal/mol and 49 kcal/mol from λ_{max} of PMC-form, respectively. Therefore, it is concluded that silica matrix forms polar moiety like as alcohol solvent.

3.2. Thermal stability

Figure 3 shows time dependence on absorption intensity at λ_{max} of PMC-form in various matrices in the dark at 25 °C. In the case of chloroform solution and PMMA matrix, intensity at λ_{max} of PMC-form decreases rapidly. Absorption intensity in silica matrix, on the other hand, keeps initial values for long period except for SP18. It is suggested that PMC-form molecules of SPOH and SPCOOH form intermolecular hydrogen bonding between a proton generated hydroxyl or carboxyl group and oxygen atom in silica matrix. Molecular vibration toward back reaction is inhibited by hydrogen bonding. Therefore, PMC-form of SPOH and SPCOOH in silica matrix is stabilized dramatically. Life-half times of intensity at λ_{max} of various PMC-form molecules are summarized in Tab. 2. Life-half times of SPOH and SPCOOH in silica matrix were estimated to be about 8×10^7 and 3×10^7 sec, respectively. Thermal stability of PMC-form in this study is about 10^5 times higher than that of other photochromic compounds reported in the last few decades.

3.3. Thermal bleaching

Thermal bleaching of PMC form is evaluated with relative intensity (I/I_0) at λ_{max} before and after heat treatment in the range between 30 and 130 °C for 1 min in the dark.

Figure 4 shows the thermal bleaching of PMC forms the thermal bleaching of SPCOOH and SPOH in silica matrix. Relative intensity of PMC form of SPCOOH was decreased rapidly by heat treatment above 40 °C. On the other hand, the degree of decreasing in that of SPOH is prevented remarkably under 100 °C. Thermal bleaching of PMC-form of SPOH around at 100 °C is about twice as high as that of SPCOOH. PMC-form of SPOH forms not only intermolecular hydrogen bonding between proton in OH group and oxygen in silica matrix but also intramolecular hydrogen bonding between proton in OH group and O⁻ generated by cleavage of spirocarbon–oxygen bond, as shown in Fig. 5. On the other hand, only intermolecular hydrogen bonding forms because of steric hindrance of carboxyl group and structural vibration of resonance COO. Therefore, it is concluded that remarkable bleaching stability of PMC-form of SPOH in silica matrix is attributed by strong hydrogen bonding. Stabilized PMC-form of SPOH converts completely into SP-form upon visible light irradiation.

4. Conclusions

Three types of spiropyran derivatives (SP18, SPOH and SPCOOH) were synthesized. Silica matrix is forms polar moiety like as alcohol solvent. PMC-form of SPOH and SPCOOH in silica matrix is stabilized dramatically. Life-half times of SPOH and SPCOOH in silica matrix were estimated to be about 8×10^7 and 3×10^7 sec, respectively. PMC-form molecules of SPOH and SPCOOH form intermolecular hydrogen bonding between a proton generated hydroxyl or carboxyl group and oxygen atom in silica matrix. Thermal bleaching of PMC-form of SPOH is about twice as high as that of SPCOOH. Thermal bleaching of PMC-form hardly does not occur up to about 80 °C. It is concluded that PMC-form of SPOH in silica matrix has high thermal stability and thermal bleaching and the application potential for optical memory and photooptical switching.

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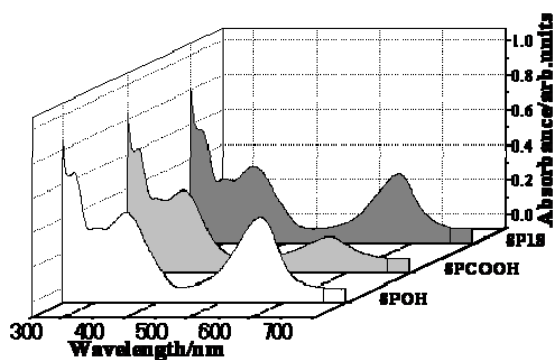


Fig. 1. UV-Vis. absorption spectra of PMC-form in chloroform solution.

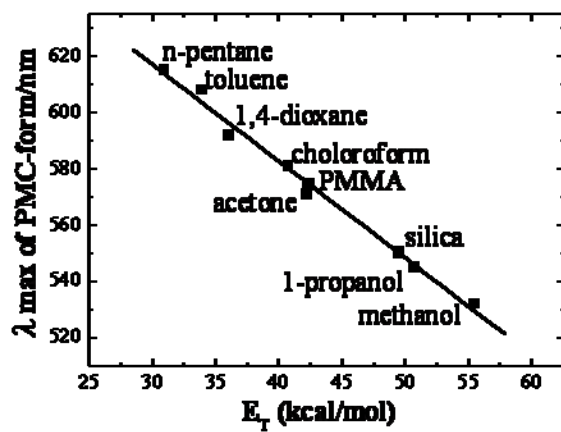


Fig. 2. Plots of λ_{max} /nm of PMC-form vs. E_T value for SP18 in various solvents.

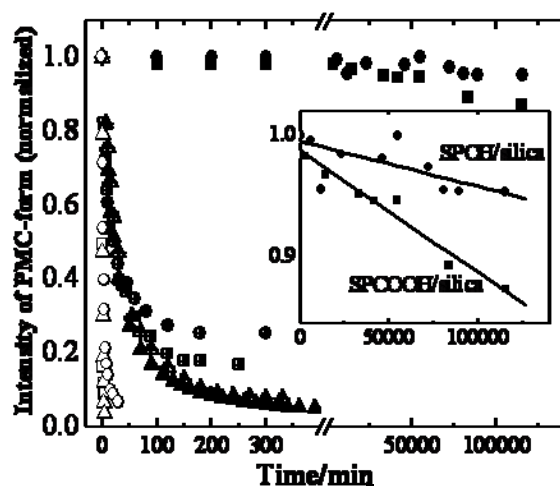


Fig. 3. Time dependence on absorption intensity at λ_{max} of PMC-form in various matrices in the dark at 25 °C; Δ (open) SP18/chloroform, (cross) /PMMA, (filled) /silica, \square (open) SPCOOH/chloroform, (cross) /PMMA, (filled) /silica, \circ (open) SPOH/chloroform, (cross) /PMMA, (filled) /silica.

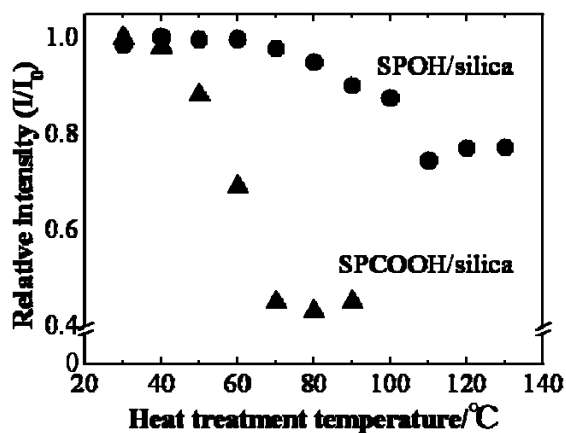


Fig. 4. Thermal bleaching of PMC-form of SPOH and SPCOOH in silica matrix.

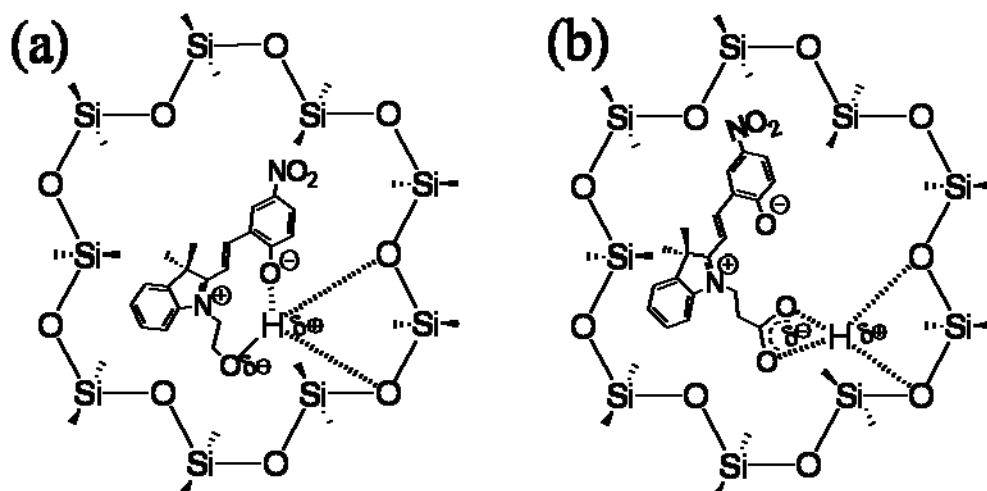
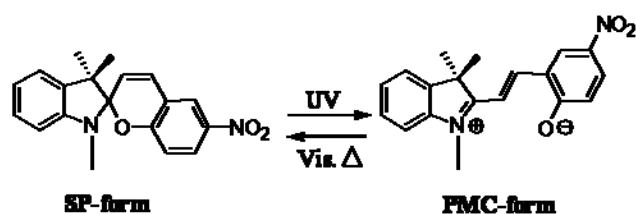
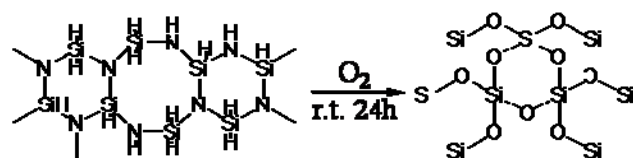


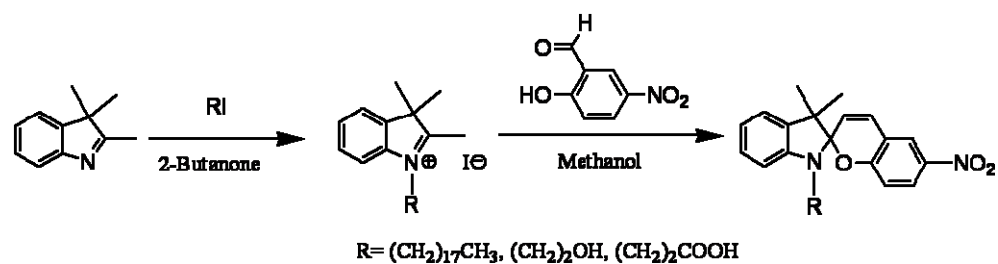
Fig. 5. Schematic representation of PMC-form of SPOH and SPCOOH in silica matrix; (a) SPOH, (b) SPCOOH.



Scheme 1. Structural change of spiropyran during photochromism.



Scheme 2. Interconversion between poly(perhydrosilazane) and silica.



Scheme 3. Synthetic procedure of spiropyran derivatives.

	$\lambda_{\text{max}}/\text{nm}$		
	Chloroform	PMMA	Silica
SP18	580	575	550
SPOH	570	560	540
SPCOOH	580	570	545

Table 1. λ_{max} of PMC-form of spiropyran derivatives in various matrices.

	$\tau_{1/2}/\text{sec}$		
	Chloroform	PMMA	Silica
SP18	84	1740	1900
SPOH	163	1260	8×10^7
SPCOOH	47	1529	3×10^7

Table 2. Life-half time of PMC-form of spiropyran derivatives in various matrices.