Stark effect on persistent spectral hole burning and dipole moment characteristics of anthraquinone derivatives doped in polymers

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We have investigated the Stark effect on the spectral hole characteristics in the photochemical hole burning reaction in systems of anthraquinone derivatives, such as 1,4-dihydroxyanthraquinone (DAQ) and 4-amino-2,6-bis(4-butylphenoxy)1,5-dihydroxyanthraquinone (ABDAQ) as guest molecules embedded in host polymers such as 2-hydroxyethyl methacrylate (PHEMA) or poly(vinyl butyral) (PVB). The hole broadening and refilling were observed by applying an external electric field to the samples. Thus, the dipole moment differences $|\Delta\vec{\mu}|$ of the guest molecules between the ground state and the excited state were estimated as follows: 0.38, 0.51 and 0.26 D in the DAQ/PHEMA, ABDAQ/PHEMA and ABDAQ/PVB systems, respectively. These material dependent characteristics of $|\Delta\vec{\mu}|$ have been able to be explained qualitatively by Hammett's substituent constant and the Taft's polar substituent constant. Furthermore, from the application view point, 5 × 5 multiple spectral holes could be formed in both the wavelength and the electric field dimensions at 4.2 K in the ABDAQ/PVB system. This result indicates that high-density data multiplexing can be achieved in both the wavelength and the electric field dimensions using the Stark effect on the spectral holes.

(Keywords: PHB; anthraquinone derivatives; polymer matrix; Stark effect; dipole moment; multiple data storage)

INTRODUCTION

Photochemical hole burning (PHB) has drawn much attention from the viewpoint of high-resolution molecular spectroscopy[1–6] and its application to high-density optical memory[2–11]. High-density optical memory using PHB of $>10^{11}$ bits cm^{-2} can be generally realized by forming multiple spectral holes in the wavelength dimension; that is, the presence and absence of a spectral hole of the absorption spectra in the wavelength dimension are coded[12] using the binary system.

PHB spectral holes can also be formed multiply in the electric field dimension according to the Stark effect[13] which can be brought about by the electric field induced redistribution of the homogeneous absorption bands of the guest molecules. A spectral hole at a wavelength λ_0, which was burnt at an initial external electric field $\vec{E}_0$, is refilled and disappears upon changing the external electric field from $\vec{E}_0$ to $\vec{E}_n$, because the initial distribution of the homogeneous absorption bands in the amorphous matrix is changed to another distribution state. Subsequently, another spectral hole at identical wavelength λ_0 can be burnt freshly at the electric field strength $|\vec{E}_n|$. In this manner, a series of spectral holes in the electric field dimension can be formed multiply at wavelength λ_0 by changing the external electric field strength. These multiple holes in the electric field dimension can also be used as multiple signals in addition to the ones formed in the wavelength dimension.

Several studies concerning the Stark effect have been reported both for inorganic[14,15] and organic PHB material systems. For organic PHB material, only such guest molecules as chlorine and its derivatives[16–18], resolfine[19] and 9-aminoacridine[20] were examined in the polymer matrix hosts. The multiple data storage in the electric field dimension was demonstrated only in the chlorine/ poly(vinyl butyral) (PVB)[21] and 9-aminoacridine/PVB[19] systems; no reports seem to have been published on the quinone derivatives.

In this work, we observed the Stark effect for the first time for PHB systems composed of 1,4-dihydroxyanthraquinone (DAQ) and 4-amino-2,6-bis(4-butylphenoxy)1,5-dihydroxyanthraquinone (ABDAQ)[22–25]. We obtained some significant experimental results as follows. First, we succeeded in producing 5 × 5 multiple spectral holes both in electric field and wavelength dimensions at 4.2 K. Second, an efficient response of the spectral hole depth to the applied electric field strength change was observed. Third, we were able to estimate the absolute value of the dipole moment difference, $|\Delta\vec{\mu}|$, of the guest molecule between the ground and the excited states. In this study, the absolute values $|\Delta\vec{\mu}|$ for DAQ and ABDAQ were estimated to be 0.38, 0.51 and 0.26 D in the DAQ/2-hydroxyethyl methacrylate (PHEMA),

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ABDAQ/ PHEMA and ABDAQ/PVB systems, respectively. We have explained such material dependences of $|\Delta\vec{\mu}|$ on the basis of the electronic characteristics of the substituents of the anthraquinone (AQ) derivatives and the microscopic dipole moment characteristics of the polymer side chain, using the Hammett's substituent constant[26,27] for the aromatic AQ derivatives and the Taft's polar substituent constant[28] for the aliphatic polymer side chain, respectively.

EXPERIMENTAL

AQ compounds such as DAQ and ABDAQ were used as the guest and PHEMA and PVB as the host. DAQ was obtained from Wako Chemical Ltd, ABDAQ from Nihon Kayaku Ltd and PHEMA and PVB from Scientific Polymer Products Inc. The solvents [tetrahydrofuran (THF) and 2-methoxy ethanol (MeOEtOH)] used for dissolving the polymers and the dyes were of spectral quality. The three kinds of samples were prepared in the form of polymer films by the following process. DAQ and PHEMA, and ABDAQ and PHEMA were dissolved in MeOEtOH and ABDAQ and PVB in THF. They were mixed thoroughly before casting. The concentration of the guest in the host polymer was 2.04×10^{-4} mol mol^{-1} in the DAQ/PHEMA system, 3.30×10^{-4} mol mol^{-1} in the ABDAQ/PHEMA system and 3.23×10^{-4} mol mol^{-1} in the ABDAQ/PVB system, respectively. Appropriate amounts of each solution were placed in a glass Petri dish, and the solvents were allowed to evaporate slowly over at least a week. In this manner, optically clear films were obtained. The thickness of the film was 270 μm in the DAQ/PHEMA sample, 170 μm in the ABDAQ/PHEMA sample and 80 μm in the ABDAQ/PVB sample, The molecular structures of the compounds used are shown in *Figure 1*.

To apply the electric field to the sample, the sample film was inserted under pressure between two glass plates at 110°C for the PVB sample and at 150°C for the PHEMA sample. The glass plates had an optically transparent inner coating which was an electrical conductor. The samples were mounted in a cryostat (Oxford Instruments CF1204) and cooled to 4.2 K. A coherent CR699-29 single-mode dye laser operated with rhodamine 6G (R-6G) was used as the light source to initiate the PHB reaction. The laser band width was 500 kHz. The hole spectra were recorded by using a CT-100C monochromator (Japan Spectroscopic Co. Ltd) equipped with a 100 W tungsten lamp and an R928 photomultiplier tube (Hamamatsu Photonics KK) and a model 5207 lock-in amplifier (EG&G). The spectral resolution of the monochromator was better than 0.01 nm. The out-put data from the lock-in amplifier were collected by a PC-8801 (NEC) computer and then treated by a Macintosh II (Apple) computer. The electric field was set by a d.c. power supply model 610C (Trek Inc.).

RESULTS AND DISCUSSION

Effect of external electric field on the spectral hole profile: Stark effect

We examined the electric field strength dependence of the spectral hole profile in the AQ derivative PHB systems. In general, the absorption band of the guest dye molecule shifts due to the interaction between the dipole moment of the guest dye molecule and the electric field when the external electric field is applied. The degree of the shift $\Delta\nu$ of the homogeneous absorption band under an electric field is expressed by equation (1)[29,30]:

$$\mathrm{h}\Delta\nu = -\mathrm{f}\Delta\vec{\mu}\vec{E} - (1/2)f^2\vec{E}\Delta\tilde{\alpha}\vec{E} \qquad (1)$$

where h is Planck's constant, $\Delta\vec{\mu}$ and $\Delta\tilde{\alpha}$ are, respectively, the differences in the dipole moment vector and the polarizability tensor of the molecule between the excited and the ground states, E is the applied electric field, $f = (\varepsilon + 2)/3$ is the local field factor and ε is the dielectric constant of the host polymer. The second term is

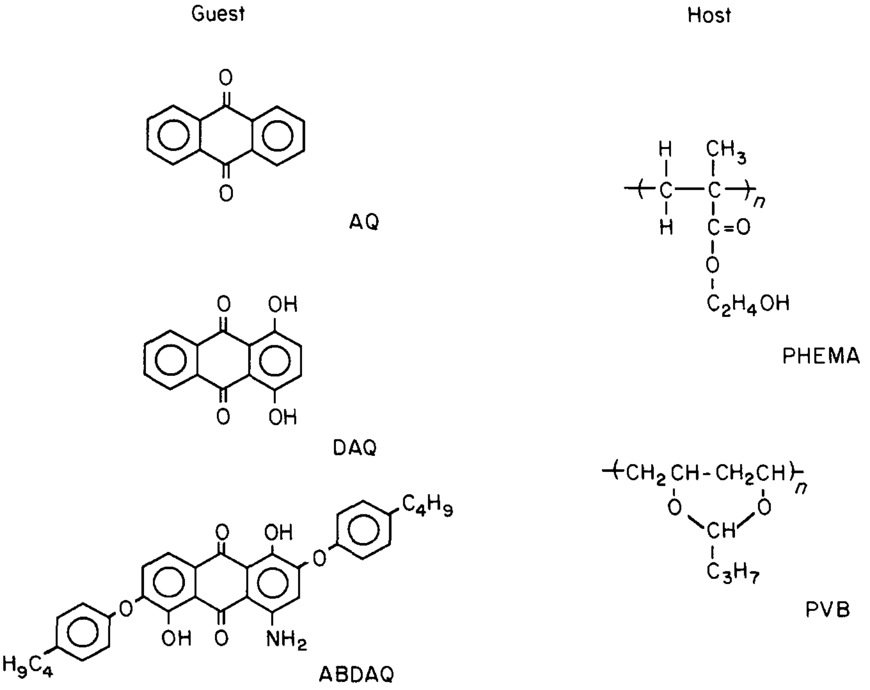

Figure 1 Molecular structures of the compounds used

generally negligible up to an electric field strength of MV cm^{-1} compared to the first term[31]. Consequently, the second term is neglected hereafter in this paper. Thus equation (1) indicates that the superimposition of the shifted homogeneous absorption bands results in symmetrical broadening of the hole profile and hole filling because the guest dye molecules orientate randomly in the amorphous host. Moreover, we can estimate the absolute value of $\Delta\bar{\mu}$, i.e. $|\Delta\bar{\mu}|$ by equation (1).

DAQ/PHEMA system. In this system, a high-density multiple hole of >300 was efficiently formed in the wavelength dimension as reported in our previous papers[22,23]. *Figure 2a* shows the initial hole profile burnt at an electric field of +18.5 kV cm^{-1} and a wavelength of 576.22 nm. The hole profiles at electric fields of 0 and −18.5 kV cm^{-1} are shown in *Figures 2b* and *c*, respectively. The Stark effect could be observed and was reversible as shown in *Figure 2d*. The initial hole width, i.e. the full width at half maximum (FWHM) in the wavelength dimension was estimated to be 0.56 cm^{-1}.

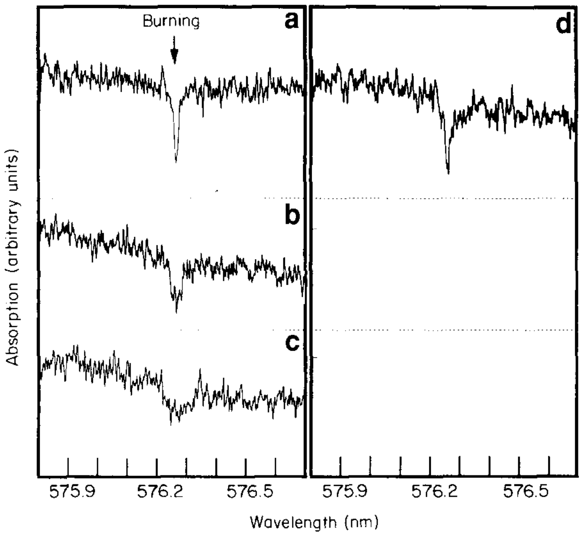

Figure 2 Hole profile change with change in the external electric field strength in the DAQ/PHEMA system: (a) E_1 = 18.5 kV cm^{-1}; (b) E_2 = 0 kV cm^{-1}; (c) E_3 = −18.5 kV cm^{-1}; (d) E_1 = 18.5 kV cm^{-1}

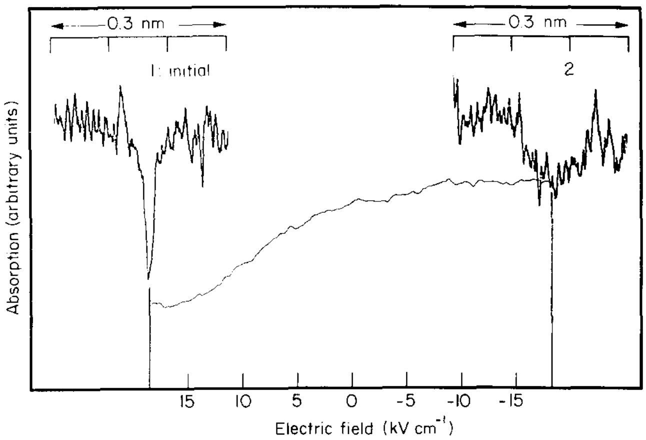

Figure 3 Hole depth variation curve *versus* the external electric field strength in the DAQ/PHEMA system. (The hole profiles are the ones in the wavelength dimension measured at the corresponding electric field)

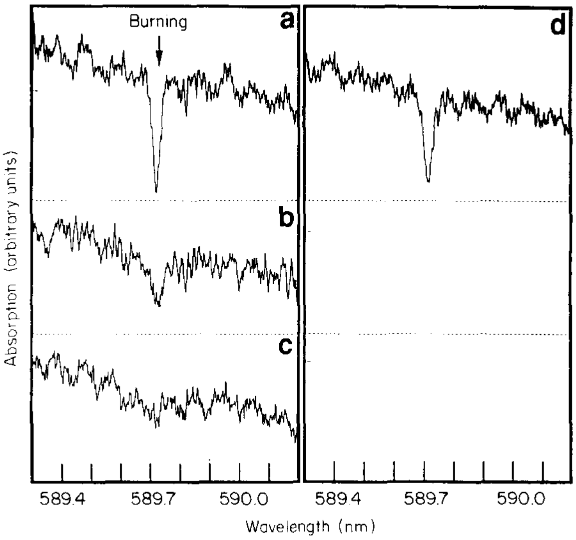

Figure 4 Hole profile change with change in the external electric field strength in the ABDAQ/PHEMA system: (a) E_1 = 26.5 kV cm^{-1}; (b) E_2 = 0 kV cm^{-1}; (c) E_3 = −26.5 kV cm^{-1}; (d) E_1 = 26.5 kV cm^{-1}

The initial hole was burnt by light irradiation with an intensity of 35 mW cm^{-2} for 15 s. *Figure 3* shows the hole depth variation against the external electric field strength. The hole width (FWHM) in the electric field dimension was estimated to be 22 kV cm^{-1} by this hole depth curve. We substituted FWHM in the wavelength for $\Delta\nu$ and twice the strength of FWHM in the electric field for $\vec{E}$, respectively, in equation (1), which might be met where the dipole moment difference and the applied electric field were parallel. Thus, the absolute value, $|\Delta\bar{\mu}|$, of the dipole moment difference of DAQ in this system was calculated to be 0.38 D, where the value of the dielectric constant of PHEMA used was 4.0 which was estimated from Tsunoda's data[32].

ABDAQ/PHEMA system. A high-density multiple hole formation of >350 in the wavelength dimension was also formed in this system[24]. *Figure 4* shows the hole profiles at three electric field strengths of +26.5, 0 and −26.5 kV cm^{-1}. The hole width (FWHM) in the wavelength dimension was measured to be 0.86 cm^{-1} from the initial hole burnt by irradiation at the wavelength of 589.7 nm with a light intensity of 20 mW cm^{-2} for 20 s. *Figure 5* shows the hole depth variation against the external electric field strength. By this hole depth curve, the hole width (FWHM) in the electric field dimension was estimated to be 25 kV cm^{-1}. As in the DAQ/PHEMA system, by using the first term of equation (1) and the change in values of the hole widths in the wavelength dimension by applying the electric field, $|\Delta\bar{\mu}|$ of ABDAQ in this system was calculated to be 0.51 D.

ABDAQ/PVB system. Figure 6 shows the hole profiles at three electric field strengths of +56.3, +28.2, 0 and +56.3 kV cm^{-1}. The hole width (FWHM) in the wavelength dimension was measured at 0.55 cm^{-1} for the initial hole profile burnt at a wavelength of 590.7 nm. The initial hole was burnt by light irradiation with an intensity of 35 mW cm^{-2} for 20 s. *Figure 7* shows the

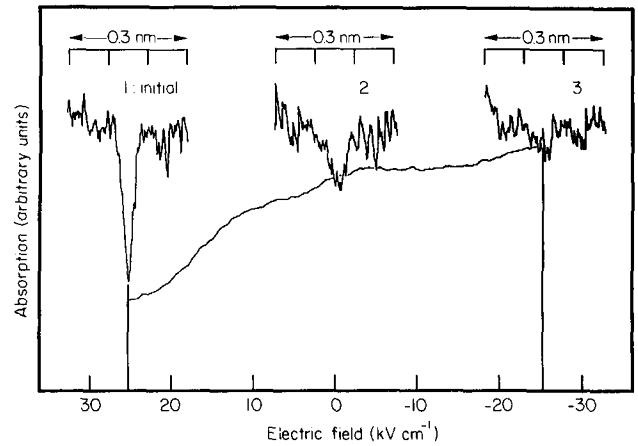

Figure 5 Hole depth variation curve *versus* the external electric field strength in the ABDAQ/PHEMA system. (The hole profiles are the ones in the wavelength dimension measured at the corresponding electric field)

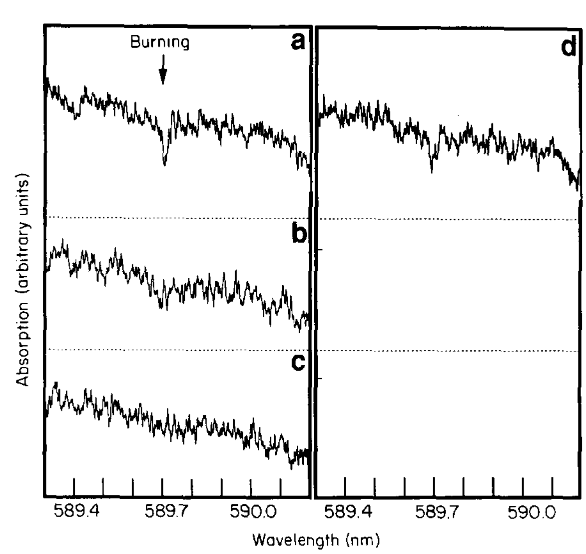

Figure 6 Hole profile change with change in the external electric field strength in the ABDAQ/PVB system: (a) $E_1 = 56.3\,\mathrm{kV\,cm^{-1}}$; (b) $E_2 = 28.2\,\mathrm{kV\,cm^{-1}}$; (c) $E_3 = 0\,\mathrm{kV\,cm^{-1}}$; (d) $E_1 = 56.3\,\mathrm{kV\,cm^{-1}}$

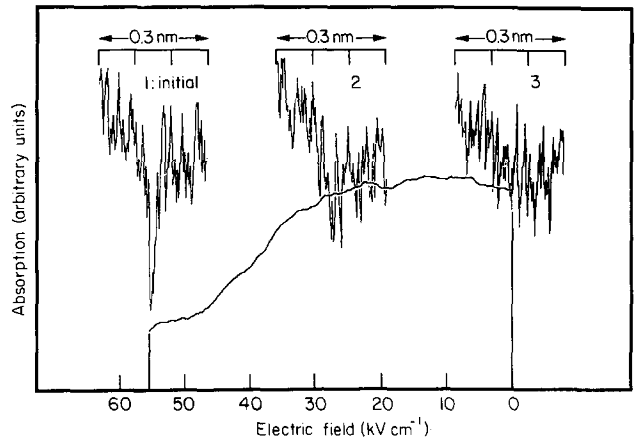

Figure 7 Hole depth variation curve *versus* the external electric field strength in the ABDAQ/PVB system. (The hole profiles are the ones in the wavelength dimension measured at the corresponding electric field)

hole depth variation curve *versus* the electric field strength. The hole width (FWHM) in the electric field dimension was calculated to be $38\,\mathrm{kV\,cm^{-1}}$ and $|\Delta\bar{\mu}|$ of ABDAQ in this system to be 0.26 D by the same treatment as in the previous two systems, where the value of the dielectric constant[28] of PVB used was 3.6.

Shape feature of the spectral hole in the electric dimension. The shapes of the spectral holes in the electric field dimension in the three systems studied here seem to have fundamentally the similar feature as that obtained by expression (11) in reference 33. As for the hole shape feature, Kador *et al.* also reported that it could be expressed by the Gaussian expression[34]. Thus, the spectral hole feature still remains to be solved quantitatively.

Effect of chemical structures of the AQ derivatives and host polymers on $|\Delta\bar{\mu}|$

The values of the hole widths and dipole moment differences in each PHB system are summarized in *Tables 1* and *2*, respectively.

First, the polymer effect on $\Delta\bar{\mu}$ will be elucidated by comparing the results between ABDAQ/PHEMA and ABDAQ/PVB. The absolute value $|\Delta\bar{\mu}|$ of ABDAQ in ABDAQ/PHEMA is 0.51 D and is about twice that in ABDAQ/PVB (0.26 D). This difference in $|\Delta\bar{\mu}|$ of ABDAQ seems to arise from the difference of the characteristics of the microscopic electronic dipole moment of the functional side chain between the two polymers PHEMA and PVB. PHEMA has two polar functional groups in its side chain. One of them is a hydroxymethyl (CH_3OH) and the other is an esteric carboxy group (CO_2), and they are separated by a methylene group (CH_2). The Taft's polar substituent constants are +0.555 and +2.00 for the hydroxymethyl and carboxy groups, respectively. On the other hand, PVB has two ether linkages in its cyclic side chain. The linkages exist symmetrically in the mirror image to reduce the polarity of the side chain as shown in *Figure 1*, although the Taft's polar substituent constant of its ether linkage is supposed to be close to the value of CH_3OCH_2 (+0.520). From the above discussions, PHEMA has a more dense dipole moment density microscopically than PVB. Hence PHEMA acts as a much more polar matrix for ABDAQ than does PVB. Consequently, ABDAQ can have a more electronically polarized structure in its excited state in the PHEMA system than in the PVB system which results in a larger absolute value $|\Delta\bar{\mu}|$ in PHEMA than in PVB.

Next, the effect of the substituents of the AQ derivatives

Table 1 Hole widths in the wavelength dimension ($\mathrm{cm^{-1}}$) and the electric field dimension ($\mathrm{kV\,cm^{-1}}$, in parentheses) in each system

	Host polymer	
Guest dye	PHEMA	PVB
DAQ	0.56 (22)	–
ABDAQ	0.86 (25)	0.55 (38)

Table 2 Dipole moment differences of the guest dye molecule in each system

	Host	
Guest	PHEMA (D)	PVB (D)
DAQ	0.38	–
ABDAQ	0.51	0.26

on $\Delta\bar{\mu}$, can be evaluated by comparison of the absolute values $|\Delta\bar{\mu}|$ of DAQ in the DAQ/PHEMA and that of ABDAQ in the ABDAQ/PHEMA system. In these systems, the absolute value $|\Delta\bar{\mu}|$ of ABDAQ is 0.51 D and is larger than that of DAQ (0.38 D). We are concerned with the electronic effect of the substituents of the AQ derivatives on the characteristics of $\Delta\bar{\mu}$. We think it is reasonable to take the *para* sigma value of the Hammett's substituent constant into account to explain the difference of $|\Delta\bar{\mu}|$ between DAQ and ABDAQ. ABDAQ has two hydroxy groups at 1- and 5-positions of the AQ molecule, two 4-butylphenoxy groups at 2- and 6-positions of AQ and an amino group at 4-position of AQ as shown in *Figure 1*. The Hammett's substituent constants of hydroxy and amino groups are -0.37 and -0.66, respectively. The Hammett's substituent value of 4-butylphenoxy group is reasonably supposed to be nearly -0.50 as the sum of the values of the phenoxy and ethyl groups. Thus, these three substituent groups have electron donating characteristics to the aromatic AQ moiety and are positively charged in the ABDAQ molecule. On the other hand, AQ possesses two carbonyl groups as the quinone function. The Hammett's substituent value of the quinone carbonyl group is supposed to be in the range 0.678–0.522 from the values of the cyano (CN) group, (+0.678), and ester (CO_2Et) group (+0.522). This result indicates that the two carbonyl groups have electron accepting nature and negative charge in the ABDAQ molecule. Thus, ABDAQ has five positively charged points and two negatively charged points. And the amino group exists to make the molecular symmetry lower. Furthermore, the distance between the positive charge on the 4-butylphenoxy group and the negative charge on the carbonyl group is very large in the ABDAQ molecule. In addition, the ABDAQ molecule has much more electronically polarized structure and enhanced dipole moment in the excited state than the DAQ molecule, which may result in a larger $|\Delta\bar{\mu}|$ in ABDAQ than in DAQ. Because DAQ only has two hydroxy groups at two symmetrical 1- and 4-positions of the AQ molecule and so DAQ may not have such a highly polarized electronic structure as that considered in ABDAQ.

Response characteristics of the spectral hole depth to the change of the electric field strength

It is one of the interesting applications of the Stark effect on the PHB to control the hole depth set by the electric field strength, because we can provide an optical filter, optical modulator or optical switch by that effect. A rectangular electric field was applied to the ABDAQ/PVB sample as indicated in *Figure 8b*. The response characteristics of the hole depth to the change in electric field strength is shown in *Figure 8a*. Although Hartmannsgruber *et al.* reported a decrease in the selective fluorescence in the course of the repetition of applying the rectangular electric field[35], such a decrease in the initial hole depth was not observed in our system, which might suggest that the hole burnt in the ABDAQ/PVB system would be stable to electric field application cycling.

Multiple spectral hole formation in both the wavelength and the electric field dimensions

The most interesting application aspect of the Stark effect on the PHB hole is to apply it to the multiple data storage in the electric field dimension in addition to the wavelength dimension.

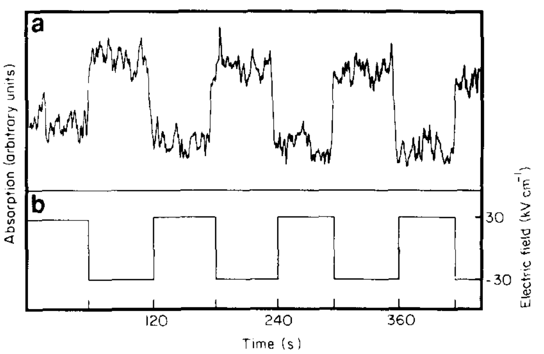

Figure 8 Response characteristics of the hole depth to the application of the rectangular electric field in the ABDAQ/PVB system. For (a) and (b) see text

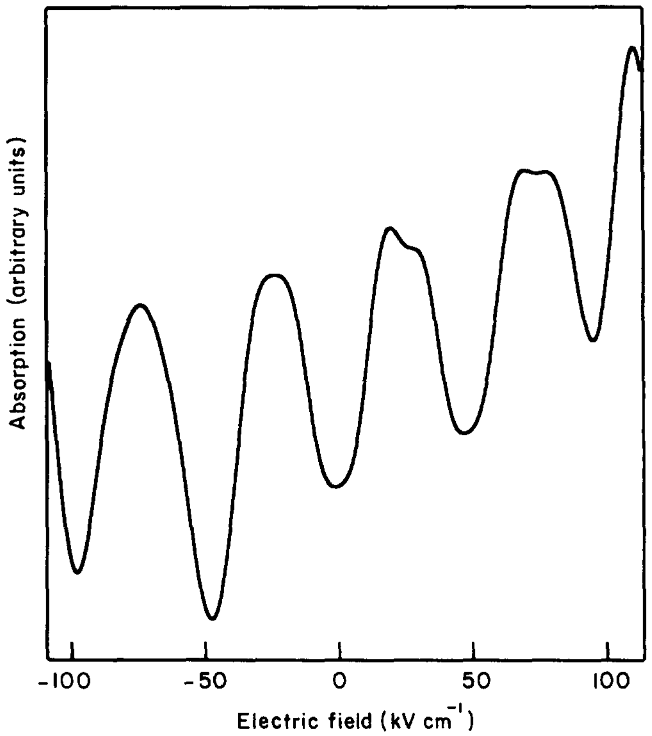

Figure 9 Multiple hole formation in the electric field dimension in the ABDAQ/PVB system

First, the multiple hole formation in the electric dimension was investigated in the ABDAQ/PVB system. A successive five multiple holes formation was carried out as shown in *Figure 9*. The holes at the 582.5 nm wavelength were burnt at electric field strengths of +97.5, +48.75, 0, −48.75 and −97.5 kV cm^{-1} where the light was irradiated at an intensity of 17.4 mW cm^{-2} for 5 s for each hole formation.

Next, the multiple holes at above the five electric field strengths were burnt at the five wavelengths from 581.0 to 583.0 nm at 0.5 nm wavelength intervals. Consequently 25 multiple holes of 5 × 5 were burnt in both the wavelength and the electric field dimensions as shown in *Figure 10*. The 5 × 5 multiple PHB holographic image storage by using both the wavelength and the electric field dimensions was reported by Caro *et al.*[36], which was carried out at 1.7 K. Our 5 × 5 multiple hole formation in both the wavelength and the electric field dimensions was, however, carried out at 4.2 K. In order

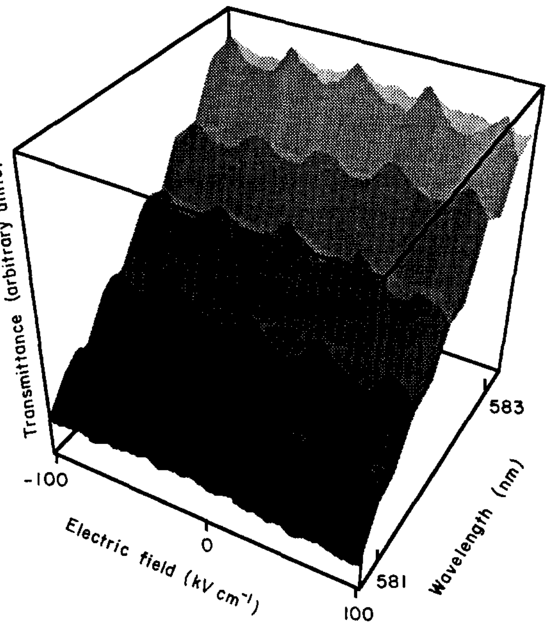

Figure 10 Multiple hole formation in both the wavelength and the electric field dimensions in the ABDAQ/PVB system

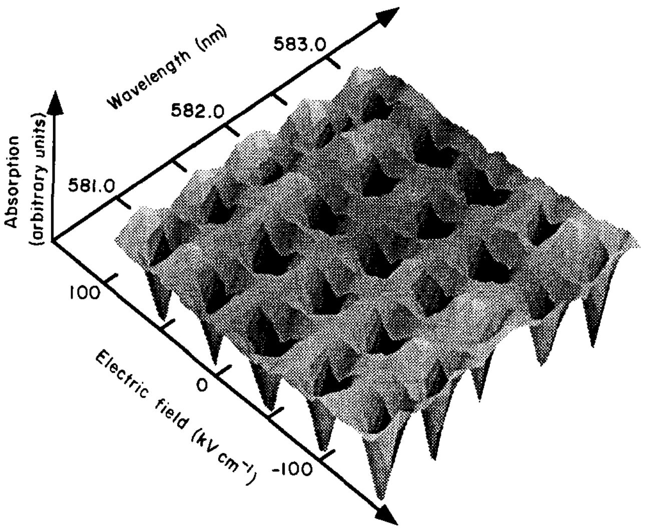

Figure 11 Bird's-eye view of the multiple spectral holes extracted as signals on the two-dimensional flat plane of the wavelength and electric field; see from the top of the hole

to show these spectral holes clearly on the two-dimensional flat plane of the wavelength and electric field, we measured the differential spectrum between, before and after hole burning by analysing the raw data in *Figure 10* by computer treatment. The result is shown in *Figure 11* where we can recognize the three-dimensional multiple holes clearly as a bird's-eye view from the top of the hole.

CONCLUSIONS

We have investigated the external electric field effect on the PHB reaction feature of the AQ derivative PHB systems and found the Stark effect in the three systems of DAQ/PHEMA, ABDAQ/PHEMA and ABDAQ/PVB. This Stark effect is the first one found in the quinone derivative PHB system. We have been able to produce multiple spectral holes of 5 × 5 in both the wavelength and electric field dimensions simultaneously, which is the highest value of the spectral hole multiplexing at 4.2 K in both the wavelength and the electric field dimensions as far as we know.

Moreover, we have shown that the absolute value $|\Delta\bar{\mu}|$ depends not only on the molecular structure of the AQ derivatives but also on the characteristics of the host polymer. We have explained these results using the Hammett's substituent constant for the effect of the AQ derivatives, and using the Taft's polar substituent constant for the polymer effect.

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