Photochemical hole burning (PHB) of tetraphenylporphin in poly(ethylene terephthalate)

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The efficiency of hole formation, Φ, the energy difference between a zero-phonon hole peak and a pseudo-side hole peak, E_s, and the thermal stability of holes burnt at 4.2 K with a 0.1–2.0 mW cm^{-2} Ar$^+$-laser-pumped ring dye laser at about 647 nm were studied for tetraphenylporphin (TPP) in poly(ethylene terephthalate) (PET) films. The value of Φ was 5.4×10^{-4} and 6.2×10^{-4} for TPP in undrawn and five-times drawn PET film, respectively, while the annealing of the drawn film at 220°C resulted in a marked decrease in Φ probably due to the aggregation of TPP molecules. The phonon frequency measured as E_s from the hole profiles of TPP in PET films was about 11–12 cm^{-1} (similar to the E_s for polystyrene), and a small increase in E_s was observed by five-times drawing the PET film, reflecting the increased order in the amorphous region of the PET film. The thermal stability of holes burnt at 4.2 K measured with hole recovery at 4.2 K after cyclic standing of the sample at 30, 50 and 80 K was markedly improved by the five-fold drawing of the PET film. The structural relaxation process affecting the spectral diffusion of PHB holes seemed to be of very local character in the vicinity of PHB molecules in the amorphous region of PET films.

(Keywords: PHB; tetraphenylporphin; poly(ethylene terephthalate); low temperature spectroscopy)

INTRODUCTION

The phenomenon of photochemical hole burning (PHB) has recently attracted considerable interest not only as a means for frequency-domain high-density optical storage[1], but also as a tool for high-resolution solid state spectroscopy at low temperatures[2–4]. The PHB consists of burning very narrow and persistent holes into the absorption bands of guest molecules molecularly dispersed in amorphous solids by narrow band excitation with a laser beam at very low temperatures.

The temperature dependence of hole profiles burnt at liquid-helium temperature is one of the important aspects of the PHB phenomenon. It gives information on electron–phonon coupling and the dephasing process from the hole width and the change in the Debye–Waller factor, and the spectral diffusion process due to local structural relaxation of the matrices. For example, the photochemical hole of free-base phthalocyanine (H_2PC) in poly(methyl methacrylate) (PMMA) burnt at 4.2 K was reported to be difficult to measure above 50 K by hole broadening and the decrease in the Debye–Waller factor. However, the hole reappeared when it was cooled to 4.2 K after cyclic annealing at 80 K (ref. 5). The cyclic annealing experiments for evaluating the temperature stability of holes burnt at 4.2 K were also carried out for quinizarin (Q) in amorphous silica (a-SiO_2)[6], free-base tetraphenylporphin (TPP) in phenoxy resin (PhR)[7], and for some other systems[8–10].

In order to increase the thermal stability of photochemical holes, we introduced main-chain aromatic polymers, such as polycarbonate, polysulphone, polyethersulphone, polyimides, and phenoxy resin[8] as matrices. Among them phenoxy resin (aromatic polyhydroxyether) proved to be an effective matrix both for the efficiency of hole formation and for the temperature stability of the hole of TPP[7], suggesting the importance of improving the packing and higher-order structure of the matrix polymer. Poly(ethylene terephthalate) (PET) is used extensively in the form of fibre and film, and the effect of orientation by drawing on the physical and microscopic properties of PET has been widely studied[11–13]. Thus we chose PET as a matrix for studying the effect of drawing and annealing on the PHB in polymer matrices.

In this study, the efficiency of hole formation and the temperature dependence of hole stability in PHB of TPP have been investigated in undrawn and drawn PET films.

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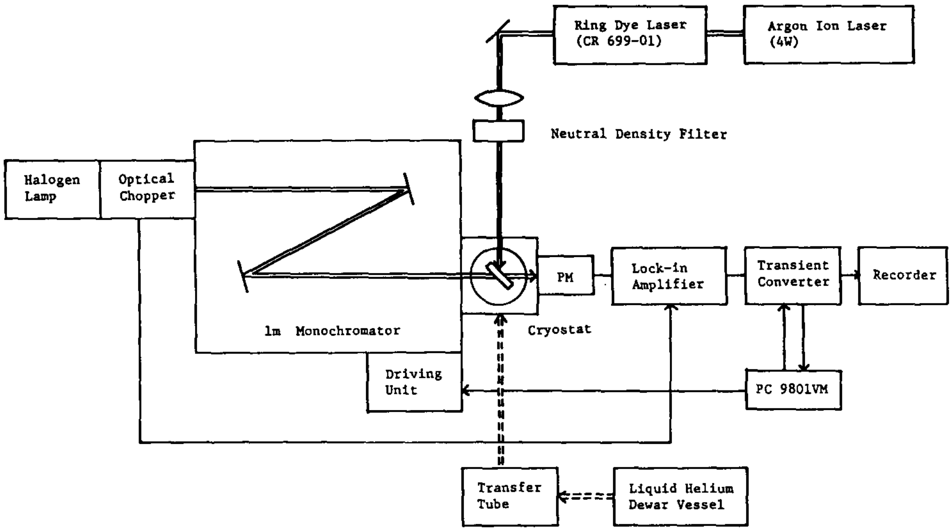

Figure 1 Schematic diagram of the hole burning and detecting system

The phonon frequency for PET reflecting the low energy excitation modes has also been determined from the energy difference between zero-phonon hole and pseudo-side hole peaks.

EXPERIMENTAL

Materials

The solution of PET and TPP (Wako Pure Chem. Ind., Tokyo) in hexafluoroisopropyl alcohol was cast, dried, and changed to a brown powder. An appropriate amount of this brown powder was mixed (1:10 v/v) with a PET pellet at 280°C in melt and pressed at 280°C for 3 min, resulting in PET film (100–200 μm thick) containing molecularly dispersed TPP. The glass transition temperature, T_g, of the film was about 80°C as determined by differential scanning calorimetry (d.s.c.). The uniaxial drawing five times in length was carried out at 220°C for 60 s. The TPP concentration was about 8×10^{-3} mol l^{-1} in all films. The density, ρ, of the undrawn, drawn and drawn-and-annealed films were 1.338, 1.368, 1.388, respectively.

PHB measurements

The system for hole burning and detection is shown in *Figure 1*. The sample was set in a continuous flow type liquid-helium cryostat (Oxford, CF1204), and irradiated by an Ar$^+$-laser-pumped single-mode continuous wave ring dye laser (Cohernt, 699-01) with 0.1–2.0 mW cm^{-2} laser power around 647 nm. The sample temperature was monitored by a Fe-doped gold *versus* chromel thermocouple. Holes were detected by the change of transmittance with a 1-m monochromator (Jasco, Tokyo, CT100C), a photomultiplier (Hamamatsu, R943-02) and lock-in amplifier (Jasco, LA126W). The data was processed with a desk-top computer (NEC, PC9801vm2). The resolution of the detecting system was about 0.3 cm^{-1} with the resolution of the monochromator being the limiting factor.

RESULTS AND DISCUSSION

Efficiency of hole formation

Figure 2 shows the absorption spectrum of TPP in PET at room temperature and 4.2 K. Holes were burnt around 647 nm in the lowest 0–0 transition of the Q band with an inhomogeneous line width, $\Delta\omega_i$, of approximately 550 cm^{-1}. The absorbance of the band increased with the decrease in temperature, and it was about one-and-a-half times larger at 4.2 K than that at room temperature.

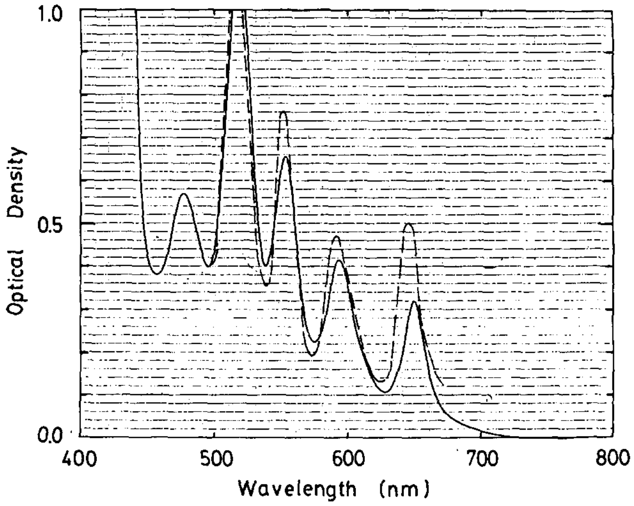

Figure 2 Absorption spectrum of TPP in five-times drawn PET film at 4.2 K (----) and at room temperature (———). The film thickness is 100 μm, and the concentration of TPP in the film is 8.0×10^{-3} mol l^{-1}

Typical photochemical holes of TPP in PET films burnt with a 0.75 mW cm^{-2} ring dye laser at 4.2 K are shown in *Figure 3*, and the changes in hole depth during laser irradiation are given in *Figure 4*. The increase in hole depth, $\Delta A/A_0$, where ΔA is the difference in absorbance produced by hole formation and A_0 is the absorbance before irradiation, does not obey a first-order plot, and $\Delta A/A_0$ levels off during irradiation.

The quantum yield for hole formation, Φ, can be calculated from the initial slope in *Figure 4*, $[\mathrm{d}(A/A_0)/\mathrm{d}t]_{t=0}$, by using equation (1):

$$\Phi = \left(\frac{\mathrm{d}(A/A_0)}{\mathrm{d}t}\right)_{t=0} A_0/[10^3 I_0(1-10^{-A_0})\varepsilon R] \qquad (1)$$

where I_0 is the incident laser intensity given in einstein

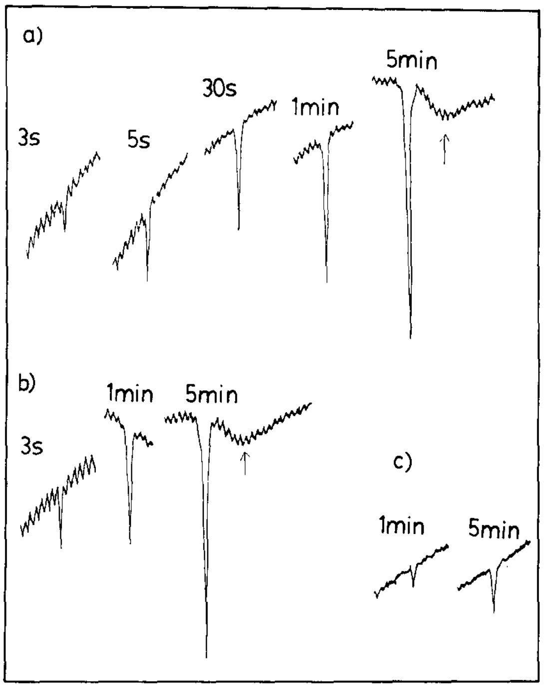

Figure 3 Typical photochemical holes of TPP at 4.2 K in undrawn (a), five-times drawn (b) PET films, and annealed PET film after five-times drawing (c). Burning times with a 0.75 mW cm^{-2} dye laser at 4.2 K are shown beside the profiles

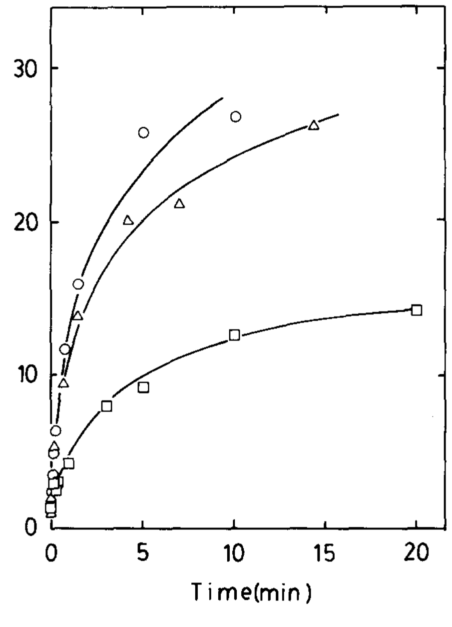

Figure 4 Change in hole depth, $\Delta A/A_0$, during 0.75 mW cm^{-2} dye laser irradiation at 4.2 K for TPP in undrawn (Δ), five-times drawn (○) PET films, and annealed PET film after five-times drawing (□)

cm^{-2} s^{-1}, ε is the molar extinction coefficient for the inhomogeneous line profile at the hole burning wave length and temperature, and $R = C_0/C_{0h} = \Delta\omega_i/\Delta\omega_h$ is the reciprocal initial fraction of TPP molecules within a homogeneous line width, $\Delta\omega_h$, at the laser frequency[7,14]. The value of Φ increased a little for the five-times drawn TPP/PET film ($\Phi = 6.2 \times 10^{-4}$) compared with the undrawn film ($\Phi = 5.4 \times 10^{-4}$), but the annealing of the drawn film at 220°C resulted in a marked decrease in Φ ($\Phi = 1.2 \times 10^{-4}$). The same tendency is also observed for the hole depth in the later stage of irradiation shown in *Figure 4*. The TPP molecules are supposed to locate in the amorphous region of PET film, and annealing at 220°C for 1 min may have brought about the aggregation of TPP molecules causing the decrease in Φ. The TPP is stable up to 350°C and vaporizes in vacuum at that temperature. The maximum value of $\Phi = 6.2 \times 10^{-4}$ for the hole formation of TPP in PET is not much smaller than that of $\Phi = 1.1 \times 10^{-3}$ for TPP in phenoxy resin[7]. Recently, Φ for TPP was shown to depend little on the nature of matrix polymers, as long as the samples were prepared in optimum conditions, i.e. with a sufficiently low concentration of TPP, evacuation of the solvent-cast sample at a temperature near the T_g of the matrix polymer and hot pressing[15].

Phonon frequency of poly(ethylene terephthalate)

A pseudo-side hole or a side hole formed at the low energy side of a zero-phonon hole (shown by arrows in *Figure 3*) gives information on the low energy excitation modes of the matrix polymer coupled with guest molecules. The energy difference E_s between a zero-phonon hole peak and a pseudo-side hole peak, called phonon frequency, corresponds to the energy for that mode, and was proved to be independent of both the temperature and the nature of the guest molecule[16]. The E_s is an inherent parameter to the matrix polymers. The values of E_s for PET and other polymers are summarized in *Table 1* together with the characteristic frequency, E_c, used to explain the excess heat capacity[17] and the energy E_1, at a peak in the region of low energy excitation modes determined by neutron inelastic scattering measurements[18]. The fact that the E_s values obtained from the PHB hole profile agree well with E_c by heat capacity and E_1 by inelastic neutron scattering measurements suggests the utility of PHB measurements for investigating the low-energy modes of phonon states of amorphous matrices[16,19]. The increase in E_s of PET by drawing five times suggests the increase in order and orientation by drawing the amorphous region of the PET film.

Thermal stability of holes burnt at 4 K

Typical changes in hole profiles during cyclic annealing of TPP in five-times drawn PET film are shown in *Figure 5*. The photochemical hole of TPP in PET burnt at 4.2 K for 10 min with a 0.75 mW cm^{-2} laser at about 646 nm becomes broader and shallower with increase in cyclic 30-min-standing temperature, and it disappeared with standing and measuring at 80 K. Three factors, namely, broadening of homogeneous width due to dephasing of the electronically excited state by electron–phonon interaction, decrease in the Debye–Waller factor, and the spectral diffusion process due to local structural relaxation of the matrix polymer are supposed to affect

Table 1 Phonon frequencies determined by PHB, E_s, heat capacity, E_c, and inelastic neutron scattering, E_1, measurements

Chromophore/amorphous polymer matrix	E_s (cm^{-1})	E_c[17] (cm^{-1})	E_1[18] (cm^{-1})
TPP/PET (undrawn)	10.9		
TPP/PET (five-times drawn)	11.8		
TPP/polystyrene	10.1	9.1	12.0
TPP/PMMA	13.1	12.0	
Quinizarin/PMMA	13.6		
TPP/phenoxy resin	15.1		
Sulphonated TPP/poly(vinyl alcohol)	23.5		
Quinizarin/poly(vinyl alcohol)	23.0		

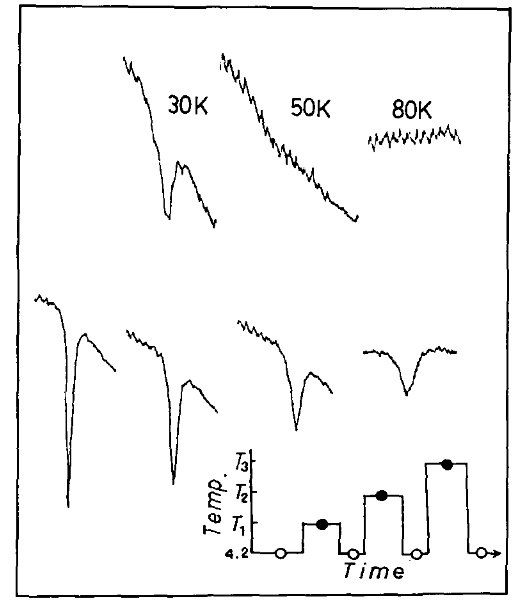

Figure 5 Typical photochemical holes of TPP in five-times drawn PET film during cyclic annealing. The upper faces correspond to the measurements at the annealing temperature (●) (shown beside the spectra) after standing for 30 min. The lower traces correspond to spectra measured at 4.2 K (○) after cooling from the annealing temperature. Insert shows the cyclic annealing procedure

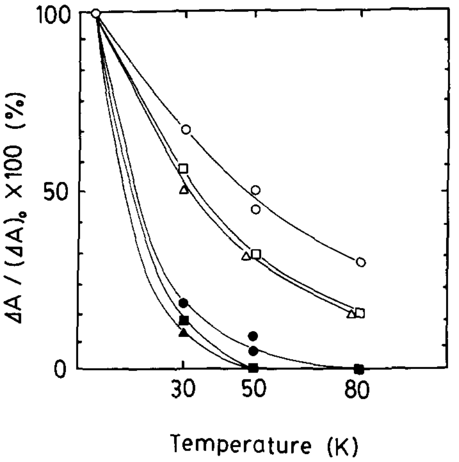

Figure 6 Change in relative hole depth, $\Delta A/(\Delta A)_0$, compared with the initial hole depth burnt at 4.2 K, during cyclic annealing measured at the annealing temperatures (▲, ●, ■) and at 4.2 K (△, ○, □) for TPP in undrawn (▲, △), five-times drawn (●, ○) PET films and annealed (at 220°C) PET film after five-times drawing (■, □)

the temperature dependence of hole profiles. The broadening of homogeneous width and the change in the Debye–Waller factor are reversible processes with change in temperature, while spectral diffusion is an irreversible process[4,15]. Thus the analysis of hole recovery observed in *Figure 5* when the sample was cooled again to 4.2 K from each annealing temperature provides information on the irreversible local structural relaxation causing hole broadening and filling.

The changes in relative hole depth, $\Delta A/(\Delta A)_0$, based on its initial value measured just after irradiation at 4.2 K, are summarized in *Figure 6* for TPP in PET films. The hole depth measured at 4.2 K after cyclic standing at a certain temperature was improved markedly by five-times drawing the PET film, but it returned to its initial value by annealing the drawn sample at 220°C for 60 s (△, ○, □ in *Figure 6*). Similar effects of drawing the PET film and further annealing of the film at 220°C were also observed for the change in hole depth measured at the standing temperatures (▲, ●, ■ in *Figure 6*). The dye molecules molecularly dispersed in PET film are known to be located in the amorphous region[20]. The orientation of the amorphous region by uniaxial drawing suppressed the local molecular motion of TPP leading to the restriction of spectral diffusion at 4–80 K. Further annealing of the drawn sample at 220°C brings about the increase in crystallinity and crystallite size, and also a disordering of non-crystalline oriented chains[12,21]. The results in *Figure 6* suggest that the disordering or structural relaxation process affecting PHB hole recovery is of very local character in the vicinity of the PHB molecule which is sensitive to the annealing of drawn film even for 60 s at 220°C.

The orientation in the amorphous region can be evaluated by visible dichroism measurements of dye molecules molecularly dispersed in PET film[20]. Though TPP in the drawn PET film showed no visible dichroism owing to its inherent inactivity to dichroism, a marked dichroism ($D = 0.28$) was induced for free-base tetrahexyloxyphthalocyanine (THPC) in PET film by drawing the film five times. Further annealing of the drawn film at 220°C for 60 s hardly changed the value of dichroism ($D = 0.27$). Thus the present condition of annealing is insufficient for rotation of the dye molecule, but is supposedly sufficient for the local relaxation affecting the PHB hole recovery.

In conclusion, the effects of drawing and annealing on the efficiency of hole formation and the temperature stability of photochemical holes of TPP have been studied for PET films. The five-times drawing of the PET film improves the temperature stability of holes by increasing the number of oriented chains in the amorphous region. The structural relaxation process affecting the spectral diffusion of PHB holes is of very local character in the vicinity of the PHB molecule.

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