12H, ring), 1.35, 1.31, 1.30 (three s, 27H, *t*-butyl).

3,6-Bis-(2-piperidyl)piperazine-2,5-dione·2TFA (11)[11].
A solution of **10** (0.260 g, 0.424 mmol) and 1 : 1 mixture
of TFA/CH_2Cl_2 (4 mL) was stirred for 2 hr at 0 °C. The
resulting mixture was concentrated *in vacuo*, and NMM
(0.154 mL, 1.40 mmol) and 0.1 M AcOH/*i*-PrOH (5.20 mL)
were added into the resultant. After heating at refluxing te-
mperature for 2 hr, a solid appeared. The solid was filtered
and recrystallized from methanol-ether to give the salt **11**
(0.040 g, 36%).

mp 204-206 °C (dec.); ^{1}H NMR (DMSO-d₆) δ 4.28 (m, 2H,
C_3-H, C_6-H), 3.40-3.22 (m, 4H, C_2'-H, C_2''-H, C_6'-H$_e$, C_6''-H$_e$),
2.80 (m, 2H, C_6'-H$_a$, C_6''-H$_a$), 1.85-1.33 (m, 12H, C_3'-H, C_4'-H,
C_5'-H, C_3''-H, C_4''-H, C_5''-H); MS (FAB) 281 (mono cation);
Anal. Calcd for $C_{18}H_{26}F_6N_4O_6$: C, 42.52; H, 5.15; N, 11.02,
found: C, 42.08; H, 5.08; N, 10.61.

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11. Compound **6, 7, 8, 9** and **10** are the mixture of diaste-
    reomers.

Thermal Bleaching Reactions of Spirooxazine in Ethanol and PMMA

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It is well known that reactions of photochromic compounds
dopped in amorphous solids follow non-single exponential
kinetics even if their elementary steps are unimolecular pro-
cesses which lead to first order reaction in solutions. Exam-
ples of deviations from first order kinetics behavior in poly-
mer matrices are thermal bleaching reaction of photochromic
compounds of azobenzenes,[1~4] indolinospirans,[5~7] and stilbe-
nes.[4,8]

In an attempt to provide explanation of the departures
from the first order kinetics of the thermal reactions in gla-
ssy matrices, distribution of local free volume,[2~4,8] distribu-
tion of activation energy,[5,6] and stretched exponential model
(Kohlraush-Williams-Watts (KWW))[9,10] were suggested. Ac-
tually, the first two models are similar in their expression
and in considering the distribution of a physical parameter
to dispersive kinetic model for hole burning.[11,12] Both the
thermal fading reaction of photochromic compounds and non-
photochemical hole burning (NPHB) (for above ~15 K) occur
via thermally activated processes and are affected by the
inhomogeneity of the surroundings of guest molecules lead-
ing to nonlinear reaction. However, the former process goes
with the structral change of guest molecules in the ground
electronic states while the latter process in the excited states
without the structral change of guest molecules. Therefore,
there is some difficulties in using the local free volume mo-
del to explain the burning process. Therefore, we expect
that in the analysis of the non-single exponential kinetics
occuring in polymers, using the dispersive kinetic model is
more general way than using the local free volume model.

In this work we investigated the matrix effect on the ther-
mal bleaching reaction of spironaphthooxazine using the dis-
persive kinetics model which is utilized to explain the persi-
stent spectral hole burning.

Experimental

1,3-dihydro-1,3,3-trimethyl-spiro[2H-indol-2,3'-[3H]naphth
[2,1-b][1,4]oxazine] (spironaphthooxazine, NSO) was pur-
chased from Tokyo Kasei Kogyo Co. and used without fur-
ther purification. Polymethylmethacrylate (PMMA) and spec-
trograde ethanol were purchased from Aldrich. Thin films
of NSO/PMMA was prepared by dissolving polymer plus
NSO in toluene and chloroform, respectively, and allowing
the solvent to evaporate from a specially designed evapora-
tion tray. After drying in air, the films were dried in a va-
cuum oven for several days at temperatures above the glass
transition temperatures of polymer involved. The weight per-
cent of NSO in the film was approximately 3%.

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Notes
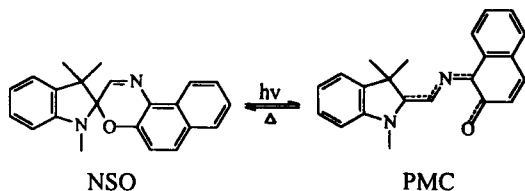
Scheme 1.

Absorption spectra of NSO in ethanol were recorded at various temperatures using a Scinco UVS-2030 spectrophotometer. The photocoloration and thermal bleaching experiments were performed at various temperatures using a temperature controllable cell holder. The photocoloration of the samples was achieved using 337 nm laser pulses from a N_2 laser (Laser photonics LN-1000). The changes of concentration of photomerocyanine (PMC) form of NSO have been monitored by recording the transmittance of the 594 nm light from a Yellow He-Ne laser (Edmund G3941) using a photomultiplier (R928). By using an oscilloscope (HP54600B), time traces of the transmission after the cessation of photoirradiation were collected and transferred to a personal computer and analysed. The laser and oscilloscope were triggered by a function generator (Wavetek 145).

Analysis of Kinetics of Thermal Fading Reaction

Upon UV irradiation, colorless NSO experience a reversible photochemical transformation to the colored PMC form.[13] This involves cleavage of the C-O bond of the oxazine ring followed by a rotation of a part of the molecule to achieve coplanarity, according to Scheme 1. Then the open PMC thermally fade to the closed NSO.

In order to explain the non-exponential thermal fading of PMC, we used a simple first-order reaction rate equation $d[PMC]/dt = -k[PMC]$. Here k is the rate constant and [PMC] represents the concentration of PMC at time t. In Arrhenius equation, the rate constant k is expressed as $k = A \exp[-E/RT]$ where A is frequency factor and E is activation energy for the thermally activated reaction. In case of reactions consisting of many decoupled additive contribution the temporal concentration of PMC is the convolution of a distribution function $g(E)$ and the individual decay function.[6,11,12]

$$[PMC] = \int g(E) \exp[-k(E)t] \, dE \qquad (1)$$

Since the energy of a PMC dopped in an disordered environment depends on a large number of internal coordinates which are subject to random fluctuation, it is a realistic assumption that the activation energy is subject to a Gaussian distribution. Then Eq. (1) can be converted to

$$[PMC] = [PMC]_0/(2\pi)^{1/2}\sigma \int_0^{+\infty}$$
$$\exp[-(E-E_m)^2/2\sigma^2] \exp[-k(E)t] \, dE \qquad (2)$$

where $[PMC]_0$ is the concentration of PMC at the end of the UV irradiation, σ and E_m are the standard deviation and mean of the activation energy, respectively. Although Eq. (2) is derived for the non-exponential reactions, it can be applied to the reactions in solution which follows first order
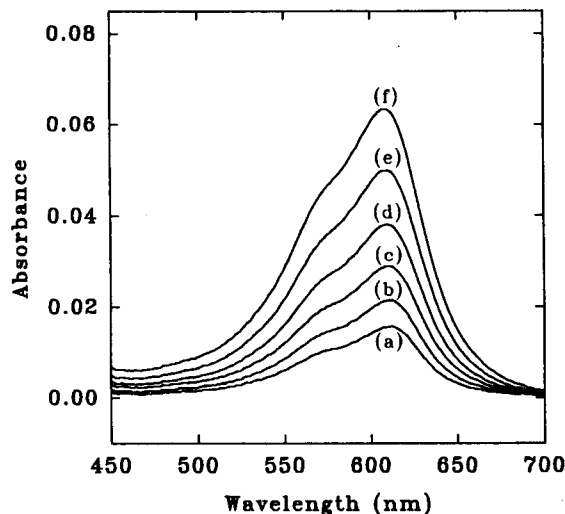

Figure 1. The absorption spectra of the colored species PMC in ethanol (2.0×10^{-3} M) at several temperatures; (a) 15 ℃, (b) 25 ℃, (c) 35 ℃, (d) 45 ℃, (e) 55 ℃ and (f) 65 ℃.

reaction by assuming the standard deviation of the activation energy is negligible compared to the average activation energy.

Results and Discussion

Figure 1 shows the absorption spectra of NSO in ethanol (2.0×10^{-3} M solution) at various temperatures. Since thermal equilibrium constant between NSO and PMC is very small ($\sim 10^{-5}$) at room temperature,[14] the absorbance in the visible region is small. The visible absorption band gradually grows as the temperature increases. From the Figure 1, the standard enthalpy change for NSO→PMC reaction in ethanol was estimated to be 23.2 kJ/mol.

The first step of the analysis of the kinetic data is to convert the transmission raw data into the normalized absorbance data, which is straight forward calculation after determining the transmission at times at $t = 0$ and $t \approx \infty$. Figure 2A shows that the thermal back reaction of PMC in ethanol follows the first-order kinetic law at various temperatures. The parameters of the least-square fitting to the first order kinetics at different temperatures are given in Table 1. From the Table 1, the calculated frequency factor and activation energy of the reaction are 2.36×10^{13} s^{-1} and 77.2 kJ/mol, respectively. Because the frequency factor is close to kT/h = 6.2×10^{12} s^{-1}, the activation entropy cannot be much in excess of 10 J/mol·K. From the equation of $\Delta H^{\neq} = E_a - RT$, the activation enthalpy change of 74.8 kJ/mol was estimated. Figure 2B represents best fits obtained with Eq. (2) for a Gaussian width of the distribution of activation energy 1 J/mol which is very small compared to its mean value. The solid curves are theoretical fits and the noisy curves are experimental data. The same mean activation energy and same pre-exponential factor obtained from Table 1 were used for all different temperatures. The good agreements between theoretical fits and experimental data can consistently be interpreted in terms of a single temperature-activated process in the temperature ranges studied.
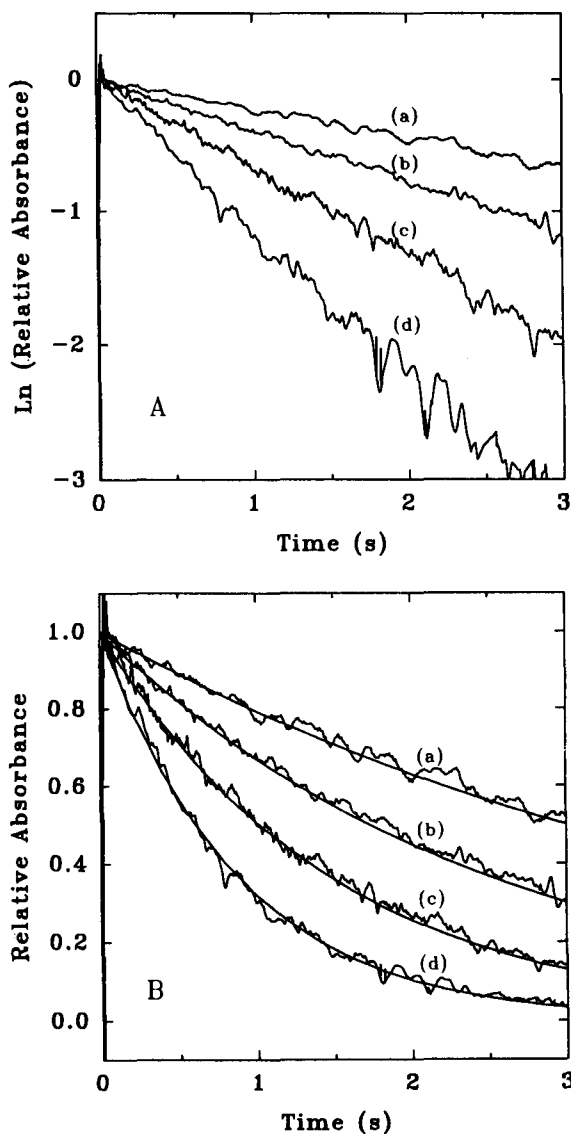
Notes

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Figure 2. (A) Experimental thermal bleaching kinetics of NSO in ethanol at various temperatures; (a) 15 ℃, (b) 20 ℃, (c) 25 ℃, and (d) 30 ℃. (B) Theoretical fits to the experimental data (A) with Eq. (2). For all different temperatures, same fitting parameters were used. The parameters used were 77.2 kJ/mol for activation energy, 2.36×10¹³ s⁻¹ for pre-exponential factor, and 1 J/mol for standard deviation; (a) 15 ℃, (b) 20 ℃, (c) 25 ℃, and (d) 30 ℃.

Figure 3. (A) Experimental thermal bleaching kinetics of NSO in PMMA at various temperatures; (a) 15 ℃, (b) 20 ℃, (c) 25 ℃, and (d) 30 ℃. (B) Theoretical fits to the experimental data (A) with Eq. (2). The same fitting parameters were used for all different temperatures. The parameters used were 4.43×10¹³ s⁻¹ for pre-exponential factor and 79.3 kJ/mol for mean activation energy. The standard deviation of the activation energy is given in Table 2. (a) 15 ℃, (b) 20 ℃, (c) 25 ℃, and (d) 30 ℃.

Table 1. The thermal bleaching rate of the colored form PMC in ethanol at various temperatures

온도 (℃)	15	20	25	30
k (s⁻¹)	0.231	0.383	0.676	1.204

Table 2. The Gaussian widths of the distribution of activation energies for thermal bleaching reaction of the colored form PMC in PMMA at several temperatures

온도 (℃)	15	20	25	30
σ (kJ/mol)	2.80	2.75	2.70	2.60

Experimental results for the normalized absorbance of PMC in PMMA (T_g=105 ℃) as a function of time at various temperatures are given in Figure 3A. It clearly shows the deviations from the first-order kinetics at every temperature studied. Figure 3B shows the plots based on Eq. (2). The
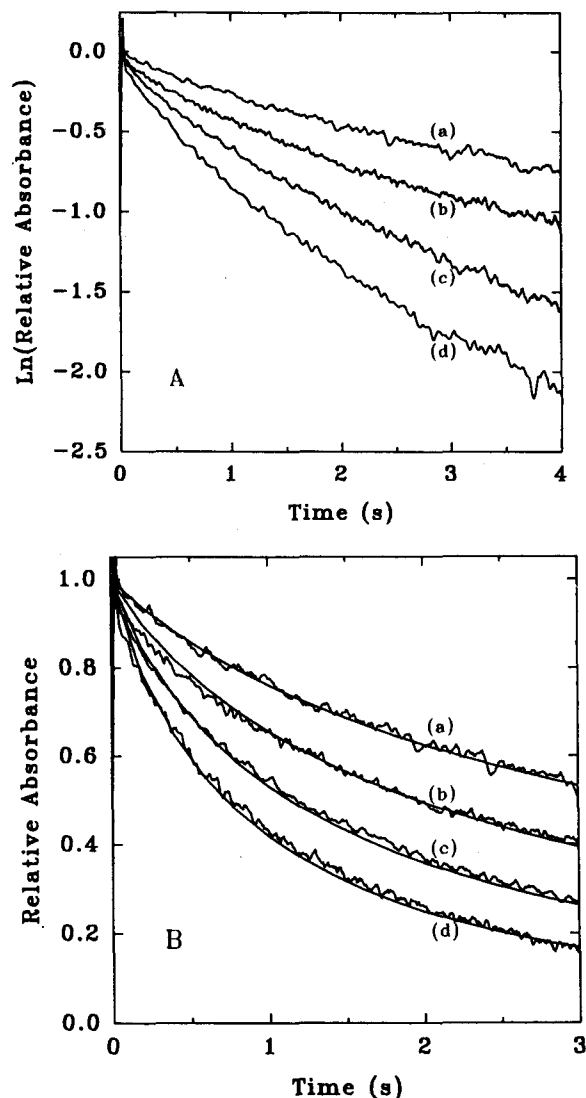
solid curves are best fits for an average activation energy 79.3 kJ/mol and for a frequency factor 4.43×10¹³ s⁻¹. The fitting procedure was performed under the assumption that both average activation energy and frequency factor are independent of temperatures. The only temperature dependent

parameter used in the fitting is the standard deviation of the activation energy which decreases with temperature as indicated in Table 2. The fact that the standard deviation of activation energy in PMMA is about 2000 times larger than those used for NSO in ethanol indicates that thermal reaction is greatly influenced by the microscopic heterogeneity of molecular environments around PMC. The wide distribution of the activation energy may be understood in terms of the inherent disorder of the polymer. The photochromic compounds trapped in a sparse and widely separated set of local potential minima, which is inherent in polymer and coupled to the guest molecules, cannot thermally access to lowest minima at temperatures below T_g. As temperature increases, the parameter σ decreases. At last the width σ at T_g is expected to be the same with that in solution resulting in the first-order reaction as observed in azo compounds.[15]

In summary, the thermal fading reaction of NSO follows the first-order reaction in ethanol solution while it shows large departure from the single exponential decay in PMMA polymer. The deviation from the first order reaction of the monomolecular photochromic reaction in PMMA was explained using disorder of the matrix which causes the thermodynamic parameters to fluctuate around average value.

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A Facile Preparation of α-Amino-β-Methoxydiazines through, the Lithianation Followed by Amination
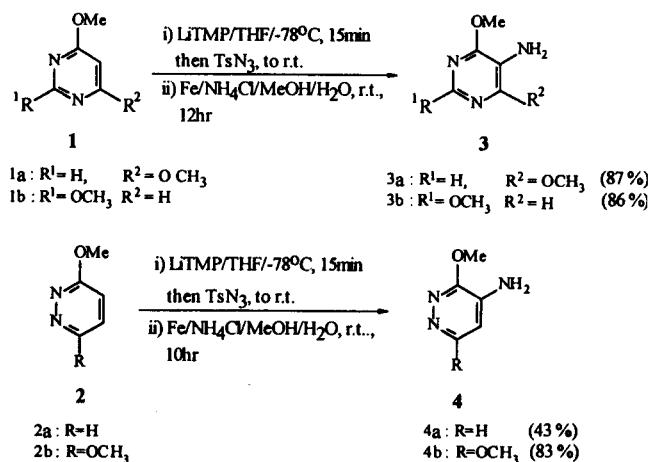
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α-Amino-β-methoxydiazines are common synthons for the construction of a variety of diazine fused heterocycles by a^2, d^0/a^1, d^n combination.[1] Several routes for preparation have been known by reaction of α-amino-β-chlorodiazine with sodium methoxide followed by Hofmann rearrangement,[2] amination of methoxydiazine by potassium amide-liquid ammonia,[3] treatment of dichlorodiazine with ammonia solution followed by the reaction with sodium methoxide.[4] However, these methods require harsh reaction conditions and result in low yields and selectivities. In connection with our project for the synthesis of diazine heterocycles, we devised an alternative method for the preparation of the α-amino-β-methoxydiazines, which included the regiospecific introduction of nitrogen functionality to methoxydiazine by directed ortho-metalation.[5] While some examples for introducing carbon electrophiles to the methoxydiazines by orthometalation have been known,[6] to the best of our knowledge, amination of diazines by the orthometalation has not been reported. We report herein a facile one-pot preparation of α-amino-β-methoxydiazines *via* the orthoazidation followed by a reduction.

Result and Discussion

Compound **1a** was treated with LiTMP in THF and the resulting lithiated compound was reacted with tosyl azide. This amination condition seems to be essential for regiospecific and efficient generation of **3a**. When TMEDA (tetramethylethylenediamine) was used as a chelating agent only a trace amount of **3a** could be obtained. The reaction mixture was treated subsequently with an excess amount of Fe/NH$_4$

1a: R^1=H, R^2=OCH$_3$
1b: R^1=OCH$_3$ R^2=H

3a: R^1=H, R^2=OCH$_3$ (87%)
3b: R^1=OCH$_3$ R^2=H (86%)

2a: R=H
2b: R=OCH$_3$

4a: R=H (43%)
4b: R=OCH$_3$ (83%)

Scheme 1.