

Persistent Spectral Hole Burning of Resazurin and Resorufin in Poly(methyl methacrylate) in the Presence and Absence of *N,N,N',N'*-Tetramethyl-*p*-phenylenediamine

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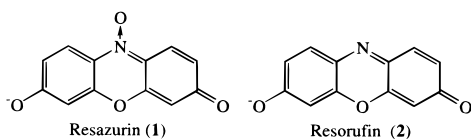
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Two similar anionic dyes, resazurin and resorufin, were used for persistent spectral hole burning (PSHB) experiments at 20 K in polymer matrixes in the presence and absence of *N,N,N',N'*-tetramethyl-*p*-phenylenediamine (TMPD). The effects of TMPD addition on PSHB phenomena were observed with regard to hole width, hole area (relative efficiency for hole formation), and thermal stability of the holes. The differences between the trends in PSHB of these two dyes are also discussed.

Introduction

Ionic dyes are often used as indicators for their “environments”, such as polarity, proton concentration, and hydrogen-bond-donating/accepting properties of the media. In the end of the 1950s, Kosower^{1a,b} established a solvent polarity parameter, *Z* value,^{1a} using *N*-alkylated pyridinium derivatives. In his early paper, he measured the *Z* value of many organic solvents using a pyridine *N*-oxide.^{1b} We have turned our attention to this *N*-oxide moiety. The characteristics of the *N*-oxide absorption in the UV region were investigated in detail by Kubota.² The absorption band is blue-shifted markedly with the increase in solvent polarity and hydrogen-bond formation. The dye mainly used in this study is the resazurin anion (**1**), which has an *N*-oxide moiety and has a structure in the remaining part similar to that of a famous ionic dye resorufin anion (**2**).



Among numerous ionic organic dyes, resorufin **2** has been studied by many photochemical and photophysical investigators.^{3–14} Contrary to resorufin **2**, a similar dye, resazurin **1**, has seldom been studied in photochemistry and photophysics¹⁵ except for biological uses^{16,17} as a pH indicator and an indicator for milk decomposition by the use of the unstable moiety *N*-oxide. But **1** would have the possibility of being utilized as a better indicator because this *N*-oxide moiety gives good solvatochromic information^{1b} on the “microenvironment” of the dye molecule. Microenvironment does not mean “bulk” physical properties but physical properties in “the very neighborhood” of the dye molecule. Among many physical properties, matrix polarity is frequently studied. Persistent spectral hole burning (PSHB)^{18–20} has become an important subject for many physical and chemical investigators. PSHB is a phenomenon that can be seen in several organic dye/crystalline or glassy matrix systems at low temperatures. Though the lowest electronic

absorption bands of some organic dyes in crystalline solids are very narrow in width at low temperatures, the absorption bands of the same dyes in glassy matrixes are broad even at low temperatures because of the inhomogeneity of their environments. The whole spectrum is broad in glassy matrixes, but the spectrum of each single molecule should still be narrow inside the broad band. So monochromatic light irradiation can photochemically excite molecules at the specific sites (frequency selectively) and shift molecules in some specific spectral sites to other sites. After irradiation, a dip is observed around the irradiated frequency in the absorption band. This partial decrease in absorption at the irradiated frequency is called PSHB. It is not only one of the promising methods for realizing ultrahigh-density optical storage but also an important method for studying photochemical properties of dyes at low temperatures.^{19,20} The first PSHB paper of **1**²¹ was reported in 1996 by the present authors, though a lot of work on PSHB of **2** has been carried out since the end of 1970s.³

We report in the present study that PSHB can be used for evaluating the environmental changes around the dye molecules in polymer matrixes induced by the addition of *N,N,N',N'*-tetramethyl-*p*-phenylenediamine (TMPD). It means that these ionic dyes can distinguish the difference in their environments in the presence or absence of TMPD and that these changes can be seen in PSHB measurements. The phenomena obtained in this study are novel and interesting and may give us some new interpretation for the basic photophysical properties of the dyes. The effect of TMPD addition has been seen in the changes in hole width, relative efficiencies of hole formation, and thermal stability of holes.

The reason why we took notice of these ionic dyes is the easiness of electron transfer, both donating and accepting in their excited states. The ease of electron transfer is not good for practical use because it causes their instability in the excited states, but it is favorable to providing good microenvironmental indicators. In past several decades, photoinduced charge transfer is one of the very important subjects in which many photochemists are interested. Many investigations have been published in regard to the electron transfer of ionic dyes in solution. For example, Vauthey et al.⁴ estimated rate constants for electron transfer between oxazine 118 or rhodamine 6G and electron donors, such as TMPD, from free radical yields and backward

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electron-transfer efficiency. Legros et al.⁵ measured the electron-transfer processes from the naphtholate anion and its derivatives (and neutral donors) to several electron-accepting substrates (aromatic cyano compounds, aromatic halogeno compounds, perylene, other aromatic compounds, and **2**). They showed that the quenching constants, k_q , were highly influenced by the hydrogen bond strength because the electron-transfer process occurred with the break of the hydrogen bonds between naphtholate anions and solvent molecules or between the acceptors and solvent molecules. Recently, Neumann et al.¹⁵ used **1** in the presence of aliphatic amines and observed **1** to be photoreduced to **2**. Their results suggest that the ionic dyes have high capability for electron transfer and are interesting as electron donors/acceptors.

Some groups have reported persistent spectral hole formation of resorufin **2** in alcoholic glasses and polymers, and most of them have attributed the hole of resorufin to be a "nonphotochemical" one. In the 1980's, Kokai et al.^{9a} found the importance of hydrogen bonds, and Völker's group⁸ investigated completely "hydrogen-bond-enhanced" PSHB of resorufin mainly in glycerol and ethylene glycol. They also investigated PSHB of **2** in PMMA.^{8a} They reported that there are two kinds of resorufin molecules, one is "free", and the other is "hydrogen-bonded". The latter is lying in the red region compared with the free molecules. In the early 1990s, Schellenberg et al.¹⁰ investigated the external pressure effect, and Renn et al.¹⁴ measured the external electric field effect (Stark effect). By measuring the temperature dependence of **2** in alcoholic and nitrile solvents, Flamigni et al.¹² found that the hydrogen bonds of **2** at low temperatures remarkably differed from those at room temperature. From their study, such ionic dyes could be thought to be highly sensitive to their environment through hydrogen bonds.

In the present study, an anionic dye, resazurin sodium salt **1**, is used for PSHB measurements and the change in the very neighborhood of the dye could be observed with the addition of a neutral, electron-donating molecule, TMPD. The hole width, the relative efficiency of hole formation, and the thermal stability of the holes was measured. The results for **1** are compared to those for a dye with a similar skeleton, resorufin sodium salt **2**, to investigate the relationships between their PSHB properties and the molecular structure. From these results, **1** can be thought of as a better indicator for their "microenvironments" than the dye with a similar skeleton, **2**.

Experimental Section

(1) Materials. Two kinds of anionic dyes, resazurin (3*H*-phenoxazin-3-one, 7-hydroxy, 10-oxide) sodium salt (**1**) (Aldrich Chemical) and resorufin (3*H*-phenoxazin-3-one, 7-hydroxy,) sodium salt (**2**) (Aldrich Chemical), were used as supplied. Spectral grade solvents, methanol and acetone (Dojin), were used without further purification. Three kinds of polymers, poly(methyl methacrylate) (PMMA), poly(vinyl alcohol) (PVA), and poly(vinyl acetate) (PVAc) were used after reprecipitation.

(2) Preparation of Polymeric Films. The samples were prepared with the solvent casting method. A dye solution in a basic mixture of acetone-methanol (1:1 v/v)³ was added to a solution of PMMA in acetone, PVA in water, or PVAc in methanol and dried at 40–45 °C to avoid decomposition of dye molecules. The concentration of sodium hydroxide was 5 mmol kg⁻¹ in each sample, which was added in order to maintain the basic condition for dyes. In the case of ref 3, hexafluoro-2-propanol was added to the solution of **2**, but in our case, it was not added because the addition of hexafluoro-2-propanol caused

the protonation and collapse of the **2** molecule. Van den Berg et al.^{8a} used CHCl₃ as a solvent for PMMA film preparation, but we did not use it because this halogenated hydrocarbon formed a "contact ion pair"²² with TMPD. The effect of an alkaline compound (sodium hydroxide) is very important because no stable samples in PMMA can be made without the addition of sodium hydroxide due to the protonation of dye anions.

(3) Measurements of PSHB Spectra. Each polymer film was set in an optical cryogenic refrigerator (Sumitomo SRD204) and cooled to 20 K for hole burning. The spectral holes were burnt at each temperature with a line-selectable He-Ne laser (Electro Optics LSTP-1010) with an intensity of 15–250 $\mu\text{W}/\text{cm}^2$ at 611.9 or 632.8 nm for the case of **1** and $\sim 700 \mu\text{W}/\text{cm}^2$ at 594.3 nm for the case of **2**. Hole spectra were measured as an intensity change in the transmitted light with a 1-m monochromator (Jasco, CT-100C) detected with a photomultiplier (Hamamatsu, R943-02) and a lock-in amplifier (Jasco, LA126W). The details of the equipment have been described elsewhere.^{25a}

The samples of **1** were irradiated at 632.8 nm (except for 1/PVA, 611.9 nm) and the samples of **2** were irradiated at 594.3 nm by using a line-selectable He-Ne laser (Electrooptics). After the hole formation, the sample was heated to an annealing temperature, held for 15 min, and then cooled to 20 K to measure the hole spectrum again. The annealing temperature was raised stepwise to examine temperature dependencies of the hole width and hole area.

For the PSHB measurements below 20 K, the samples were set in a liquid helium flow-type cryostat (Oxford, CF1204), cooled to 4.2–17 K, and irradiated with an Ar⁺-laser (Coherent, Innova 70)-pumped ring dye laser (Coherent, 699-01) using DCM as the lasing dye.

Absorption spectra at room temperature were measured with a double-beam UV-visible spectrophotometer (Jasco, UVIDE-660).

Results

(1) Hole Burning at 20 K. Absorption spectra (at room temperature and at 20 K) and zero phonon holes (with/without TMPD) were measured for **1** and **2** molecularly dispersed in PMMA films. Absorption spectra of 1/PMMA films at room temperature with and without TMPD are shown in Figure 1. No significant spectral change of **1** is induced by the addition of TMPD. Typical hole spectra of 1/PMMA are shown in Figure 2 for the absence and presence of TMPD. The difference spectra of 1/PMMA and 2/PMMA after hole burning without TMPD are given in Figure 3. An antihole (an increased part in the spectra corresponding to the frequency of photoproducts) is noticed in the red region for **1**. Since the burned wavelength is on the longer (red) side of the absorption band of **1**, the antihole of **1** is formed on the opposite side from the absorption maximum. On the other hand, the antihole of **2** is observed on the shorter (blue) side.

The increases in hole width and hole area during laser irradiation are shown in Figures 4 and 5, respectively. With the addition of TMPD, a typical width of the observed hole increased from 2.5 to 3.6 cm⁻¹ for **1**, and this increase was also observed for **1** in all polymers. These typical values are listed in Table 1. The increase in hole width with TMPD addition was also observed for 2/PMMA. The hole width for 2/PMMA in the absence and presence of TMPD is 2.5 and 5.0 cm⁻¹, respectively. The relative efficiency of hole formation

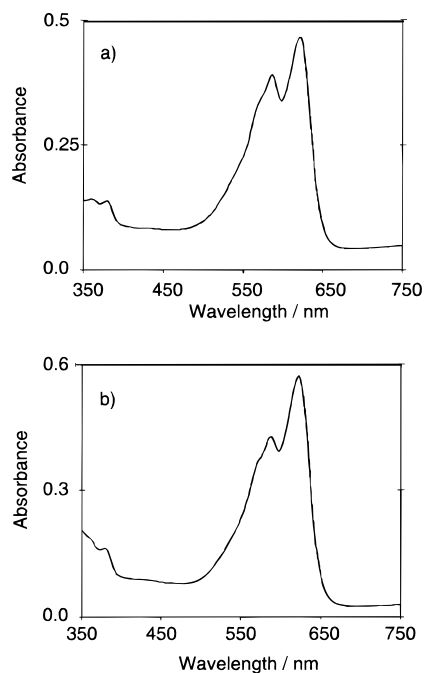


Figure 1. Absorption spectra of 1/PMMA films (2.8×10^{-4} mol kg $^{-1}$, ~ 1 μ m thickness) at room temperature: (a) without TMPD and (b) with TMPD.

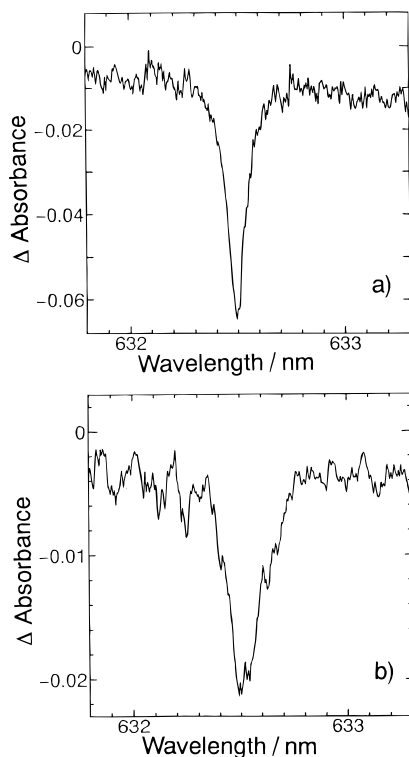


Figure 2. Typical hole spectra (difference spectra) of 1/PMMA at 20 K after 15 min irradiation: (a) without TMPD and (b) with TMPD.

decreased with the addition of TMPD only for 1/PMMA but was not significantly affected by the addition of TMPD for 2/PMMA.

(2) Temperature-Excursion Experiments. The changes in hole width and hole area measured at 20 K during the temperature-excursion experiments for the holes burned at 20 K are shown in Figures 6 and 7, respectively. The increase in hole width with the increase in excursion temperature is suppressed in the presence of TMPD for 1/PMMA but is enhanced for 2/PMMA (Figure 6). The decrease in hole area

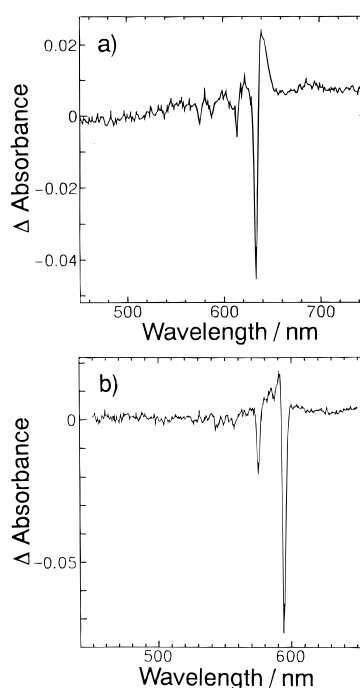


Figure 3. Change in absorption spectra of 1/PMMA and 2/PMMA with hole burning in the absence of TMPD at 20 K: (a) 1/PMMA; (b) 2/PMMA.

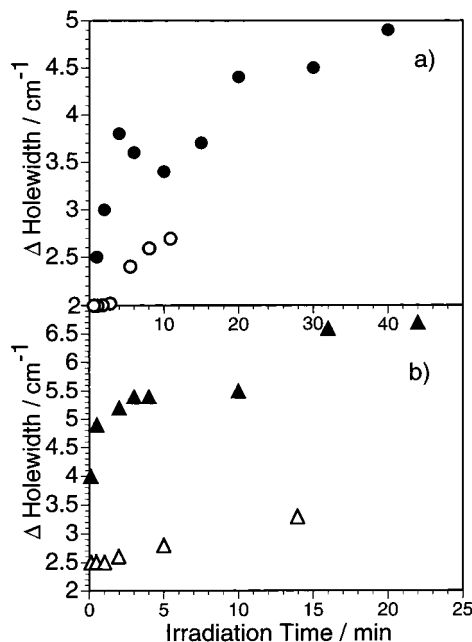


Figure 4. Change in hole width with hole burning at 20 K in the absence (○, △) and presence (●, ▲) of TMPD: (a) 1/PMMA with 210 μ W cm $^{-2}$ He-Ne laser; (b) 2/PMMA with 340 μ W cm $^{-2}$ He-Ne laser.

is suppressed in the presence of TMPD for 1 but is not affected by the presence of TMPD for 2 (Figure 7). With the addition of TMPD, the thermal stability of the spectral hole is improved for 1/PMMA but is not significantly affected by the addition of TMPD for 2/PMMA.

(3) Burning-Temperature Dependence of Hole Width for 1/PMMA. The burning-temperature dependence of hole widths was measured for 1/PMMA at 4.2–17 K. The hole width decreases with decreasing burning temperature, and at all temperatures measured, the hole width is larger in the presence of TMPD than in its absence. It means that the total dephasing time, T_{total} , is shortened by the presence of TMPD. T_{total} is

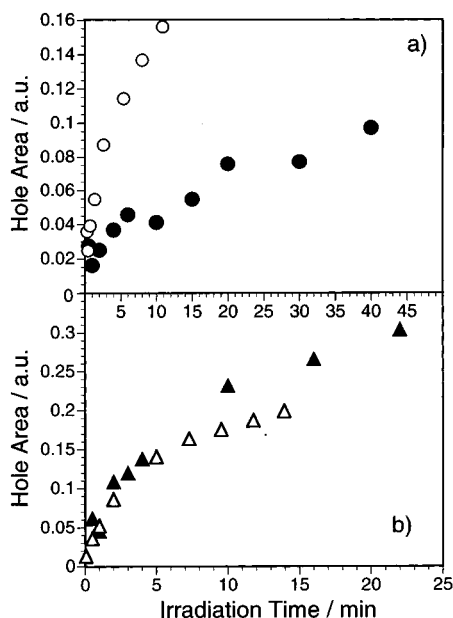


Figure 5. Hole-area change with hole burning at 20 K in the absence (○, △) and presence (●, ▲) of TMPD: (a) 1/PMMA with 210 μW He-Ne laser; (b) 2/PMMA with 340 $\mu\text{W cm}^{-2}$ He-Ne laser.

TABLE 1: Typical Hole Widths^a of Resazurin 1 in PVA, PVAc, and PMMA Films^b

	PVA ^c	PVAc ^d	PMMA
without TMPD			
concn of 1 (mol kg ⁻¹)	3.4×10^{-4}	1.2×10^{-4}	2.8×10^{-4}
hole width (cm ⁻¹)	2.9	4.2	2.5
with TMPD			
concn of 1 (mol kg ⁻¹)	6.8×10^{-4}	1.2×10^{-4}	2.8×10^{-4}
concn of TMPD (mol kg ⁻¹)	1.0×10^{-2}	6.5×10^{-3}	6.8×10^{-3}
hole width (cm ⁻¹)	6.9	7.6	3.6

^a These values are not extrapolated to "zero-burning time". ^b Irradiation wavelengths were 632.8 nm except for PVA (611.9 nm). ^c Irradiated for 10 min with 2.5 mW/cm². The zero phonon holes were almost saturated and broadened under this condition. ^d Irradiated for 2 min with 2.0 mW/cm². The zero phonon hole were already saturated under this condition.

defined as follows.

$$1/T_{\text{total}} = 1/(2T_1) + 1/T_2 \quad (1)$$

where T_1 is the lifetime of the excited state and T_2 is the pure dephasing time. The relationships of T_{total} to the observed hole width extrapolated to zero burning energy (Γ_{hole}) are described as^{25b}

$$\Gamma_h = (\Gamma_{\text{hole}} - \Gamma_1)/2 \quad (2)$$

$$\Gamma_h = 1/(\pi c T_{\text{total}}) = (1/(\pi c))\{1/(2T_1) + 1/T_2\} \quad (3)$$

where Γ_h is the homogeneous width, $\Gamma_1 = 0.3 \text{ cm}^{-1}$ is the constant due to the apparatus limit, and c is the light velocity.

The change in homogeneous width Γ_h with burning temperature T is shown in Figure 8.

Discussion

(1) Preparation of Samples. Since all samples were dried at $\sim 45^\circ\text{C}$, which is below the T_g (glass-transition temperature) of PMMA, a small portion of solvents, i.e., methanol and acetone, must have remained in PMMA films. Since the hydrogen bond enhances the PHB efficiency of 2, as suggested

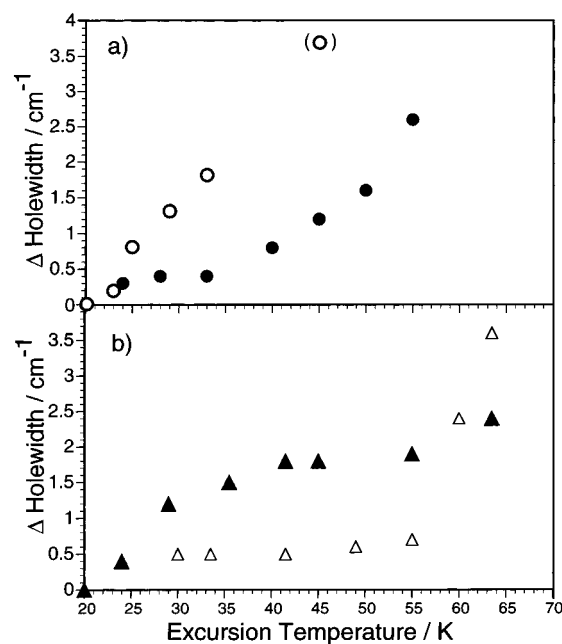


Figure 6. Change in hole width with temperature excursion for a hole burned at 20 K in the absence (○, △) and presence (●, ▲) of TMPD: (a) 1/PMMA; (b) 2/PMMA

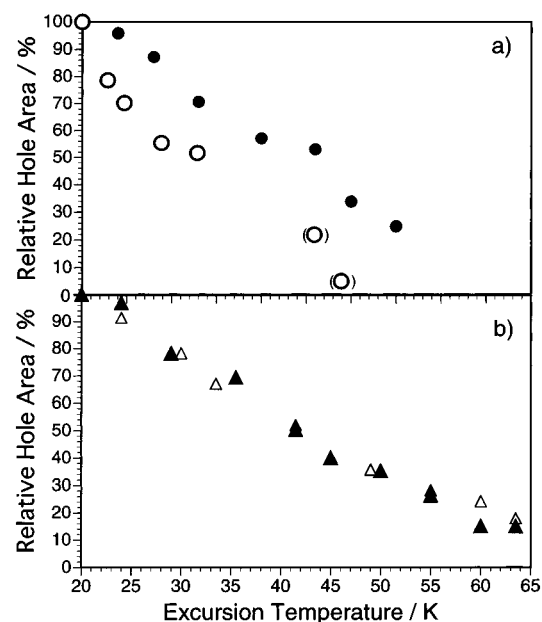


Figure 7. Change in hole area with temperature excursion in the absence (○, △) and presence (●, ▲) of TMPD: (a) 1/PMMA; (b) 2/PMMA.

by the results of van den Berg et al.⁸ and Kokai et al.,⁹ the residual solvents are thought to have assisted hole burning in our cases also. The reason why we did not use chloroform (the solvent in ref 8) is to avoid its interaction with TMPD molecules. These halogenated hydrocarbons are thought to form charge-transfer (CT) complexes with TMPD.²² All cases of ours and other groups except ref 8 used basic solutions of the dyes (in our case for both 1 and 2, in others for 2). Excess sodium cation is not needed to remove the counteranion from the dye anion. PMMA is not usually thought of as a highly electron-donating or -accepting molecule, but the absorption band of the Ni-complex^{23a} in PMMA shows that PMMA has a moderate coordination ability to Ni^{23b} as strong as that of frozen acetone.^{23a} Acetone, methanol, and ethyl acetate (as a low

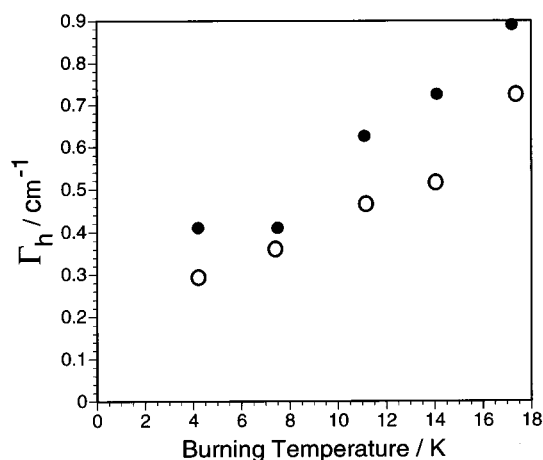


Figure 8. Burning-temperature dependence of the hole width for 1/PMMA with (●) and without (○) TMPD.

molecular-weight model for PMMA) give the following values for Swain's solvent parameters:²⁴ $A = 0.25, 0.75$, and 0.21 (A : anion-solvating tendency) and $B = 0.81, 0.50$, and 0.59 (B : cation-solvating tendency), respectively. From these results, the PMMA matrix seems to prefer cations instead of its surroundings compared with anions and methanol seems to prefer anions instead of its surroundings.

(2) Hole Burning at 20 K. As is seen in Figure 3, there is no significant new band appearing in the absorption spectrum after hole burning (in the UV–visible region), and main products appear on the red side of the hole for **1** and the blue side of the hole for **2**. These photoproducts correspond to the same dye molecules (**1** or **2**, respectively) found in the different sites. In ref 8a, the absorption bands of hydrogen-bonded **2** molecules are red-shifted from those of free **2** molecules in the UV–visible spectrum. On the other hand, absorption bands of *N*-oxide molecules are known to be blue-shifted with hydrogen-bond formation.^{2,26} The results that the “hydrogen-bonded” **2** molecules have a higher efficiency for hole formation than the “free” molecules^{8a} agree with our results of antihole formation on the blue side for **2**, suggesting hole formation for “hydrogen-bonded” **2** molecules. The antihole position on the red side of the hole for **1** and on the blue side for **2** can be explained by the higher tendency of hole formation for the “hydrogen-bonded” molecules compared with the tendency of the “free” molecules and the weakening or breaking of hydrogen-bonds between the dyes and the surroundings by hole burning. Thus, the observed hole is supposed to be formed by the change in the hydrogen bonds between the dye molecule and the solvent molecule not only for **2** but also for **1**. No significant change was observed in the antihole formation with or without TMPD.

The $S_0 \rightarrow S_1$ absorption maximum of **1** is bathochromically shifted with a decrease in solvent polarity, though that for **2** was not shifted much. This means that **1** is a better indicator for the microenvironment than **2** is.

By the addition of TMPD, the changes in hole profiles during hole burning for **1** and **2** become completely different from each other except for the increase in hole width. The increases in hole width with the addition of TMPD are observed for both **1** and **2** (Figure 4), which means decreases in total dephasing time T_{total} . The values of $1/T_{\text{total}}$ are on the order of 10^{11} s^{-1} . These values are too small for T_1 , so the hole width is thought to be controlled mainly by the pure dephasing time T_2 .

Van den Berg et al.^{8b} used triethylamine in their PSHB experiments for **2** as a “hydrogen-bond inhibitor” and found that the “hydrogen-bonded species” decreased and “free mol-

TABLE 2: Fluorescence Lifetimes (τ_f) of Dyes 1 and 2

dye	τ_f at room temp/ns	τ_f at low temp/ns	source
1	1.2 ± 0.1 (in methanol, at 25 ± 1 °C)		15
2	4.9 (in alcohol, ^a at 293 K)	2.9 (in alcohol, ^a at 87 K)	12
	5.5 (in nitrile, ^b at 293 K)	4.1 (in nitrile, ^b at 87 K)	12
		~ 8 (in PMMA, PE) ^c	8e
		3.9 (in C ₂ H ₅ OH, at 1.5 K)	11
		4.2 (in C ₂ H ₅ OD, at 1.5 K)	11
		3.5 (in glycerol, at 1.5 K)	11
		4.8 (in PVB, ^d at 77 K)	14

^a Ethanol/methanol (4:1 v/v). ^b Propionitrile/butyronitrile (4:5 v/v).

^c The extrapolated value from PHB (at 0.3–4.2 K). PE: polyethylene (high density). ^d Polyvinylbutyral.

ecules” increased in the excitation spectra with the addition of triethylamine. If TMPD worked in the present case mainly as an inhibitor of hydrogen-bonding as in the case of triethylamine van den Berg et al.^{8b} used, the relative efficiency of hole formation would have been reduced, since the hole formation seems to depend on the intermolecular hydrogen bonds between the dye and the matrix.^{8a}

Berg et al.^{11a} and Pack et al.^{11b} observed the deuteration effect for PSHB and the photon echo of **2**^{11a} and cresyl violet (CV; 5,9-diamino-5*H*-phenoxazininium perchlorate)^{11a,b} in ethanol. From their results, deuterium had no effect on the dephasing time (in both PHB and photon echo experiments) at all temperatures measured. Also, no significant change in hole width was seen in fluorinated solvents.^{9b} To summarize the effect, the increase (decrease) in the strength of the hydrogen bond corresponds to the increase (decrease) in the efficiency of hole formation and the decrease (increase) in the lifetime of the excited state (τ_f listed in Table 2) and gives no significant change in hole width. The deuteration effect causes a decrease in the efficiency of hole formation in some cases.^{11a} The potential barrier of the TLS model^{29,30} was supposed to be raised by deuteration in the excited and/or ground states. Rasimas et al.¹³ observed the transient absorption spectroscopy and time-resolved fluorescence spectroscopy of **2** in *n*-butyl and *tert*-butyl alcohols at room temperature and reported the ultrafast kinetic behavior of **2** in solution and the dissociation constants of the sodium salt of **2**. On the other hand, in Brownian rotation of dye molecules, the hydrogen bond makes the environment from “slip” to “stick”.³¹ But in the backward processes in the electronically excited states, the hydrogen bond shortens the relaxation time because it works as the driving force for the backward processes.³¹ The hydrogen bond also causes some effect on the rotor shape of dye molecules.^{32–34} These suggest the importance of hydrogen bondings for the dye molecules. So it is important to know how the additives work on the hydrogen bond between the dye and the matrix.

In our case, if TMPD were only a “hydrogen-bond inhibitor”, the relative hole-formation efficiency could have decreased. In fact, the hole-formation efficiency of 1/PMMA decreased in the presence of TMPD (Figure 5a), which suggests that the decrease in the number of hydrogen bonds between *N*-oxide and solvents in 1/PMMA with the addition of TMPD would be the reason for the decrease in its hole-formation efficiency.

However, no significant change in the relative efficiency of hole formation for 2/PMMA (Figure 5b) or no significant change

TABLE 3: Tendencies with the Addition of TMPD Observed in PSHB Measurements for Resazurin 1 and Resorufin 2 in PMMA, and the Supposed Reasons

	resazurin 1	resorufin 2
	Hole Width	
result with TMPD reasons	increase in Γ_{hole} and decrease in T_2 the weakening of hydrogen-bonding and/or the change in intra- and/or intermolecular electron transfer in the excited state	increase in Γ_{hole} and decrease in T_2 the weakening of hydrogen-bonding and/or the change in intra- and/or intermolecular electron transfer in the excited state
	Relative Efficiency of Hole Formation	
result with TMPD reasons	decreased efficiency decrease in the number of weak sites of <i>N</i> -oxide hydrogen bonds	no significant change no change in the number of hydrogen bonds causing the hole formation
	Thermal Stability	
result with TMPD reasons	improved stability the decrease in the weak sites of hydrogen-bonds between <i>N</i> -oxide and solvent	no change in hole area; increase in hole width dephasing does not occur in large scale; the weakening of hydrogen-bonds

in the positions of satellite holes was found. So we guess that mainly the effect of TMPD on the hole burning of 2/PMMA is not the inhibition of “hydrogen-bond” formation in the excited state but is the induction of some intra- and/or intermolecular charge transfer in the electronically excited states as van den Berg et al. mentioned.^{8a}

(3) Temperature-Excursion Experiments. As the change in hole width with increasing excursion temperature becomes large with the addition of TMPD for 2, the microenvironment of the dye molecule becomes softened and the hydrogen bond between the dye and the solvent seems to be a little weakened but not broken or free, since the decrease in hole area during temperature excursion is not affected by the addition of TMPD. On the other hand, the marked thermal-stability improvement in 1/PMMA with the addition of TMPD is obviously related to the presence of the *N*-oxide moiety. It is known that when pyridine *N*-oxide derivatives are hydrogen-bonded with protic solvents, their vibrational modes are red-shifted^{28a,b} in infrared spectroscopy, and in contrast to pyridine *N*-oxide, the vibrational modes of pyridine are blue-shifted^{28c,d} in infrared spectroscopy. Both of them show new absorption bands in infrared spectroscopy with the formation of hydrogen-bonds with solvent molecules that do not appear in the absence of hydrogen bonds. One of the new bands in pyridine *N*-oxide with methanol is stronger than that in pyridine with ethanol.^{28b,d,e} Thus, it is supposed that the decrease in the number of hydrogen bonds with the addition of TMPD caused the improvement in thermal stability of 1/PMMA in the presence of TMPD in both hole width and hole area and that it also caused the increase in hole width of 2/PMMA in the presence of TMPD, although no significant change was observed in the positions of satellite holes. With the addition of TMPD, the weak *N*-oxide part of 1 is thought to be less flexible and the ratio of going over the potential barrier for hole formation in the excited state decreased, leading to a decrease in the relative efficiency of hole formation. On the other hand, the stiffness given by TMPD improved the thermal stability of the burned hole of 1/PMMA.

(4) Burning-Temperature Dependence of Homogeneous Width for 1/PMMA. The hole burning of 1/PMMA in the presence and absence of TMPD was carried out at temperatures between 4.2 and 17.3 K. The homogeneous width $\Gamma_h(T)$ increases with an increase in burning temperature T (Figure 8). Fitting of the data in Figure 8 with eq 4

$$\Gamma_h(T) = \Gamma_0 + \alpha T^\beta \quad (4)$$

gives the values of $\beta = 1.5$ and 1.9 for 1/PMMA without TMPD and with TMPD, respectively, which would reflect the changes in the pure dephasing time T_2 .

The homogeneous widths in Figure 8 are much broader than those expected from the singlet excited-state lifetimes measured from fluorescence decay, $\tau_f = 1.2 \pm 0.1$ ns, for 1 in methanol.¹⁵ The values of τ_f for 1 and 2 are listed in Table 2. The values of τ_f and the extrapolated value from PHB measurement for 2 lie between 2.9 and 8 ns with a tendency of increasing lifetime with a decrease in hydrogen-bond-donating ability of the solvents.

(5) Difference between Resazurin and Resorufin. The summary of the results of the effects of TMPD addition and the supposed reasons are given in Table 3. The hole widths for both dyes increase with TMPD addition, which would be due to the decrease in T_2 . The reason for the T_2 decrease is not so clear. But in speculation, the changes in hole width for both dyes seem to have some relationship with photoinduced intra- and/or intermolecular charge transfer. The occurring of charge transfer might cause bigger changes in hydrogen bonds around the dye molecules.

The efficiency of hole formation for 1/PMMA decreased markedly with the addition of TMPD, while that for 2/PMMA was not changed with the TMPD addition as is shown in Figure 5. The decrease in the number of hydrogen bonds causing hole formation between the dyes with the solvent in the matrix by the addition of TMPD would be the reason for the decrease in the efficiency for 1, but in the case of 2, no significant change in the hydrogen bonds causing the hole formation is suggested from the results. This difference would be due to the difference in the electronic structure of N in *N*-oxide for 1 from that of N in the oxazine ring for 2. The significant point is the polarity of the charge on ring N and N in *N*-oxide. The results of the calculation with a semiempirical method, AM1,³⁵ are shown in Figure 9. Both the ground state and the first excited state were fitted for each dye molecule. In the first excited state of 2 and other phenoxazine or phenothiazine dyes, the negative ring-N charge is very important, since the ring-N atom in 2 and other phenoxazine or phenothiazine strongly abstracts the H atom in its neighborhood. The previously reported different feature in the IR spectra change²⁸ of ring N (blue shift) and *N*-oxide (red shift) with hydrogen-bond formation also supports the different feature in our PSHB results for 1 (*N*-oxide) and 2 (oxazine ring). From thermal stabilities of holes, in the absence of TMPD, the environment around *N*-oxide is not tightly fixed with the hydrogen bonds between 1 and the residual solvent molecules (maybe methanol) and the environment around the phenoxazine-ring N seemed to show no change with the hydrogen bonds between 2 and the residual solvent molecules.

The flexibility of the *N*-oxide causes a thermal stability for 1/PMMA in the absence of TMPD (see Figure 7a, ○) that is

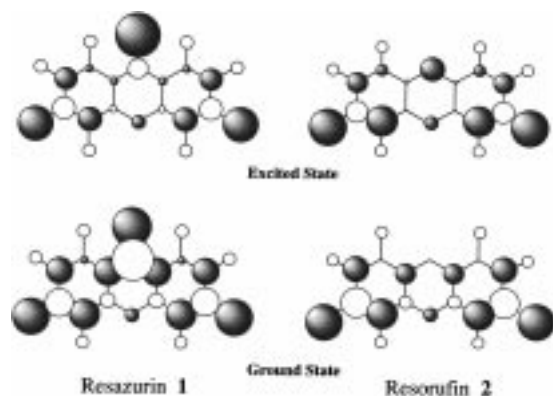


Figure 9. Electron charge densities in the ground/excited states of **1** and **2**. Filled and open circles correspond to negative and positive charges, respectively.

lower than the stability for **1**/PMMA in the presence of TMPD (see Figure 7a, ●). The decrease in relative efficiency of hole formation for **1**/PMMA with TMPD addition would be due to the decrease in the number of weakly hydrogen-bonded sites because the PSHB hole is formed by a change in its hydrogen bond between the dye and the matrixes. Thermal stability for **2**/PMMA in the absence of TMPD (see Figure 7b, △) showed no difference from the stability for **2**/PMMA in the presence of TMPD (see Figure 7, ▲). The lack of *N*-oxide structure is supposed to reduce the effect of thermal flicker.

In conclusion, the differences of the results in the absence and presence of TMPD are suggested to originate from the structural differences between **1** and **2**, especially from the presence and absence of flickering and solvatochromic *N*-oxide structure. The trends in PSHB for **1** and **2** are completely different, and the effects of the hydrogen bond on hole profiles and stabilities have been proved to be important.

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