# Remarkable Electric Field Effect on the Absorption Intensity of a Molecular Aggregate of Photomerocyanine in a PMMA Polymer Film

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Electroabsorption spectra of merocyanine (PMC) produced by an photochromic reaction of spiropyran (SP) in a PMMA polymer film have been measured. The intensity of the sharp absorption band assigned as an aggregate of PMC was found to be remarkably reduced by an external electric field. The photochromic reaction from the aggregate of PMC to SP is suggested to be markedly enhanced by an electric field.

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Plots of the electric-field induced change in absorption intensity as a function of wavelength, i.e., the so-called electroabsorption spectra, are well known to give the information about the electric properties in the excited states. In fact, the magnitude and orientation of the change in electric dipole moment and molecular polarizability following photoexcitation had been examined in many polyatomic molecules, based on the electroabsorption measurements.[1,2] The electroabsorption spectra are also expected to give the information about the field-induced change in absorption intensity, which may be induced by a change in the magnitude of the transition moment or by a change in the number of the molecules concerned. In the present study, the electroabsorption spectra of photomerocyanine produced by a photochromic reaction of spiropyran doped in a PMMA polymer film have been measured with different concentrations.

5'-Chloro-3',3'-dimethyl-6-nitro-1'-octadecyl 8-[docosanoylomethyl]-spiro[2H-1-benzopyran-2,2'-indoline], which is shown in Figure 1 and hereafter denoted by SP, was purchased from Nippon Kanko Shikiso and used without any further purification. With a UV light irradiation to SP, photomerocyanine, denoted by PMC, which shows an absorption band in the visible region, is produced.[3] PMC is considered to have a resonance structure of zwitterion and quinoid (see Figure 1).[4] PMC is converted to SP by a visible light irradiation or by a thermal process.

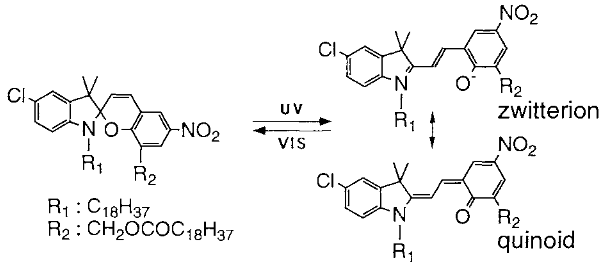

**Figure 1.** Molecular structure of spiropyran and its photoisomer (merocyanine) with a zwittenionic or quinoidal structure.

A purification of PMMA and a sample preparation of the polymer film are the same as reported elsewhere.[5] Briefly, SP dissolved in benzene solution of PMMA was poured onto an ITO coated quartz plate with a spin-coating method and kept in dark at room temperature for a few days. Then, a semitransparent aluminum (Al) film was deposited on the polymer film. A typical thickness of the polymer films was ~1 μm.

All the optical measurements were carried out at room temperature under vacuum conditions, and the electroabsorption spectra were measured using electric field modulation spectroscopy. 150 W xenon light dispersed by a monochromator was used for excitation. A sinusoidal ac voltage was applied between ITO and Al films, and a small amount of ac component of the excitation light at excitation wavelength, $\lambda$, $\Delta I(\lambda)$, synchronized with the applied ac voltage was detected with a lock-in-amplifier at the second harmonic of the modulation frequency (40 Hz). The field-induced change in the absorbance at $\lambda$ ($\Delta A(\lambda)$) was determined using a relation of $-\Delta I(\lambda)/2.303I(\lambda) = \Delta A(\lambda)$, where $I(\lambda)$ is the transmitted excitation light intensity.[6] $\Delta A(\lambda)$ at the first harmonic of the modulation frequency was negligibly small in the whole region, indicating that molecules are not oriented by the external field.

The absorption spectra of SP doped in a PMMA polymer film are shown in Figure 2. With an irradiation of UV light, the absorption spectra are changed, and an absorption band with a peak at 590 nm appears at 4.5 wt%. This band is assigned as that of PMC, which is the photoisomer of SP.[3] As the dopant concentration of SP is increased to 9.0 wt%, a shoulder with a peak at ~ 550 nm newly appears following a UV irradiation (see Figure 2b), though the absorption spectra of SP are essentially the same (see Figure 2a). The absorption spectra shown in

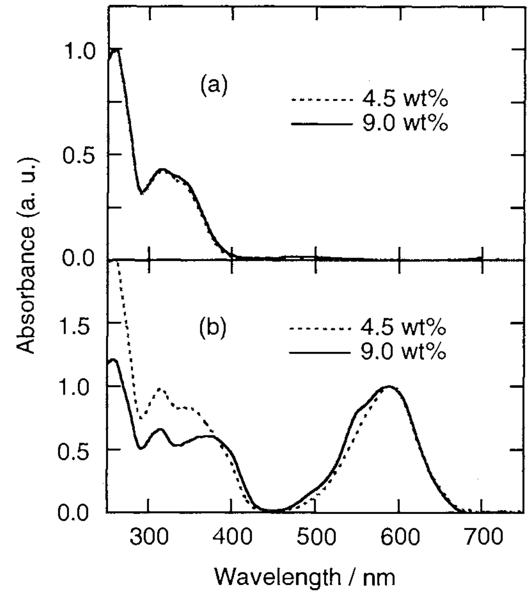

**Figure 2.** Absorption spectra of spiropyran (a) and a mixture of spiropyran and merocyanine following photoexcitation at 365 nm (b) with a concentration of 4.5 or 9.0 wt%.

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Figure 2b must be regarded as those of a mixture of SP and PMC, but the spectra in the visible region are regarded as the ones of PMC. The shoulder at 550 nm, which was not observed at concentrations lower than 4.5 wt%, is attributed to a molecular aggregate of PMC. The absorption spectrum of PMC at 4.5 wt% was subtracted from the spectrum at 9.0 wt% by assuming that the intensities at the peak at 590 nm are the same. The resulting spectrum shown in Figure 3a, which gives a sharp peak at 550 nm, may be regarded as the spectrum of the aggregate of PMC, as far as the visible region is concerned.

Electroabsorption spectra of PMC were observed at 4.5 and 9.0 wt% with a field strength of 0.8 MV/cm. The results are shown in Figure 3. The corresponding absorption spectra are regarded as the ones shown in Figure 2b. As is shown in Figure 3, the magnitude of $\Delta A(\lambda)$ is very large at 9.0 wt%, especially in the region from 500 to 650 nm. If the field effects on the absorption spectrum come from the Stark shift induced by a change in electric dipole moment or in molecular polarizability, the electroabsorption spectra observed at the second harmonic of the modulation frequency are given by the second derivative or the first derivative of the absorption spectrum, respectively. In fact, the electroabsorption spectrum of PMC in the visible region observed at 4.5 wt% could be interpreted in terms of the Stark shift, as will be described in detail elsewhere.[7] As is shown in Figure 3a, however, the electroabsorption spectrum of PMC in the visible region observed at 9.0 wt % is essentially the same in shape as the absorption spectrum of the aggregate of PMC, indicating that the absorption intensity of the aggregate is reduced by an electric field.

The magnitude of the decrease in $\Delta A(\lambda)$ of the aggregate relative to the total intensity of the aggregates, i.e., $\Delta A(\lambda)/A(\lambda)$, was evaluated to be about 1 % with a field strength of 0.8 MV/cm. The decrease of the absorption intensity may be attributed to the field-induced decrease in the transition moment and/or to the field-induced decrease in the number of the aggregates of PMC.

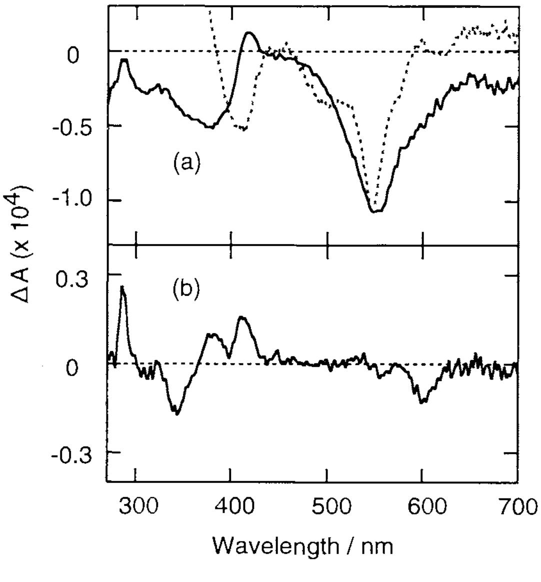

**Figure 3.** Electroabsorption spectrum of a mixture of spiropyran and merocyanin at 9.0 wt% (a) and 4.5 wt % (b). The spectrum obtained by a subtraction of the absorption spectrum at 4.5 wt% from the spectrum at 9.0 wt% is also shown by a dotted line in (a).

As is shown in Figure 3, only the aggregate shows a remarkable decrease of the absorption intensity, but the absorption intensity of the normal PMC is not so affected by an electric field. It seems to be unlikely that the transition moment of PMC is largely affected by an electric field only for the aggregate, as far as the molecular structure of PMC is the same. As mentioned above, a photochromic reaction occurs from PMC to SP following excitation into the PMC band. Then, the remarkable field effect on the absorption intensity of the aggregate may indicate that the photochromic reaction from PMC to SP by a visible light irradiation is markedly enhanced by an electric field only for the aggregate of PMC, not for the normal PMC. Note that the field-induced decrease of the absorption intensity can be induced by a change in the concentration of PMC, even when the transition moment is not affected by an electric field.

The aggregation type, whether J-type or H-type, was shown to depend on the molecular structure of the photochromic compound.[8] The absorption band of the present aggregate of PMC gives the sharp band and locates in the wavelength region a little lower than that of the corresponding absorption band of the normal PMC. Therefore, the present aggregate of PMC, whose intensity is markedly reduced by an electric field, may be regarded as an aggregate with a rather loose H-stack structure.

A field-induced shift of thermal equilibrium among stereo-photoisomers in PMMA was reported, based on the static electric field effect on the position of the absorption band of photoisomers.[9] The interconversion rate constants of photo-isomers were reported to be as small as 0.2 ~ 0.4 sec$^{-1}$, suggesting that the present modulation frequency (40 Hz) is too high to induce a shift of the thermal equilibrium of the stereo-photoisomers. In fact, this kind of field effect was not observed in the present study both for the normal PMC and for the aggregate.

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