Photochemical hole burning of tetraphenylporphin in an aromatic polyimide

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(Received 6 July 1990; accepted 23 August 1990)

Photochemical hole burning (PHB) was performed in free-base tetraphenylporphin (TPP) doped into an aromatic polyimide (PI). The microscopic ordered structure of PI, low energy excitation modes, and thermal stability of a hole burnt at 4.2 K were studied with the PHB measurements. Low energy excitation modes reflected microscopic ordered structure. Thermal stability of a hole showed little dependence on the ordered structure. It could be interpreted that the structural relaxation leading to the instability of a hole is a larger scale relaxation than the low energy excitation modes. This interpretation is consistent with the fact that the thermal energy for annealing temperature (30–80 K) is larger than the low energy excitation modes ($\sim 10\ \mathrm{cm}^{-1}$).

(Keywords: photochemical hole burning; tetraphenylporphin; polyimide; low temperature spectroscopy)

INTRODUCTION

Photochemical hole burning (PHB) in polymer systems has been investigated intensively in recent years[1–6]. PHB has attracted much interest as a very sensitive probe for the dynamics in polymer systems as well as a possible means for optical data storage. Hole profiles give much information on the microenvironment around photoreactive guest molecules. The PHB technique has revealed the subtle relaxation process around the guest molecules and the intrinsic low energy excitation modes in amorphous polymers[2]. Relaxation processes in various polymer systems at low temperatures have been monitored with cyclic annealing experiments, i.e. measurement of the change of hole profile during cyclic annealing[1,3,4,6]. Low energy excitation modes in amorphous polymers, which lead to excess heat capacity at low temperatures, are estimated from the position of a pseudo-phonon side hole[2].

An aromatic polyimide (PI) has excellent thermal and mechanical stability. The microscopic ordered structure of PIs leading to the thermal and mechanical stability was elucidated by small angle X-ray scattering measurements[7]. Molecular aggregation of PIs affecting the microscopic ordered structure was monitored by fluorescence spectra[8]. This microscopic ordered structure is attained by the main chain rigidity and by strong intermolecular interaction caused by the stacking of aromatic rings. Cold drawing of a PI precursor, poly(amic acid) (PAA), followed by thermal imidization also led to development of the ordered structure[9]. The PI host system might be expected to have microscopic rigidity leading to good thermal stability of a photochemical hole due to this microscopic ordered structure.

In the present paper, the relaxation process and low energy excitation modes in an aromatic polyimide are studied with the PHB measurements in order to obtain information on the relationship between the microscopic ordered structure of the aromatic polyimide, relaxation processes and the low energy excitation modes.

EXPERIMENTAL

The DMAc solution of a PI precursor, PAA, prepared from biphenyltetracarboxylic dianhydride (BPDA) and *p*-phenylenediamine (PDA) was supplied by Ube Industries, and used without further purification. The concentration of PAA was 10%, and the viscosity of the solution was $\sim 500\ \mathrm{N\,m^{-2}\,s}$. Free-base tetraphenylporphin (TPP) obtained from Wako Pure Chemical

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0032-3861/91/122167-05

Table 1 Imidization conditions, hole formation efficiencies at 4.2 K, Φ, low energy excitation modes, E_s, and densities for various TPP/PI samples

Sample	Imidization condition	$\Phi \times 10^4$	E_s (cm^{-1})	Density (ref. 8) ($g\,cm^{-2}$)
A	150°C, 2 h; 200°C, 5 h	6.8	10.9	1.4194
B	270°C, 2 h	0.63	12.0	1.4465
C	320°C, 2 h	0.48	11.5	1.4655
D	150% drawn PAA 150°C, 2 h; 200°C, 5 h	7.0	13.3	
E	150°C, 24 h	11.0	12.5	

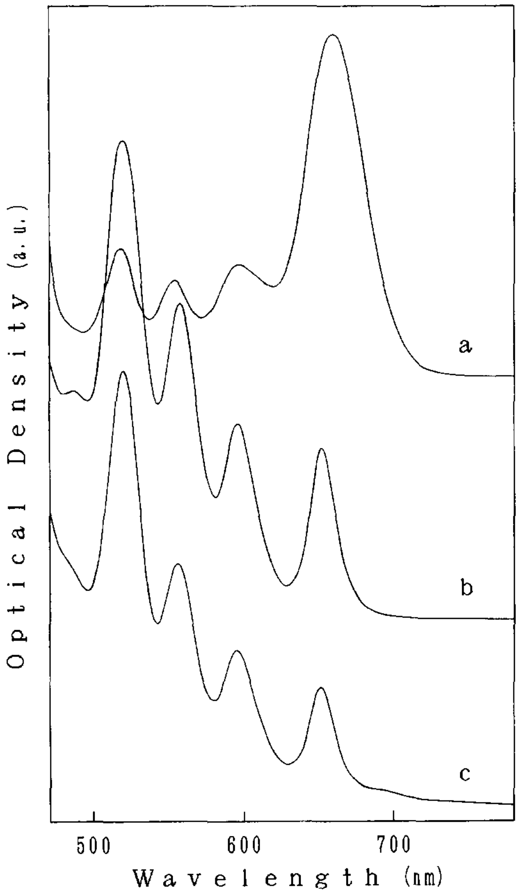

Figure 1 Absorption spectra of TPP/PAA (curve a) and TPP/PI (curve b, sample E; curve c, sample C)

Industries, was used without further purification as a photoreactive guest molecule whose hole burning reaction occurs as the phototautomeric reaction of internal protons. TPP-doped PAA films, TPP/PAA, were prepared by casting a mixed DMAc solution of PAA and TPP onto a glass substrate at 50°C for 2 h in an air oven, and then drying in a vacuum oven at 50°C for 20 h. The concentration of TPP was 1.7×10^{-3} mol l^{-1} and the film thickness was ~0.1 mm. Imidization of TPP/PAA films was carried out thermally at 150–320°C in a vacuum oven. The 150% drawing of TPP/PAA film was performed before the imidization in some cases.

Samples were set in a continuous flow type cryostat (Oxford, CF1204) and irradiated by an Ar^+ laser-pumped single-mode continuous wave dye laser (Coherent, 699-01) with 0.075–0.75 mW cm^{-2} laser power around 640 nm corresponding to the absorption band of the lowest O–O transition of TPP. Holes were detected by the change of transmittance with a 1 m monochromator (Jasco, CT100C), a photomultiplier and a lock-in amplifier. Details of the apparatus have been given previously[3].

RESULTS AND DISCUSSION

Table 1 shows the imidization conditions, hole formation efficiencies, Φ, low energy excitation modes, E_s, and densities[8] for various TPP/PI samples. I.r. measurements were made to ensure that the imidization was completed at these imidization temperatures, except for sample E[10]. Generally, the packing density of PI is higher as the imidization temperature of PAA rises. This relation is shown for samples A, B and C[8]. The imidization reaction of sample E, probably a copolymer of PI and PAA, is not completed. The other characteristics of PHB for various samples will be discussed later.

Figure 1 shows the absorption spectra of TPP/PAA and TPP/PI. TPP/PAA shows an absorption peak of a protonated TPP around 660 nm due to the acidity of PAA. This absorption peak also appeared when TPP was doped into poly(methyl methacrylate) (PMMA) containing acetic acid. The absorption peak of a protonated TPP disappeared when TPP/PAA was imidized. The absorption spectra of samples C (curve c) and E (curve b) are almost the same as that of TPP in an aprotic solvent, except for a small peak around 690 nm in sample C, which is probably due to aggregation of TPP. This explanation is supported by the low efficiency of hole formation of sample C, mentioned below.

Figure 2 shows the irradiation time dependence of the hole profile at 4.2 K for sample E. Laser intensity

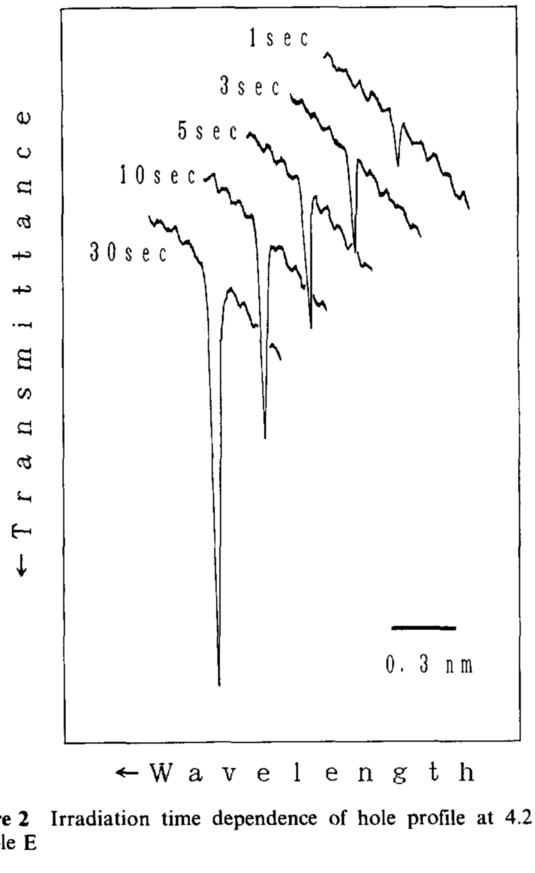

Figure 2 Irradiation time dependence of hole profile at 4.2 K for sample E

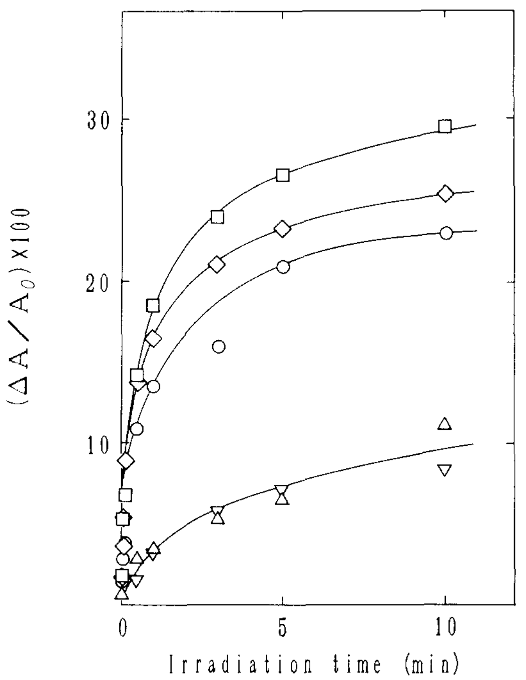

Figure 3 Irradiation time dependence of hole depth, $\Delta A/A_0$ for samples A (○), B (▽), C (△), D (◇) and E (□)

was 0.75 mW cm^{-2}. Initial hole width was ~0.7 cm^{-1}. *Figure 3* shows the irradiation time dependence of hole depth, $\Delta A/A_0$, estimated from the measurements shown in *Figure 2* for various samples at 4.2 K, where ΔA is the difference in absorbance produced by hole formation and A_0 is the absorbance before irradiation. Hole formation efficiency, Φ, was calculated using the initial slope of irradiation time dependence of hole depth shown in *Figure 3* and initial hole width, by taking into account the site selectivity of hole formation[3]. The hole formation efficiencies for various samples are listed in *Table 1*. Sample E shows almost the same value of Φ as for TPP doping in other polymer systems (1.1×10^{-3})[11]. Samples A and D show similar values of Φ to that of sample E, but samples B and C show extremely low values of Φ. These facts suggest that imidization above 200°C leads to the aggregation of TPP and results in a low Φ value due to interaction among TPP molecules. The low Φ value due to the aggregation of TPP was also reported in the TPP/poly(ethylene terephthalate) system when the sample underwent thermal treatment at 220°C for 1 min[6].

Low energy excitation modes, E_s, estimated with the position of a pseudo-phonon side hole are also listed in *Table 1*. Since the E_s values reflect microscopic order in host matrices[4,6], they should correlate to the densities of PIs which reflect microscopic order. Therefore it is expected that a PI with high density, also has a large E_s value, as indicated in *Table 1*. The larger E_s value of sample B than sample C is thought to be due to the influence of the aggregation of TPP mentioned above. Sample D has the largest E_s value, which suggests that this sample has the most ordered structure, probably due to the 150% drawing of PAA. Sample E shows a rather large E_s value in spite of the relatively low imidization temperature. A possible interpretation is that sample E is a copolymer of PI and PAA with a rather large E_s value. This interpretation was supported by the fact that the partially imidized PAA sample showed a large E_s value (14.3 cm^{-1}).

Cyclic annealing experiments up to 80 K were performed for various samples. *Figure 4* shows the temperature dependence of the hole profile during the cyclic annealing experiment for sample E. An initial hole was burnt at 4.2 K with 0.75 mW cm^{-2} laser power for 1–5 min. Annealing time was 30 min at each elevated temperature, and hole profiles were measured after cooling down to 4.2 K. As shown in *Figure 4*, hole area became small at elevated temperatures and was restored at 4.2 K. This phenomenon could be interpreted as the temperature dependence of the Debye–Waller factor which is the fraction of a zero-phonon line in the integrated absorption of a photoreactive guest molecule[2,12].

Figure 5 shows the annealing temperature dependence of hole area during the cyclic annealing experiments. Hole areas decreased gradually as the annealing temperature rose, but almost 80% of the initial hole area was conserved as long as it was measured at 4.2 K. This suggests that hole-filling due to thermally activated structural relaxation and/or backward reaction hardly occurs. It is consistent with the existence of a potential barrier to the internal proton exchange in the porphyrin ring which cannot be crossed thermally at least up to 80 K, as elucidated by n.m.r. spectroscopy[13]. It could be said that thermally activated spectral diffusion caused by the redistribution of non-equilibrium conformations in the matrix is the dominant process for the change of hole profile in this temperature range. The dependence of hole area on annealing temperature during the cyclic

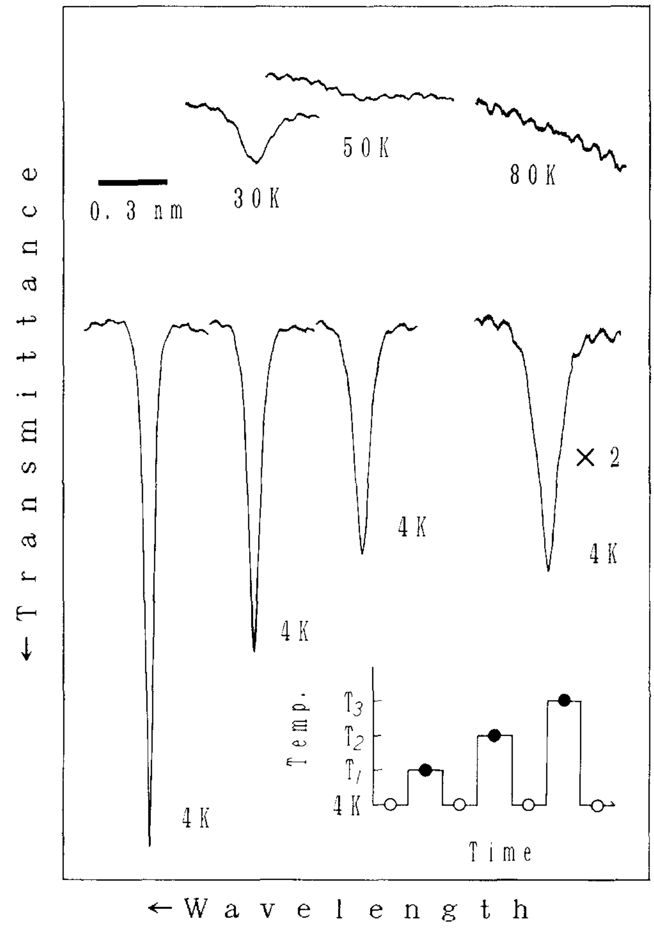

Figure 4 Temperature dependence of hole profile during the cyclic annealing experiment for sample E. Sensitivity for the hole profile after annealing at 80 K is twice as large as the others

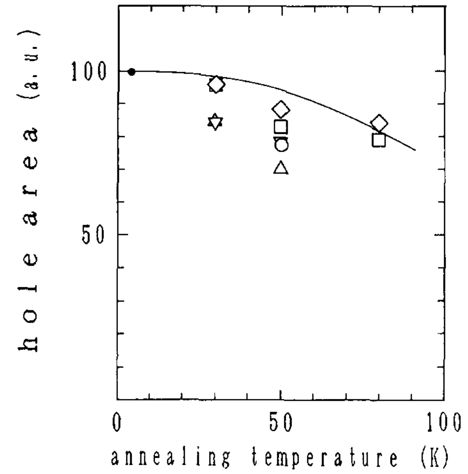

Figure 5 Annealing temperature dependence of hole area during the cyclic annealing experiments. Hole area was measured at 4.2 K after temperature cycle. Symbols as in *Figure 3*

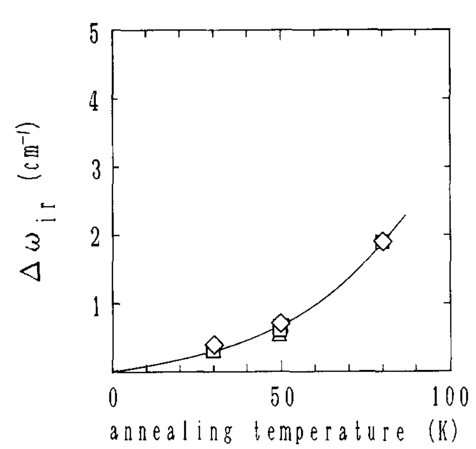

Figure 6 Annealing temperature dependence of irreversible change in hole width, $\Delta\omega_{ir}$, during the cyclic annealing experiments. Hole width was measured at 4.2 K after temperature cycle. Symbols as in *Figure 3*

annealing experiments did not depend very much on the sample preparation conditions. Furthermore, the amount of conserved hole area is almost the same as for other TPP/amorphous polymer systems[14].

Figure 6 shows the annealing temperature dependence of irreversible change of hole width, $\Delta\omega_{ir}$, during the cyclic annealing experiments. The $\Delta\omega_{ir}$ reflects the extent of thermally activated spectral diffusion at the annealing temperature. In spite of the difference in the E_s values, annealing temperature dependence of $\Delta\omega_{ir}$ did not depend on the sample preparation conditions. This is consistent with the fact that the thermal energy for annealing temperature is larger than the E_s value.

In some cases during the cyclic annealing experiments irradiation was at a different wavelength from the initial hole burnt at 4.2 K. Irradiation was performed at the lower energy side of the initial hole with 0.75 mW cm^{-2} laser power for 10 min at each elevated temperature. The energy separation between the initial hole and the irradiation was 50–100 cm^{-1}. *Figure* 7 shows the annealing temperature dependence of hole area during cyclic annealing experiments with and without laser irradiation for sample D. The hole width did not change, irrespective of the laser irradiation. Similar results were obtained for samples with other imidization conditions. The hole area decreased considerably with laser irradiation. This hole filling process is thought to be caused by photoinduced structural relaxation and not by heating due to irradiation[14]. The photoinduced structural relaxation is not suppressed in the TPP/PI system. It is probably due to the absence of hydrogen bonding and/or crosslinked structure in the TPP/PI, which was observed to restrict the laser-induced hole filling in TPP/phenoxy resin, TPP/epoxy resin, and sulphonated TPP/poly(vinyl alcohol)[14].

There are thus three classes of motion or relaxation which affect the PHB phenomena at 4.2–80 K: low energy excitation modes, E_s, which could reflect microscopic order of host matrices; thermally activated spectral diffusion caused by structural relaxation after temperature cycling; and photoinduced structural relaxation which leads to hole filling. The energy ranges of these three classes of motion are different; that of the E_s value is the smallest, followed by that of thermally activated spectral diffusion. The microscopic ordered structure of PI affects the E_s value, but hardly affects the extent of thermally activated spectral diffusion and photoinduced structural relaxation. The range of energy which could be changed by the microscopic order of PI would be rather small (~ 10 cm^{-1}) at 4.2–80 K, probably due to the lack of motion of a main chain in this temperature region. Therefore, the motions in the larger energy ranges depend very little on the microscopic ordered structure of PI.

CONCLUSIONS

The low excitation modes, E_s, reflect the microscopic ordered structure of PI. When imidization was performed at high imidization temperature or after drawing of PAA, the E_s value increased, correlating with the ordered structure. But the thermal stability of a hole burnt at 4.2 K during cyclic annealing experiments did not depend on the microscopic ordered structure. It could be interpreted that the structural relaxation leading to hole filling and spectral diffusion leading to the irreversible broadening of a hole are larger scale relaxation processes than the low energy excitation modes.

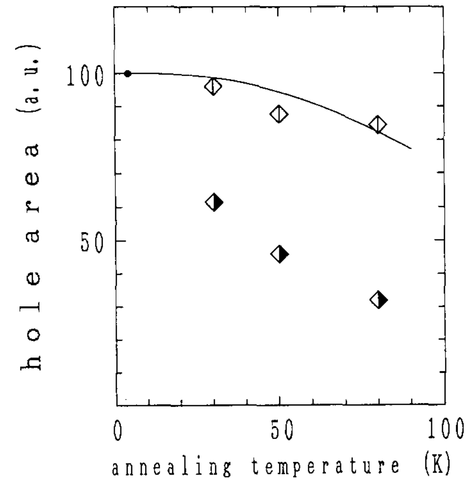

Figure 7 Annealing temperature dependence of hole area during the cyclic annealing experiments with laser irradiation (◆) at elevated temperatures and without irradiation (◇) for sample D

ACKNOWLEDGEMENTS

The authors express their thanks to Dr R. Yokota for his kind supply of PAA and to Dr N. Hasegawa for fruitful suggestions.

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