

## Photochemical Hole Burning of Tetraphenylporphine Glycosides

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Glycosides of tetraphenylporphine were synthesized and studied by photochemical hole burning (PHB) spectroscopy. The derivatives with lactosyl groups in poly(vinyl alcohol) (PVA) shows excellent thermal stability against cyclic annealing, which is superior to that of sulfonated tetraphenylporphine (TPPS) in PVA. It is supposed that the hydroxyl groups of the glycosides as well as those of PVA would contribute to reducing irreversible structural relaxation by forming hydrogen bonds.

Photochemical hole burning (PHB) is a useful method for scientific research on solid materials, and also an attractive candidate for an optical frequency-domain information storage.<sup>1,2)</sup> High-temperature PHB at 77 K was performed for a water-soluble derivative of 5,10,15,20-tetraphenyl-21*H*,23*H*-porphine (TPP) in poly(vinyl alcohol) (PVA) system<sup>3)</sup> and for TPP in phenoxy resin.<sup>4)</sup> Hydroxyl groups of the matrix polymers are thought to play an important role for high temperature PHB. Hydrogen bonds would be formed by hydroxyl groups and suppress the structural relaxation of the matrices. The relaxation process would result in a reduction of spectral hole area and broadening of hole width. Another candidate for high temperature PHB is inorganic hole burning materials.<sup>5–7)</sup> However, the quantum efficiency for hole formation of inorganic hole burning materials is much lower than those of the porphyrin/polymer systems.

A wide range of investigation has been undertaken to study glycosides. In order to develop new advanced materials, a large number of glycosides have been synthesized.<sup>8,9)</sup> Porphyrin glycosides were synthesized as a new class of water-soluble porphyrins. Non-ionizable glycosyl substituents are so bulky that the faces of the porphyrins would be protected and that the aggregation of the porphyrins would be prevented.<sup>10)</sup>

Our preliminary work showed that the derivative of tetraphenylporphine with four lactosyl groups on to the para position of *meso*-phenyl groups ((*p*-Lac)<sub>4</sub>-TPP) in PVA is superior to sulfonated TPP (TPPS) in PVA about thermal stability of a spectral hole.<sup>11)</sup> Contrary to this improvement, xylosylated TPP ((*p*-Xyl)<sub>4</sub>-TPP) in phenoxy resin (PhR) does not show any significant difference from TPP in PhR. In the present work other four glycosides of TPP with xylosyl or lactosyl groups on to the ortho or meta position of *meso*-phenyl groups have been studied by PHB spectroscopy. Thermally-induced relaxation process was examined through cycle annealing experiments. It has become clear that all of the lactosylated TPP would interact with the matrix polymer, PVA, by forming hydrogen bonds and make

improvements in thermal stability of a spectral hole. The lactosylated derivatives of TPP in PVA were found to be the most stable hole burning material against heat among the porphyrin systems. And it is suggested that the glycoside with xylosyl groups on to the meta position of *meso*-phenyl groups would interact with the matrix polymer through hydrogen bonds. The position of the xylosyl substituents would be important on the interaction between the chromophore and the matrix.

## Experimental

**Materials and Sample Preparation.** The chemical structure and the abbreviations of the porphyrins used as chromophores are shown in Fig. 1. The syntheses of the glycosylated TPPs were performed according to the literature<sup>10)</sup> with some modifications.<sup>12)</sup> Instead of helicene, *o*-, *m*-, and *p*-hydroxybenzaldehyde were used as the starting materials. The *o*-, *m*-, and *p*-isomer of hydroxybenzaldehyde are obtainable easily. Helicine is a natural product and can be converted to the glycosides of TPP with the substituents only on to the ortho positions of *meso*-phenyl groups. The *m*-, or *p*-substituted glycosides were synthesized with the isomers of hydroxybenzaldehyde. The TPP and 5,10,15,20-tetrakis(4-sulfophenyl)-21*H*,23*H*-porphine (TPPS(H)) were purchased from Wako Pure Chemical Industries, Ltd. Tetra-

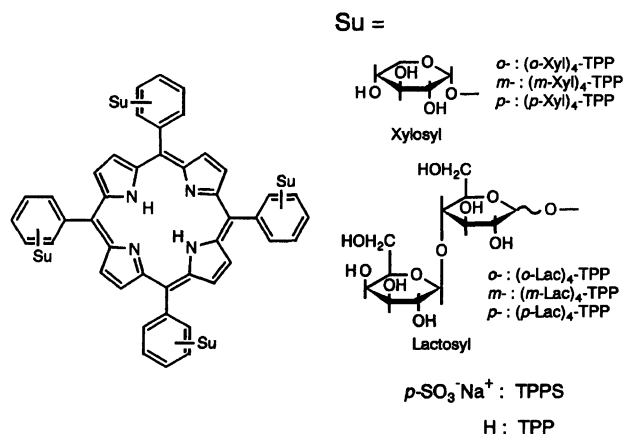


Fig. 1. The structure and abbreviations of the chromophores used.

sodium (5,10,15,20-(4-sulfonatophenyl)-21*H*,23*H*-porphine) (TPPS) was obtained by neutralization of TPPS(H) with sodium hydroxide. The polymers used as matrices were poly(methyl methacrylate) (PMMA), phenoxy resin (PhR), and poly(vinyl alcohol) (PVA). The chemical structure is shown in Fig. 2. PMMA and PVA were purchased from Wako Pure Chemical Industries, Ltd., and PhR was from Union Carbide Japan. PMMA and PhR were purified by reprecipitation. The PHB samples were prepared with solvent cast method from DMF, chloroform or water. The samples where PMMA or PhR were used as the matrix polymer were evacuated and hot-pressed above the glass transition temperature in addition to the casting process. The concentrations of the chromophores in film samples are in the order of  $10^{-3}$  mol kg $^{-1}$ . The details of the sample preparation were depicted elsewhere.<sup>13)</sup>

**Measurements.** The apparatus used for PHB measurements is the same one used in the previous work.<sup>13)</sup> The samples were cooled to 20 K in a cryostat with a closed-cycle helium refrigerator (Sumitomojuki, SRD204). Spectral holes were formed with a dye laser (Coherent, CR699-01) and DCM laser dye. A cw argon ion laser (Coherent, Innova 70) was used for pumping the dye laser. The transmission spectra of the spectral holes were measured with a one meter monochromator (JASCO, CT-100C), a photomultiplier (Hamamatsu, R943-02), and a lock-in amplifier (JASCO, LA-126W). The resolution of the detecting system was about 0.3 cm $^{-1}$  and limited by the resolution of the monochromator.

The quantum efficiency for hole formation,  $\Phi_{\text{PHB}}$ , can be defined as the following Eq. 1;<sup>13,14)</sup>

$$\Phi_{\text{PHB}} = -\{dN(t)/dt\}_{t=0} / \{(P/h\nu)(1 - T_0)\}, \quad (1)$$

where  $N(t)$  is the number of centers within a homogeneous line width of the laser frequency,  $P$  is the laser power,  $h$  is Planck's constant,  $T_0$  is the transmittance at  $t=0$ . Equation 1 can be transformed into Eq. 2 and  $\Phi_{\text{PHB}}$  was calculated by using the following Eq. 2,

$$\Phi_{\text{PHB}} = \{-(dA/dt)_{t=0}\} / \{10^3 I_0 (1 - 10^{-A_0}) \epsilon R\}, \quad (2)$$

where  $A$  is time-varying absorbance,  $A_0$  is the absorbance before irradiation,  $I_0$  is the incident laser intensity given in einstein cm $^{-2}$  s $^{-1}$ ,  $\epsilon$  is the molar extinction coefficient for inhomogeneous line profile at the hole burning wavelength and

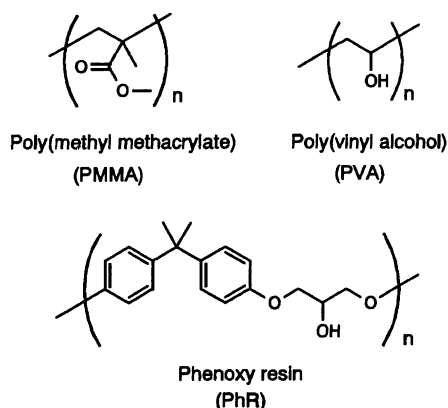


Fig. 2. The chemical structure and abbreviations of matrix polymers.

temperature, and  $R = \Delta\omega_i / \Delta\omega_h$  is the reciprocal initial ratio of a hole width,  $\Delta\omega_h$ , to an inhomogeneous line width,  $\Delta\omega_i$ . Hole depth was plotted against irradiation energy shown in Fig. 3. The  $-(dA/dt)_{t=0}$  in Eq. 2 was obtained from the initial slope of the fitting curve.

The details of cycle annealing experiments are depicted below. The hole formation was performed at 20 K and the transmission spectrum was measured. Then the temperature of the system was elevated and annealed. After the annealing for 15 min the sample was cooled to the initial hole burning temperature, 20 K, and a hole profile was measured again. The hole area was calculated as the absorbance change at the wavelength of the hole bottom multiplied by the hole width. This temperature cycle was repeated with stepwise raising of the annealing temperatures from 20 K up to 100 K by about 10 K. The experimental procedure is depicted in Fig. 4.

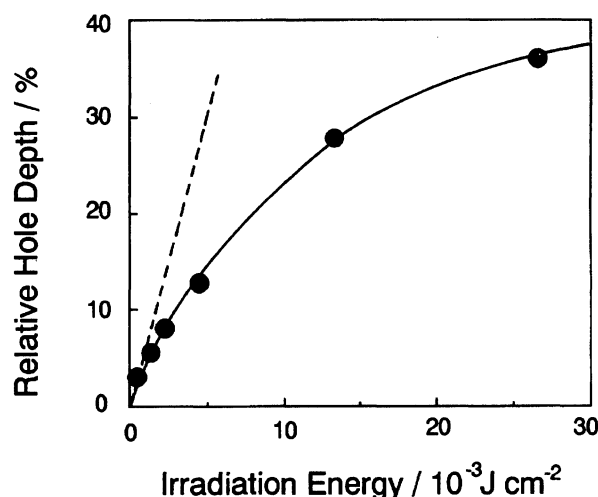


Fig. 3. Hole growth with increasing irradiation energy. The sample was (*p*-Lac) $_4$ -TPP/PVA at 20 K. The irradiation dose was  $4.42 \times 10^{-4}$  J cm $^{-2}$  s $^{-1}$ . The quantum efficiency for hole formation was calculated from the initial slope of fitting curvature.

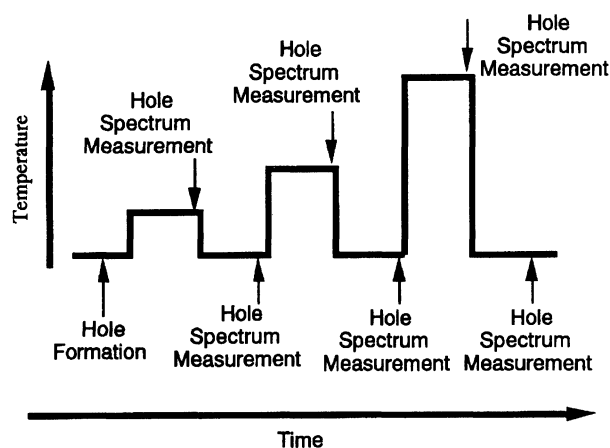


Fig. 4. Temperature change in cycle annealing experiments. Annealing was performed for 15 min. At the lowest temperature, 20 K, the hole spectra were measured twice.

A spectral hole profile ( $g(\omega)$ ) would be denoted by a convolution of homogeneous spectrum ( $h(\omega)$ ) and inhomogeneous distribution function ( $IDF(\omega)$ ).<sup>2)</sup>

$$g(\omega) = \int_0^\infty d\omega' h(\omega - \omega') IDF(\omega'). \quad (3)$$

Since  $h(\omega)$  is a reversible function of temperature, irreversible change of IDF can be extracted by cycle annealing experiment. The hole profiles at 20 K and at annealing temperatures are shown in Fig. 5.

## Results and Discussion

**Cycle Annealing Experiments.** The results of the cycle annealing experiments for the lactosylated TPPs and TPPS in PVA are shown in Fig. 6. The decrease of hole area should be ascribed to the change of

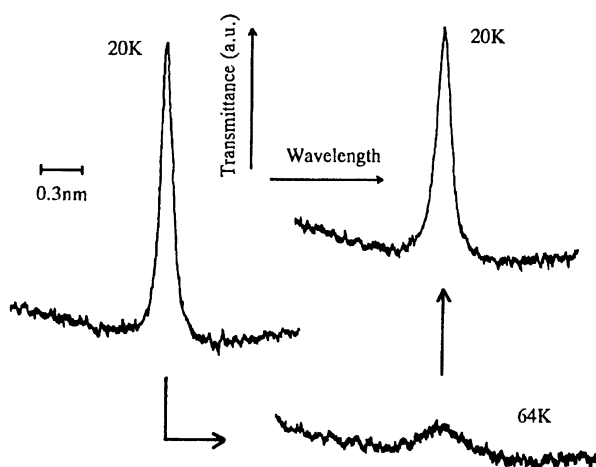


Fig. 5. Spectral hole profiles at 20 K and at annealing temperature. Holes become wider and shallower at annealing temperatures than those at 20 K. Hole areas recover to some extent by cooling down to 20 K.

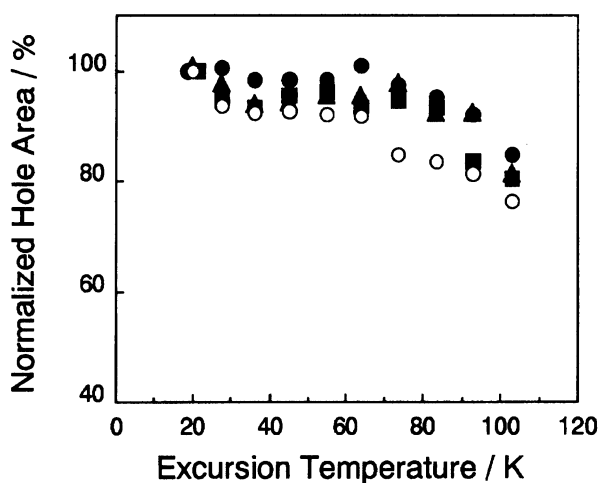


Fig. 6. Cycle annealing experiments at 20 K. TPPS/PVA (○), (*p*-Lac)<sub>4</sub>-TPP/PVA (●), (*m*-Lac)<sub>4</sub>-TPP/PVA (▲), and (*o*-Lac)<sub>4</sub>-TPP/PVA (■). The glycosides with lactosyl groups shows higher stability against heat than TPPS/PVA.

IDF( $\omega$ ) in Eq. 3. It corresponds to the thermally-induced relaxation of the dye-matrix system. It is well-known that TPPS/PVA is one of the best system for high temperature hole burning among the organic dye-polymer systems. A large number of hydrogen bonds, resulting from the high spatial density of hydroxyl groups, would contribute to making the TPPS/PVA system fixed.<sup>15)</sup> The rigidity of the system would reduce the thermally-induced relaxation, corresponding to the excellent stability against high temperature. The glycosides of TPP with lactosyl groups in PVA were shown to have higher thermal stability than TPPS in PVA has at 70–90 K. It would be considered that the lactosyl groups of the glycosides would contribute to fixing the environment around the glycosides molecules with abundant hydroxyl groups.

The results for the xylosylated TPP and TPP in PhR are shown in Fig. 7. A small improvement appears on the thermal stability of a spectral hole for (*m*-Xyl)<sub>4</sub>-TPP/PhR compared to TPP/PhR at 90–100 K. The agreement between (*p*-Xyl)<sub>4</sub>-TPP/PhR and TPP/PhR are found within the experimental error, less than 10%. (*o*-Xyl)<sub>4</sub>-TPP/PhR, however, shows less stability against heat than TPP/PhR. This may result from the low spatial density of hydroxyl groups of PhR matrix. There is one hydroxyl group in the monomer unit of PVA and PhR, however, the monomer unit of PhR is much more bulky than that of PVA. Molecular weight of the monomer unit of each polymer is 284 (PhR), or 44 (PVA). So, the spatial density of hydroxyl groups in PhR is much smaller than that in PVA. The hydrogen bonds between the xylosylated TPP and PhR would be less effective than that of lactosylated TPP/PVA system. The interaction between the xylosylated TPPs and PhR would depend on the position

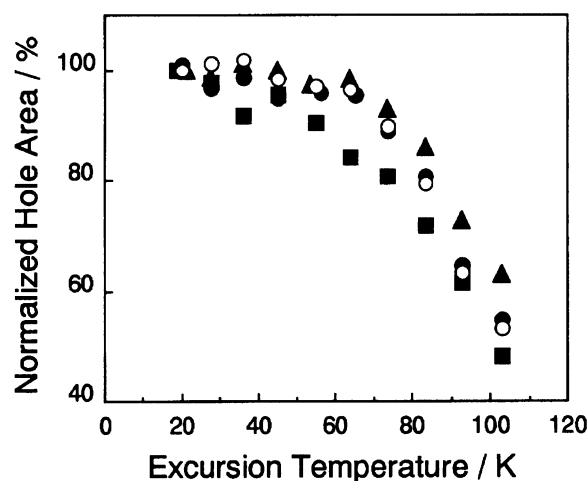


Fig. 7. Cycle annealing experiments at 20 K. TPP/PhR (○), (*p*-Xyl)<sub>4</sub>-TPP/PhR (●), (*m*-Xyl)<sub>4</sub>-TPP/PhR (▲), and (*o*-Xyl)<sub>4</sub>-TPP/PhR (■). The (*m*-Xyl)<sub>4</sub>-TPP/PhR would be improved in the thermal stability.

of the xylosyl groups on the *meso*-phenyl groups.

The increase in hole width after cycle annealing is depicted in Figs. 8 and 9. The relaxation of the dye-matrix system also appears as the increase of hole width. Each system shows monotonous increase with annealing temperature. The hydrogen bonds between the glycosides and the matrix would have little influence on the increase in hole width.

Normalized hole areas measured at annealing temperatures in cycle annealing are shown in Figs. 10 and 11. The lactosylated TPPs/PVA does not show significant differences from TPPS/PVA, but hole area for (*m*-Xyl)<sub>4</sub>-TPP/PhR remains more than that for TPP/PhR. Not only at 20 K but also at higher temperatures the xylosyl substituents of (*m*-Xyl)<sub>4</sub>-TPP would make

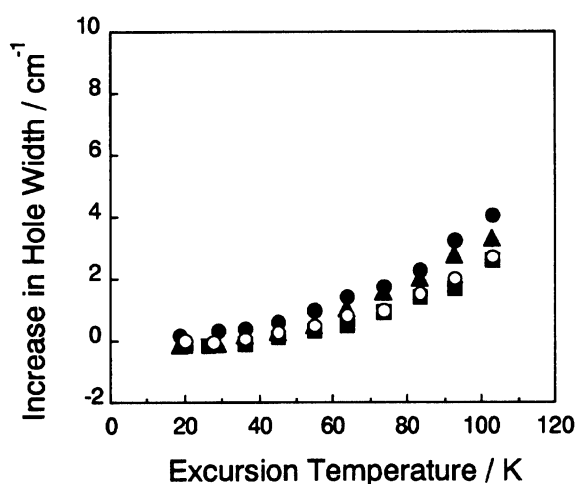


Fig. 8. The increase in hole width in the cycle annealing experiment for TPPS/PVA (○), (*p*-Lac)<sub>4</sub>-TPP/PVA (●), (*m*-Lac)<sub>4</sub>-TPP/PVA (▲), and (*o*-Lac)<sub>4</sub>-TPP/PVA (■). The hole grows wider with elevating temperature monotonously.

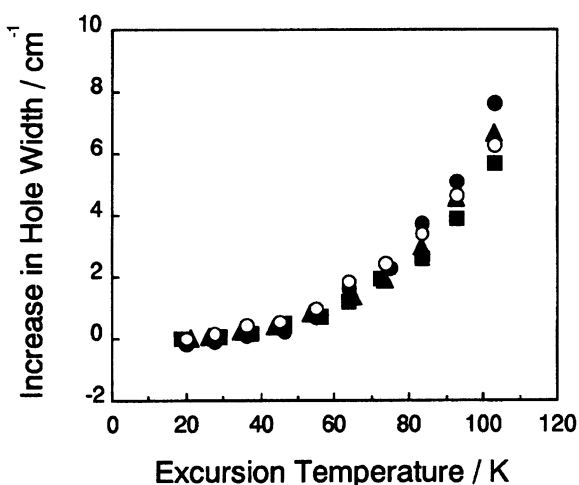


Fig. 9. The increase in hole width in the cycle annealing experiment for TPP/PhR (○), (*p*-Xyl)<sub>4</sub>-TPP/PhR (●), (*m*-Xyl)<sub>4</sub>-TPP/PhR (▲), and (*o*-Xyl)<sub>4</sub>-TPP/PhR (■). The broadening of holes for the PhR matrix is larger than that for PVA matrix.

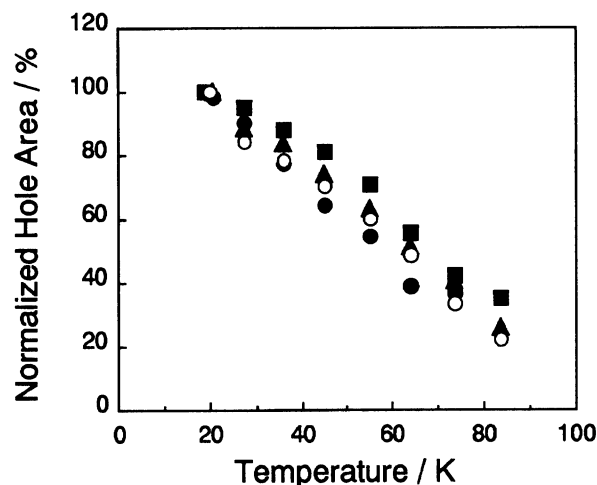


Fig. 10. Hole area measured at annealing temperature in cycle annealing experiments. The samples are TPPS/PVA (○), (*p*-Lac)<sub>4</sub>-TPP/PVA (●), (*m*-Lac)<sub>4</sub>-TPP/PVA (▲), and (*o*-Lac)<sub>4</sub>-TPP/PVA (■). No significant differences appear among each samples.

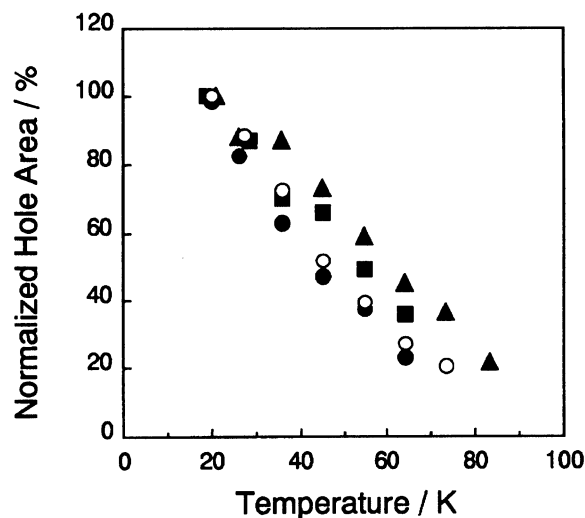


Fig. 11. Hole area measured at annealing temperature in cycle annealing experiments. The samples are TPP/PhR (○), (*p*-Xyl)<sub>4</sub>-TPP/PhR (●), (*m*-Xyl)<sub>4</sub>-TPP/PhR (▲), and (*o*-Xyl)<sub>4</sub>-TPP/PhR (■). The (*m*-Xyl)<sub>4</sub>-TPP/PhR shows less hole filling than TPP/PhR, coinciding with the results at 20 K.

the structural relaxation reduced by forming hydrogen bonds. At high temperature spectral hole profiles become wide and shallow, so that the estimation of hole area contains serious errors. This may be why no differences of hole area appeared for the lactosylated TPPs and TPPS in PVA at annealing temperatures.

**Quantum Efficiency for Hole Formation.** The quantum efficiency for hole formation,  $\Phi_{\text{PHB}}$  at 20 K, is shown in Table 1. Estimated error ranges are also shown in Table 1. The polymer matrix influences the values of  $\Phi_{\text{PHB}}$ . For example,  $\Phi_{\text{PHB}}$  of xylosylated TPP in PMMA matrix is much lower than that in PhR, and lac-

Table 1. The Values of  $\Phi_{\text{PHB}}$  and  $\Delta\omega_h$  at 20 K  
Spectral holes were burnt at the peak of  $Q_x(0,0)$  band of each samples.  $\varepsilon$  is calculated from the absorbance at the peak of  $Q_x(0,0)$  band of solution at room temperature.

Sample	Preparation	$10^3 \Phi_{\text{PHB}}$	$\Delta\omega_h/\text{cm}^{-1}$
( <i>p</i> -Xyl) <sub>4</sub> -TPP/PhR	Hot-press	1.4±0.2	1.2
( <i>p</i> -Xyl) <sub>4</sub> -TPP/PMMA	Hot-press	1.3±0.2	1.7
( <i>m</i> -Xyl) <sub>4</sub> -TPP/PhR	Hot-press	1.4±0.2	1.1
( <i>m</i> -Xyl) <sub>4</sub> -TPP/PMMA	Hot-press	0.6±0.1	1.2
( <i>o</i> -Xyl) <sub>4</sub> -TPP/PhR	Hot-press	1.4±0.2	1.2
( <i>o</i> -Xyl) <sub>4</sub> -TPP/PMMA	Hot-press	1.1±0.2	1.1
( <i>p</i> -Lac) <sub>4</sub> -TPP/PhR	Hot-press	<0.1	1.1
( <i>p</i> -Lac) <sub>4</sub> -TPP/PMMA	Hot-press	0.9±0.1	1.7
( <i>p</i> -Lac) <sub>4</sub> -TPP/PVA	Cast	2.2±0.4	1.6
( <i>m</i> -Lac) <sub>4</sub> -TPP/PhR	Hot-press	0.2±0.1	1.1
( <i>m</i> -Lac) <sub>4</sub> -TPP/PVA	Cast	2.8±0.3	1.2
( <i>o</i> -Lac) <sub>4</sub> -TPP/PhR	Hot-press	0.3±0.1	1.2
( <i>o</i> -Lac) <sub>4</sub> -TPP/PVA	Cast	1.5±0.2	1.2
TPPS/PVA	Cast	4.4±1.0	1.2
TPP/PhR	Hot-press	1.5±0.2	1.2

tosylated TPP in PhR matrix is much less efficient for hole formation than that in PVA. It is known that  $\Phi_{\text{PHB}}$  of TPP in various polymer matrices does not change much as long as the dye is well molecularly dispersed in the matrices.<sup>13)</sup> It is considered that the solubility of the chromophores in the matrices would cause the difference due to the matrices. Generally low dispersivity of chromophores makes  $\Phi_{\text{PHB}}$  much smaller. The baselines of the absorption spectra for the low  $\Phi_{\text{PHB}}$  samples are strongly dependent on wavelength, and this scattering would be caused by aggregation of the porphyrins. The absorption spectra of the lactosylated TPPs in PVA samples showed little scattering similarly to those of the porphyrins in water- or DMF-solution. The (*p*-Lac)<sub>4</sub>-TPP/PMMA sample showed the same degree of scattering as (*p*-Lac)<sub>4</sub>-TPP/PhR sample, however the  $\Phi_{\text{PHB}}$  of (*p*-Lac)<sub>4</sub>-TPP/PMMA was much higher than that of (*p*-Lac)<sub>4</sub>-TPP/PhR. There would be small aggregates in (*p*-Lac)<sub>4</sub>-TPP/PhR. The dimensions of the aggregates would be too small to scatter the light in visible region.

Little difference appears between *ortho*-, *meta*-, and *para*-substituted porphyrin as far as a series of each glycosylated substituent is concerned. By NMR measurement about 10% of protecting group, acyl group, may remain without elimination in the case of (*o*-Lac)<sub>4</sub>-TPP. This may cause  $\Phi_{\text{PHB}}$  of (*o*-Lac)<sub>4</sub>-TPP/PVA to be reduced to some extent because of its low solubility in PVA matrix. The xylosylated and lactosylated TPPs have the values of  $\Phi_{\text{PHB}}$  approximately in the same order of magnitude as TPP has.

It should be noted that  $\Phi_{\text{PHB}}$  shows wavelength dependence<sup>16)</sup> due to the existence of vibronic sublevels in the lowest energy absorption band of TPP derivatives and phonon-assisted absorption.<sup>17)</sup> Hence, the present

$\Phi_{\text{PHB}}$  values have been obtained based on the measurements at the peak wavelength of the lower energy absorption bands of each chromophore. The values of  $\Phi_{\text{PHB}}$  for TPPS and carboxylated TPP in PVA based on pure zero-phonon absorption are estimated to be in the order of  $10^{-2}$ .<sup>17,18)</sup> The temperature dependence of  $\Phi_{\text{PHB}}$  has also been discussed for TPP in PhR<sup>4)</sup> and TPPS in PVA<sup>3,15)</sup> systems.

In conclusion, porphyrin glycosides, especially lactosylated TPP in PVA show more excellent thermal stability of spectral holes than TPPS in PVA does. The hydroxyl groups of the glycosides in the porphyrins interact through hydrogen bonds with those of the matrix polymer, PVA, to suppress the thermally-induced structural relaxation leading to hole filling. The density of the hydroxyl groups of PhR is too small to interact with the porphyrin glycosides.

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