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Persistent Spectral Hole Burning of Phenoxazine and Phenothiazine Derivatives in Poly(vinyl alcohol) and the Effect of the Addition of *N*,*N*,*N*′,*N*′-Tetramethyl-*p*-phenylenediamine

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The photochemical behavior at cryogenic temperatures of phenoxazine and phenothiazine dyes in poly(vinyl alcohol) was investigated by using persistent spectral hole burning. The importance of hydrogen-bondings has been confirmed by measuring the effects of the addition of *N*,*N*,*N*′,*N*′-tetramethyl-*p*-phenylenediamine on the holewidth and the hole area of various cationic dyes at 20 K. The hydrogen bonds around the ring-N atom affect the total dephasing time, while the hydrogen bonds around the amino groups as the substituents and around the ring-N atom control the efficiency of hole formation.

Persistent spectral hole burning (PSHB) is not only one of the promising methods for realizing high-density optical data storage, but is also known as a rather new method of high-resolution spectroscopy for investigating the photochemical properties of organic dye molecules at low temperatures.[1—3] PSHB can detect several microscopic interactions between dye molecules and matrices as a change in the holewidth and/or hole area, even in cases where each molecule carries out no chemical reaction, but suffers from some physical change in the environment, such as a rearrangement of hydrogen-bonding. Van den Berg et al. measured PSHB using high-resolution fluorescence spectroscopy for resorufin[4] (**2** in molecular structures below) in glycerol, ethylene glycol, poly(methyl methacrylate) (PMMA), and polyethylene, and have found the effect of hydrogen bonds.[4b] Kanematsu et al.[5] discussed the dispersive burning kinetics, reflecting various configurations of the surrounding molecules in amorphous hosts by using the time dependence of the hole profiles of resorufin (**2**) or other dye-doped polymers during light irradiation. Shu and Small[6] have found from the polarized nonphotochemical hole-burning spectra that the cresyl violet (**5** in molecular structures below) molecule seems to rotate during photo-excitation at 15 K. Iino et al. have established the intra- and inter-molecular hydrogen-bond rearrangement mechanism of PSHB phenomena for other kinds of dyes, quinizarin and 1,4-diamino substituted anthraquinone derivatives;[7] also the mesoscopic structure of dye-polymer complexes has been discussed.[7c]

Phenoxazine and phenothiazine derivatives are famous ionic dyes, which are widely used for various applications. Although they have been widely and frequently studied, those studies have usually been carried out in solutions. As photophysical probes, Blanchard and Cihal[8b] found a different behavior concerning the rotational diffusion of cresyl violet in several alcohols. Two different rotor shapes for polar molecule reorientation, prolate and oblate, were noticed for orientational anisotropy decays of cresyl violet in 1-dodecanol (approximate prolate rotor at 26 °C, oblate rotor at 37 °C), and in ethylene glycol (oblate rotor at 26 °C).[8a,9] Under these conditions, the environment (sticking or slipping)[8b,9] around the dye molecules varies according to the solvents. Any estimate of the microenvironments requires a proper combination of dyes and the environment (matrix). If we choose some proper combinations of dyes and matrices, we can precisely control the condition of the dyes and utilize them for new kinds of applications, such as molecular devices. Since phenoxazine and phenothiazine derivatives can easily accept electrons and be reduced electrochemically or photochemically, they have a possibility of providing information about their circumstances in their ground and excited states.[10,11] However, systematic studies on the effect of the chemical structure of these dyes on their interaction with environments in the solid states have scarcely been reported.

We reported in a previous paper on the photochemical behavior at cryogenic temperature of anionic phenoxazine dyes, resazurin (**1**) and resorufin (**2**) (Chart 1), using the PSHB method, and showed the importance of hydrogen-bondings and the electronic structures of the dye molecules in their excited states.[12] The results concerning the effect of the addition of *N*,*N*,*N*′,*N*′-tetramethyl-*p*-phenylenediamine

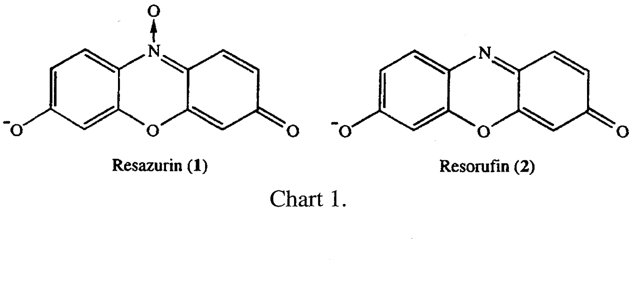


Chart 1.

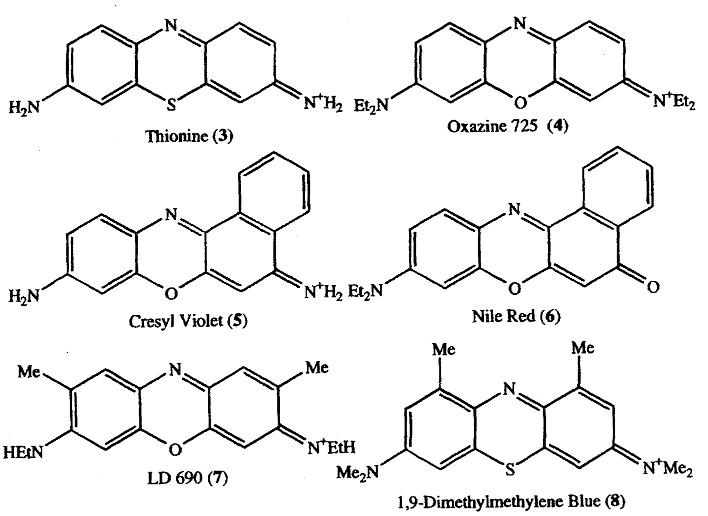


Chart 2.

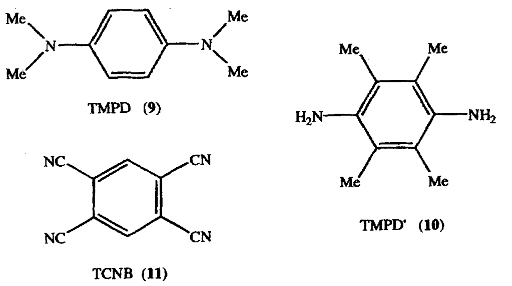


Chart 3.

(TMPD) were different from each other. For resazurin (**1**), the holewidth and the relative efficiency of hole formation increased and decreased, respectively, with TMPD addition. On the other hand, for resorufin (**2**), although the holewidth increased with TMPD addition, as in the case of resazurin (**1**), the relative efficiency of hole formation has not significantly changed. The differences in their behavior concerning the PSHB results could be explained to result from their structural difference, the presence or absence of N-oxide.[12—15]

In the present study we investigated the photochemical behavior at cryogenic temperature of cationic dyes, phenoxazines, benzophenoxazines, and phenothiazines by using PSHB techniques. These dyes have attracted much interest in photochemistry[16] and applications for optical, electrochemical and photochemical devices.[17] They are usually used in various kinds of organic solvents and aqueous solution, and their properties have been well established in solutions. However, their properties in solid matrices still remain unknown. It is very important to study their photochemical properties in polymeric solids and to clarify the relationships between their photochemical properties and chemical structures. The change in the holewidth and hole area due to the addition of TMPD for the hole-burning spectra at 20 K of cationic phenoxazine and phenothiazine dyes with various chemical structures in poly(vinyl alcohol) have been measured in the present study. A detailed consideration has been made of the hydrogen-bonds around the dye molecules and the relationships between the effect of TMPD addition and the chemical structures of these dyes. The hydrogen-bonds around the nitrogen atom in the ring structures were revealed to affect the total dephasing time; also, the hydrogen-bonds around the substituent amino-structures were found to control the yields of hole burning during light irradiation.

Experimental

Preparation of Dye Dispersed Films. Thionine (**3**) (3,7-diamino-3*H*-phenothiazin-3-iminium) chloride, and dimethylmethylene blue (**8**) (1,9-dimethyl-7-dimethylamino-3*H*-phenothiazine-3-dimethyliminium) chloride were used as phenothiazines; cresyl violet (**5**) (9-amino-5*H*-benzo[*a*]phenoxazin-5-iminium) acetate or chloride and Nile red (**6**) (9-diethylamino-5*H*-benzo[*a*]phenoxazin-5-one) were used as benzophenoxazines; oxazine 725 (**4**) (7-diethylamino-3*H*-phenoxazin-3-diethyliminum) perchlorate and LD 690 (**7**) (2,8-dimethyl-7-ethylamino-3*H*-phenoxazin-3-ethyliminium) perchlorate were used as phenoxazine (Chart 2).

Two kinds of diamines, *N*,*N*,*N*′,*N*′-tetramethyl-*p*-phenylenediamine (TMPD) (**9**) and 2,3,5,6-tetramethyl-*p*-phenylenediamine (TMPD′) (**10**), and 1,2,4,5-tetracyanobenzene (TCNB) (**11**) were used as additives (Chart 3). All of dyes were commercial products, and were used without further purification. A solvent for casting films was fluorescence-grade water. Poly(vinyl alcohol) (PVA) was supplied by Wako Chemicals and used as a matrix polymer after reprecipitation from water to acetonitrile and dried in a vacuum at 80 °C. TMPD and other additives were added to a PVA aqueous solution after the addition of a dye into the polymer solution, and the samples were made by a solvent cast onto a glass plate and dried overnight at 60 °C. The concentrations of dyes in the films were ca. 10^{-4} mol kg^{-1}. The concentration of additives **9**, **10** or **11** in the films were $(1—3)\times 10^{-2}$ mol kg^{-1}.

PSHB Measurements. 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 using a line-selectable He–Ne laser (Electro Optics LSTP-1010) with an intensity of 200 μW cm^{-2}—2 mW cm^{-2} at 611.9 nm for **6** or 632.8 nm for **3**, **5**, **7**, and an Ar^{+}-laser (Coherent, Innova 70)-pumped ring dye laser (Coherent, 699-01) using DCM as a lasing dye with ca. 2 mW cm^{-2} at 660 nm for **4** and **8**. The intensity changes in the transmitted light before and after laser irradiation were measured using a 1-m monochromator (JASCO, CT-100C), a photomultiplier (Hamamatsu, R943-02), and a lock-in amplifier (JASCO, LA126W), and were transformed to difference spectra between the absorbances before and after irradiation (hole spectra). The resolution of the equipment is ca. 0.3 cm^{-1}. The details concerning the equipment have been described elsewhere.[18)]

The absorption spectra at room temperature were measured with a double-beam UV-visible-IR spectrophotometer (JASCO, UVIDEC-660 or V-570).

Results

At first, we chose two cationic dyes, thionine (**3**) and oxazine 725 (**4**), for hole-burning measurements, since they have no substitutions near to the ring-N atom. The absorption spectra, hole spectra and PSHB results of thionine (**3**) are shown in Figs. 1, 2, and 3, respectively. We then measured the PSHB of the benzophenoxazines, such as **5** and **6**, and of the methyl-substituted dyes, such as **7** and **8**. The PHB results of all the dyes are sorted out in three groups according to their chemical structure.

Phenothiazines. The absorption spectra at room temperature, and hole spectra at 20 K of thionine (**3**) are shown in Figs. 1 and 2, respectively, as examples. The main peaks in Fig. 1 are assigned in Table 1. The shoulder at 570 nm in Fig. 1 corresponds to the dimer absorption of thionine molecules. The monomer absorption of **3** at 610 nm is independent of the addition of TMPD or TCNB, showing no occurrence of substantial complex formation in the ground state between the dye and the additives in films. The absorption spectra of the other dyes in the films are not shown here, but no significant change in their absorption spectra was observed upon the addition of TMPD. Typical changes in the hole profiles of thionine (**3**) in PVA upon TMPD addition are shown in Fig. 2. Although the holewidth becomes broad with the addition of TMPD (Fig. 2(**b**)), the hole area does not change very much with TMPD addition.

For the case of thionine (**3**) in PVA, the effects of three additives, i.e., TMPD (**8**), TMPD′ (**9**), and TCNB (**10**), on the change in the holewidth and hole area were examined (Fig. 3). The addition of both TMPD (**8**) and TMPD′ (**9**), electron-donating diamines, increased the holewidth and hole area of thionine (**3**). On the other hand, the addition of TCNB (**10**), an electron-accepting molecule, increased the holewidth, but decreased the hole area of thionine (**3**). The ratios of the holewidth and hole area of TMPD-added samples, compared to the those for the corresponding samples without TMPD, R_w, and R_a, respectively, are also shown in Fig. 3. Although the increase in the holewidth upon the addition of TMPD

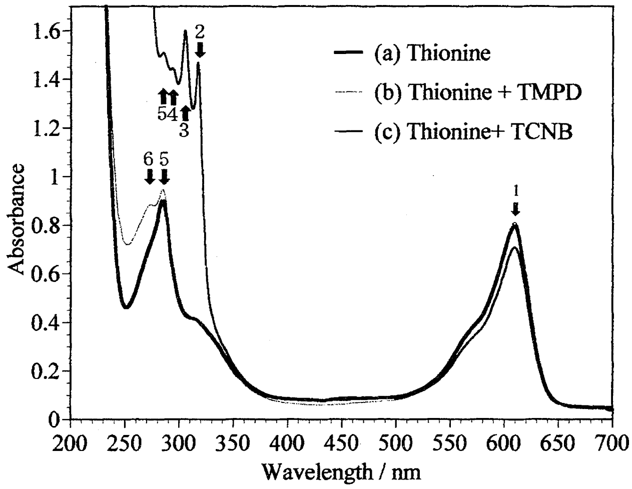


Fig. 1. UV-visible spectra of thionine (**3**) (5.6×10^{-4} mol kg^{-1}) in PVA at room temperature. (a) without TMPD, (b) with TMPD (2.8×10^{-2} mol kg^{-1}) and (c) with TCNB (1.3×10^{-2} mol kg^{-1}).

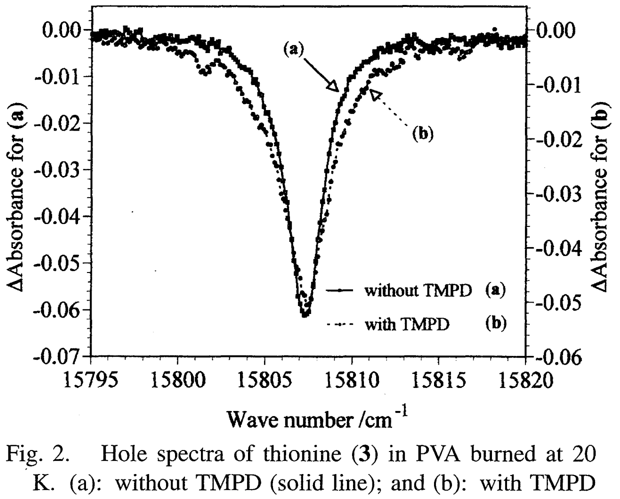


Fig. 2. Hole spectra of thionine (**3**) in PVA burned at 20 K. (a): without TMPD (solid line); and (b): with TMPD (dotted line).

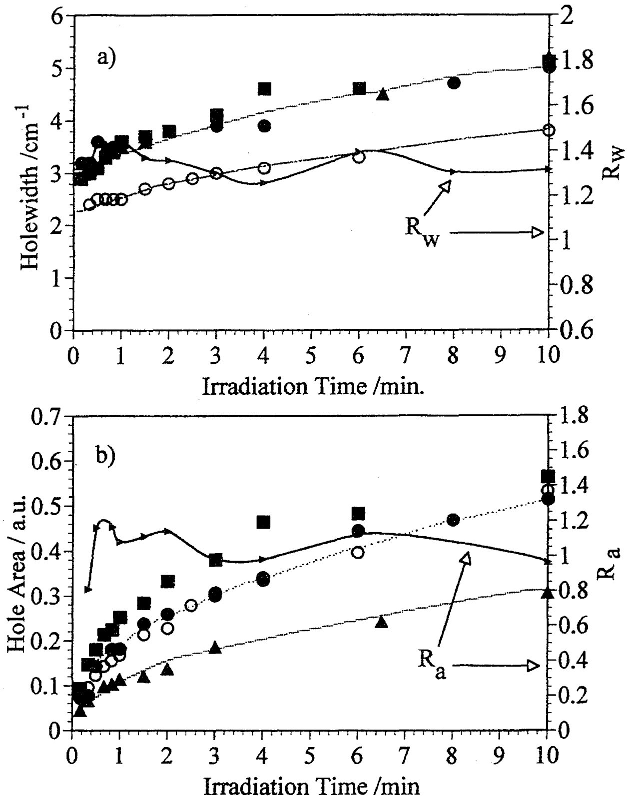


Fig. 3. Holewidth (a) and hole area (b) for PSHB of thionine (**3**) in PVA without (○) and with (●) TMPD, with TMPD′ (■) and with TCNB (▲). The ratios of holewidth and hole area in the presence and absence of TMPD, R_w and R_a, are also shown.

Table 1. Peaks of Absorption Spectra for Thionine (**3**) in PVA in the Presence and Absence of TMPD or TCNB

Dye	Assignment / Peak (nm)						Fig. 1
	1	2	3	4	5	6	
Thionine	Thionine / 609.5				Thionine / 285.0		(a)
Thionine+TMPD	Thionine / 609.5				Thionine / 285.0	TMPD / 274.0	(b)
Thionine+TCNB	Thionine / 610.0	TCNB / 317.5	TCNB / 305.5	TCNB / 293.5	Thionine / 285.0		(c)

becomes small for 1,9-dimethyl-substituted phenothiazine (**8**) (Fig. 4), the tendency for a change in the hole area of **8** upon the addition of TMPD is also the same as that of **3**.

Phenoxazines. The changes in the holewidth and hole area upon the TMPD addition for cationic phenoxazine dyes, oxazine 725 (**4**) and LD690 (**7**), are shown in Figs. 5 and 6, respectively. Although oxazine 725 (**4**), having no substituent groups near to the ring-N atom, showed a large increase in the holewidth upon the addition of TMPD, LD690 (**7**), having two methyl substituents at the 2,8 positions, showed only a small increase in the holewidth upon TMPD addition. The hole area decreased lightly upon TMPD addition for both cases.

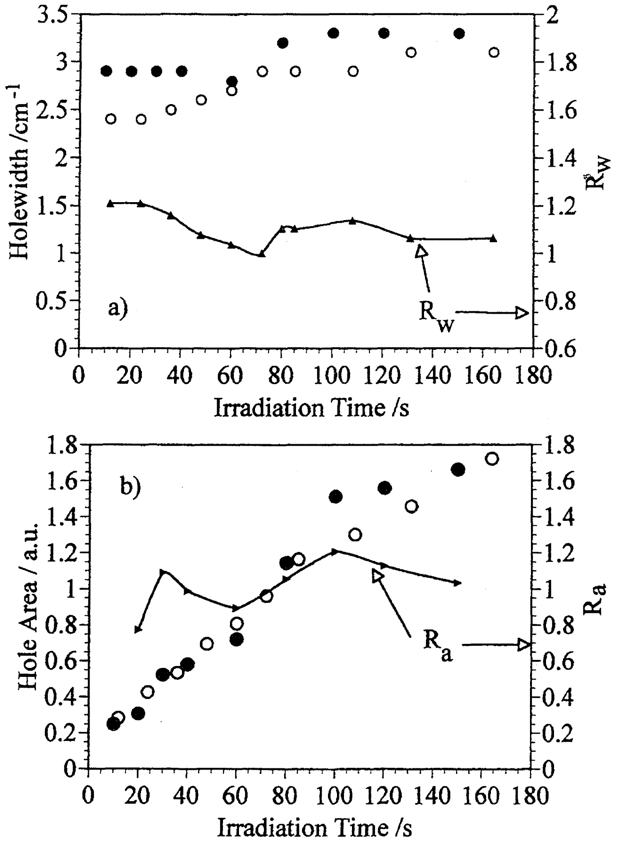


Fig. 4. Holewidth (a) and hole area (b) for PSHB of 1,9-dimethylmethylene blue (**8**) in PVA without (○) and with (●) TMPD. The ratios of holewidth and hole area in the presence and absence of TMPD, R_w and R_a, are also shown.

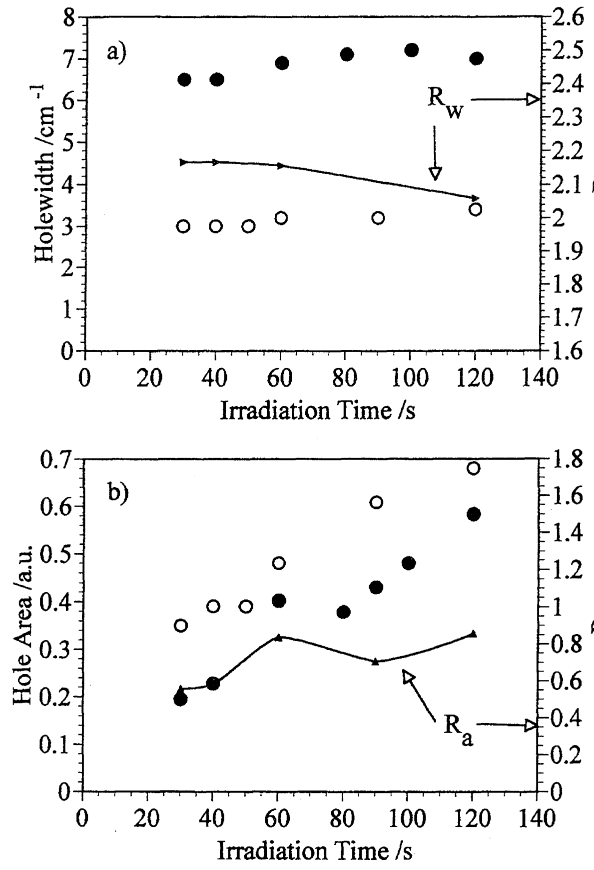


Fig. 5. Holewidth (a) and hole area (b) for PSHB of oxaznine 725 (**4**) in PVA without (○) and with (●) TMPD. The ratios of holewidth and hole area in the presence and absence of TMPD, R_w and R_a, are also shown.

Benzophenoxazines. No significant holewidth change upon the addition of TMPD was observed for PSHB measurements of cresyl violet (**5**) in PVA films (Fig. 7a). On the other hand, the relative efficiency of hole formation greatly increased with the addition of TMPD (Fig. 7b) for cresyl violet (**5**). Nile red (**6**) showed only a very shallow hole at 20 K. Since the signal/noise ratio was very small, the PHB data of **6** are not shown here; however, the tendency was similar to the results for cresyl violet (**5**), and no significant change in the holewidth was noticed upon the addition of TMPD.

Discussion

Holewidth. The mechanism of hole formation in the

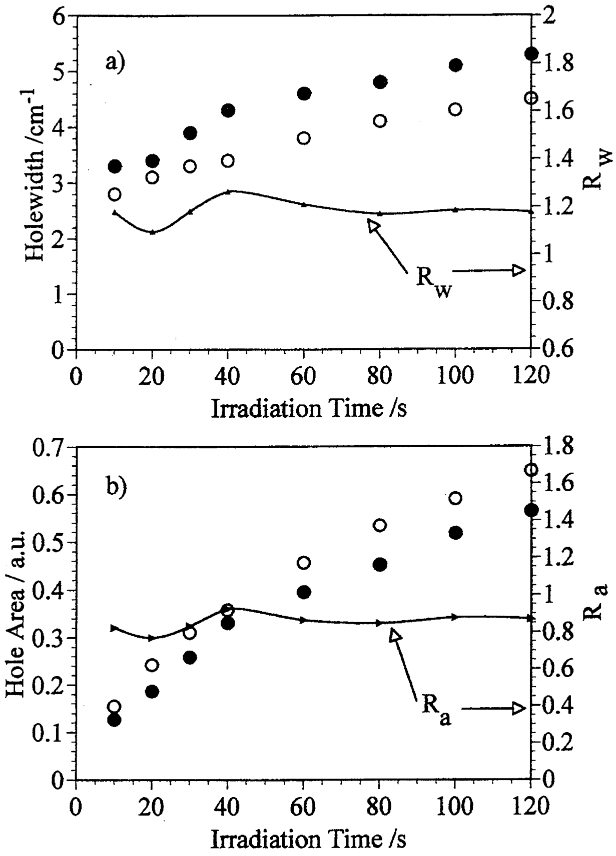


Fig. 6. Holewidth (a) and hole area (b) for PSHB of LD690 (**7**) in PVA without (○) and with (●) TMPD. The ratios of holewidth and hole area in the presence and absence of TMPD, R_w and R_a, are also shown.

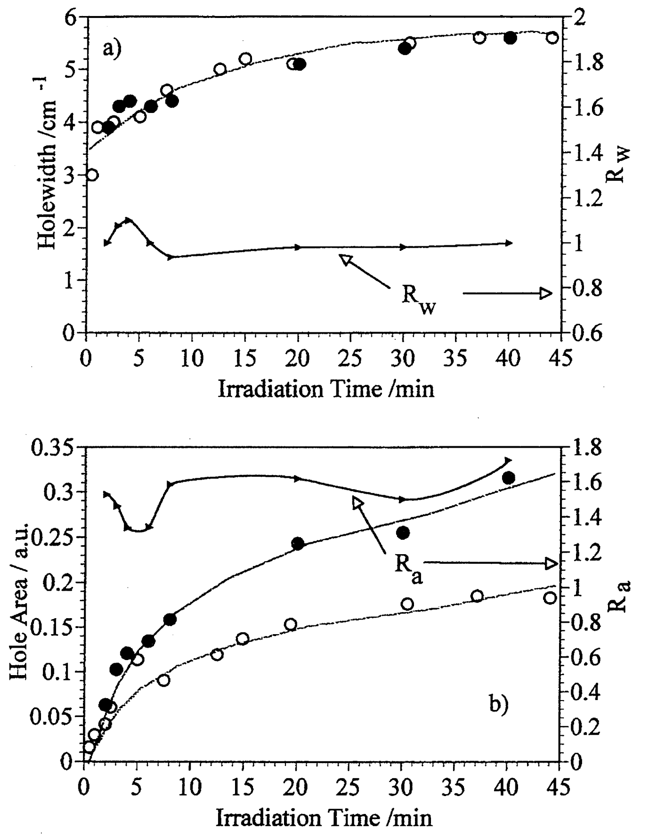


Fig. 7. Holewidth (a) and hole area (b) for PSHB of cresyl violet (**5**) in PVA without (○) and with (●) TMPD. The ratios of holewidth and hole area in the presence and absence of TMPD, R_w and R_a, are also shown.

present system of cationic dyes in PVA is supposed to be due to a hydrogen-bond rearrangement between the dyes and the surroundings, caused by photo-excitation and successive deactivation, as in the cases of anionic dyes, already discussed in previous papers,[12)] since the dyes themselves carry out no photochemical reactions. The addition of TMPD for the cases of anionic dyes, resazurin (**1**) and resorufin (**2**) in PMMA, increased the holewidth, thus suggesting a weakening of hydrogen-bonding and/or a change in the intra- and intermolecular electron transfer in the excited state.[12b)]

An important factor concerning the change in the holewidth related to the chemical structure of dyes has been found in the present study. The change is evaluated using the ratio of the holewidth change by TMPD addition, (R_w), where R_w = (holewidth in the presence of TMPD) / (holewidth in the absence of TMPD).

The average values of R_w for various dyes in PVA are listed in Table 2 with decreasing order of magnitudes.

The values of R_w are in the range 1.0—2.2, and the biggest change upon the addition of TMPD was observed for oxazine 725 (**4**). The values for LD690 (**7**) and 1,9-dimethylmethylene blue (**8**) become rather small, and no significant change was observed for cresyl violet (**5**). From these results, the factor for changing the holewidth with TMPD addition seems to be a steric effect near to the oxazine or thiazine ring-N atom. The bigger and nearer is the benzo-ring or methyl substituents around the ring-N atom of the dyes, the less becomes the effect of TMPD addition on the holewidth. This corresponds to the degree of difficulty of TMPD, approaching the very surrounding of the ring-N atom of the dyes.

The holewidth reflects the total dephasing time, T_{total}.[1)] T_{total} is expressed by

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

where T_1 is the lifetime of the excited state and T_2 is the pure dephasing time. The relationships of T_{total} with the observed holewidth extrapolated to zero burning energy (Γ_{hole}) are described as[12,18b)]

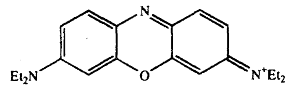
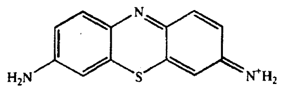
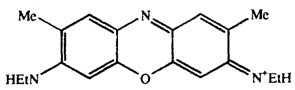
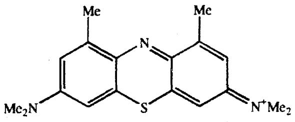
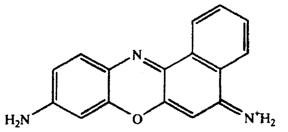
$$\Gamma_h = (\Gamma_{\text{hole}} - \Gamma_l)/2, \qquad (2)$$

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

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

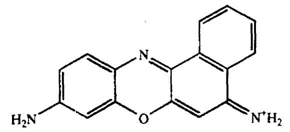
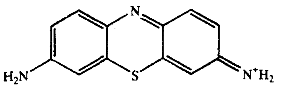
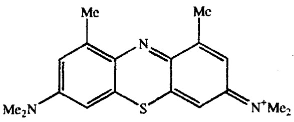
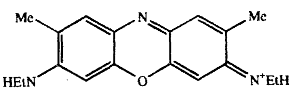
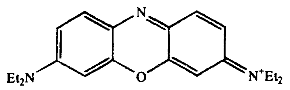
Since the total dephasing time is reflected by the holewidth, it depends on the strength of the steric effect against the approach of TMPD around the ring-N atom. Thus, the interaction of the TMPD molecule with the dyes in the excited state would be the main factor for enhancing the total dephasing process in the cases of oxazine 725 (**4**) and thionine (**3**).

Table 2. The Ratio, R_{w}, of Holewidth Change by the Addition of TMPD for PSHB of Cationic Dyes in PVA

Dye	No.		R_{w} a)
	4	Oxazine 725	2.14
	3	Thionine	1.35
	7	LD 690	1.18
	8	Dimethylmethylene blue	1.11
	5	Cresyl violet	1.01

a) Each R_{w} value contains an experimental error which depends on the experimental conditions in the range of ±0.1.

Table 3. The Ratio, R_{a}, of Hole Area Change by the Addition of TMPD for PSHB of Cationic Dyes in PVA

Dye	No.		R_{a} a)
	5	Cresyl violet	1.51
	3	Thionine	1.05
	8	Dimethylmethylene blue	1.02
	7	LD 690	0.85
	4	Oxazine 725	0.71

a) Each R_{a} values contains an experimental error which depends on the experimental conditions in the range of ±0.2.

The weakening of hydrogen-bonds between the ring-N atom and the OH group in PVA upon the addition of TMPD[12] might also influence T_{total}. The differences in R_{w} for oxazine 725 (**4**) and thionine (**3**) would be attributed to the electron-density difference between the oxazine ring-O atom and the thiazine ring-S atom.

Relative Efficiency of Hole Formation. The importance of hydrogen-bonding for hole formation for these ionic dyes in alcoholic solvents or glassy polymers has already been pointed out.[4,19] However, it has not yet been identified which hydrogen-bonds onto dye molecules are responsible for hole formation. The present study shows obvious evidence for the participation of the ring-N atom and amino-H atom for hydrogen-bondings.

The ratio of the hole area change by the TMPD addition, (R_{a}) is given by R_{a}= (the hole area in the presence of TMPD) / (the hole area in the absence of TMPD).

The average values of R_{a} for various dyes in PVA are listed in Table 3 with decreasing order of magnitudes. R_{a} has different meanings in the early and later stages of hole formation, i.e., the relative efficiency of hole formation in the early stage and its limiting value in the later stage of hole formation. Under the present experimental conditions, the holes do not yet arrive at saturation, and no significant time dependence of R_{a} is observed. We thus believe that the R_{a} values show the relative changes in the efficiencies of hole formation upon TMPD addition.

Dyes with NH_2 groups, i.e., no substitution on amino moieties, such as cresyl violet (**5**), shows the ratio $R_{\mathrm{a}} \geq 1$; with increasing bulkiness of substitutions in the amino moieties, R_{a} decreases from the value for cresyl violet (**5**). The decrease is proportional to the bulkiness of the amino substitutions. The smallest value is obtained for oxazine 725 (**3**) with $R_{\mathrm{a}} \approx 0.71$. The reason for the large R_{a} values for dyes with NH_2 groups seems to be new hydrogen-bond formation between the dye molecule and dimethylamino moiety of TMPD.

Type I $\{$Dye: $-NH_2\cdots HO{-}C{-}$: Polymer matrix$\}$

Type II $\{$Dye: $-NH_2\cdots N(CH_3)_2-$: TMPD$\}$

Thus, this hydrogen-bond formation is effective if the dye molecule is a strong hydrogen-bond donor (HBD). Since cresyl violet (**5**)[7,9,11,20] is a strong HBD in these listed ionic dyes, the enhancement of the relative hole formation upon TMPD addition was realized because of the Type II hydrogen-bond formation. Although thionine (**7**) is also a strong HBD, in the case of thionine (**7**), the addition of TMPD would weaken the Type III hydrogen-bonds between the ring-N atom and PVA, resulting in a decrease in hole formation and R_{a}, which negates the increasing effect of the NH_2 groups on R_{a}.

Type III $\{$Dye: –ring-N$\cdots HO{-}C{-}$: Polymer matrix$\}$

On the other hand, Oxazine 725 (**3**) and LD690 (**4**) are weak HBDs and strong hydrogen-bond acceptors (HBA). Their values of the relative hole formation ratio (R_{a}) are below 1, because these dyes form hydrogen-bonds in mainly the Type III mechanism, which are weakened by the addition of TMPD. In the case of 1,9-dimethylmethylene blue (**8**), which has dimethyl substituents in the amino moieties, the steric effect around the ring-N atom hinders the weakening of the Type III hydrogen-bond upon the addition of TMPD, resulting in the R_{a} value approaching unity. From these results, the hydrogen bonds around the amino moieties as well as the hydrogen bonds between the ring-N atom and the matrix polymer have been revealed to be effective for the yields of hole formation caused by a hydrogen-bond rearrangement.

Conclusion

From PSHB measurements of cationic dyes in PVA with or without TMPD, new insight concerning hydrogen-bond formation in ionic dyes could be obtained. The hydrogen-bond formation around the oxazine or thiazine ring-N atom is important for controlling the total dephasing time and the efficiency of hole formation. The hydrogen-bond formation around the H atoms of the amino moieties of the dyes is also important, but works only on the efficiency of hole formation. TMPD and other diamines are regarded not only as being an inhibitor of hydrogen-bondings between the dye molecules and polymer matrices, but also as a new hydrogen-bond acceptor for hydrogen-bond donating dyes. For hydrogen-bond accepting dyes, TMPD works only as an inhibitor of hydrogen bonding.

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