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HYDROPHILIC POLYMERS CONTAINING MEROCYANINE DYES AS PENDANT GROUPS: THE SWOLLEN THIN FILM AS SPECTRAL SENSITIZER FOR SEMICONDUCTOR PHOTOELECTRODES

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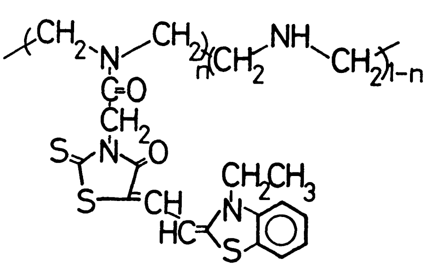
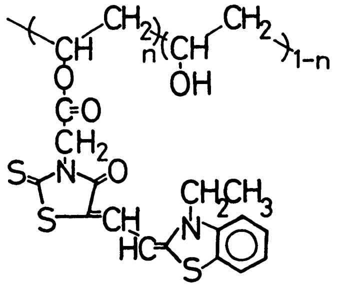
Hydrophilic polymers, such as polyethylenimine and poly(vinyl alcohol), containing merocyanine as grafted pendants were deposited on SnO_2 optically transparent electrode by spin coating technique. Under illumination of visible light, the electrode showed remarkable sensitized photocurrent in an electrochemical photocell. With a thin polymer-dye film, an intrinsic current quantum efficiency of 0.6 was obtained. It is evidenced that the polymer-dye film should be swollen with electrolyte to yield photocurrent.

Spectral and photoelectrochemical behavior of organic dyes confined to polymer matrices have been the subjects of our continuing study with the eventual aim of designing efficient artificial systems for conversion of light energy. We have come across some remarkable observations originated from the ability of the polymer-dye film to act as an effective spectral sensitizer for semiconductor photoelectrode processes.[1)] This article describes spectroscopic aspect of some polymer-dyes(polymer containing dyes as grafted pendants) and photosensitizing effect of the swollen films on the photocurrent at semiconductor electrodes. Linear polyethylenimine (PEI)[2)] and poly(vinyl alcohol)(PVA) were used as hydrophilic backbones and merocyanine(Mc) as a pendant dye. Since an efficient solar cell with a solid thin-film of Mc was reported,[3)] increasing attention has been given to the dyes of this homolog.[4,5)] The carboxylic group of this dye was used to combine with these polymers through amide or ester bond, respectively, as reported previously.[1)] The related monomer model compounds were prepared by using diethylamine and isopropanol as the related monomer models for PEI and PVA, respectively. The details of the syntheses of these polymer-dyes and the monomer models will be reported elsewhere.[6)]



PEI-Mc



PVA-Mc

Absorption spectra of the polymer-dye were considerably dependent on the solvent. As shown

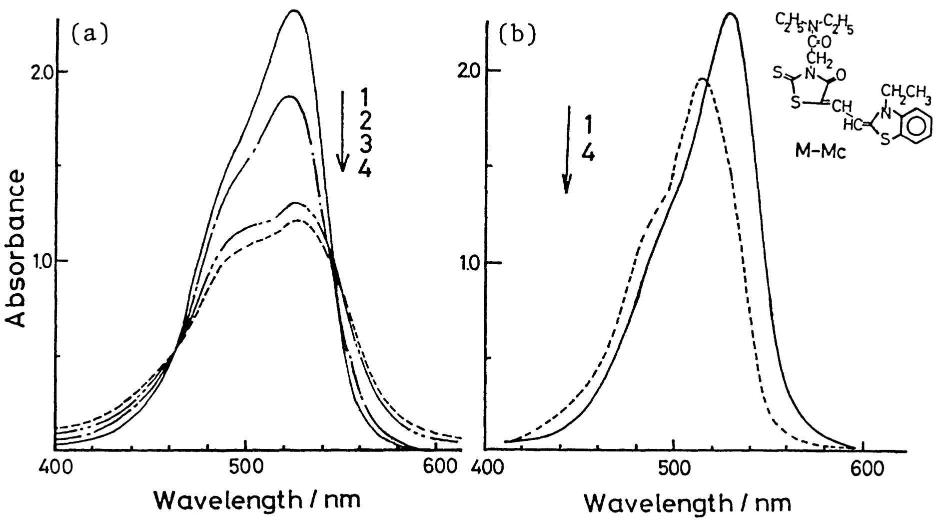


Fig.1. Absorption spectra of PEI-Mc(4 mol%)(a) and M-Mc(monomer model)(b) in DMF for curve 1 and in benzene/DMF mixture for 2-4: DMF contents are 10, 1, 0.1 vol% for 2, 3, 4, respectively.

in Fig.1(a), an addition of benzene into a N,N-dimethylformamide(DMF) solution of PEI-Mc(4 mol%)(PEI containing 4 mol% of Mc) by maintaining the residual concentration of Mc at constant led to a sharp decrease of the absorption peak at 525 nm (assigned to monomeric dye). As a result, a shoulder intensity at about 500 nm (assigned to dimeric dye) relative to the peak at 525 nm increased. The absorption spectra of the related monomer model also exhibited solvent effect but in different manner. Namely, as shown in Fig.1(b), the monomer model showed almost identical spectrum with that of PEI-Mc(4 mol%) in DMF. However, the peak assigned to monomeric dye shifted to shorter wavelength by ca.15 nm in benzene(containing 0.1 vol% of DMF), accompanied by a decrease of the intensity by ca.15 %. Such a solvent effect, frequently encountered with a variety of merocyanines, has been interpreted in terms of the stabilization effect of polar structure of the dyes by polar solvents.[7] Since benzene is a poor solvent for the polymer-dye, an addition of this solvent would cause considerable shrinkage of the polymer coil giving rise to more chance for the dye residues to form dimer. Table I lists the fluorescence intensity of

Table I Relative Fluorescence Quantum Yield ($\Phi_{f,rel}$) of Polymer-Dyes in DMF Solution at Room Temperature

Dyes	λ_{em}/nm[a)]	$\Phi_{f,rel}$[b)]
M-Mc(monomer model)	549	1
PEI-Mc(4 mol%)	552	1.16
PEI-Mc(13 mol%)	553	0.72
PEI-Mc(25 mol%)	554	0.31

a) Emission maximum. b) Excitation wavelength, 525 nm; each sample solution was adjusted to have the same absorbance at 525 nm.

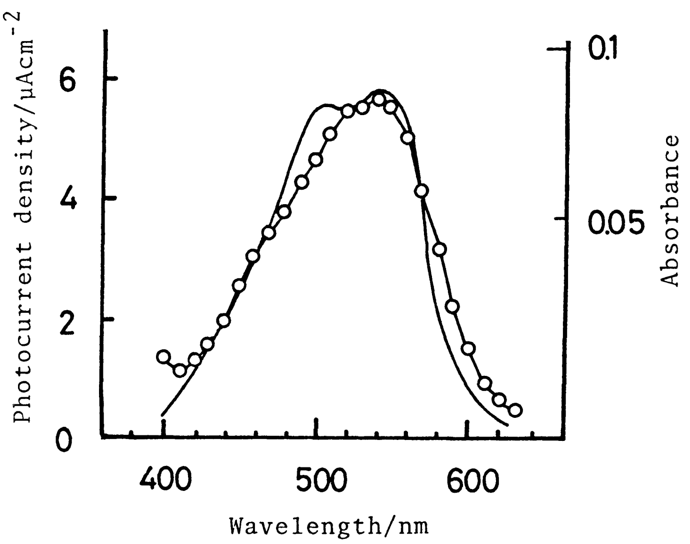


Fig.2. Photocurrent(—○—) and absorption(——) spectra of PVA-Mc(35 mol%) film deposited on SnO_2 OTE: Photocurrent was measured at 0.3 V vs.SCE.

PEI-Mc with various Mc contents relative to that of the related monomer model. The fluorescence intensity of Mc of the polymer-dye sharply decreased with increasing content of the dye in the polymer. These observations indicate that in the polymer with high dye contents the dyes are held sufficiently close together along the backbone to allow an excited dye to interact with neighboring dyes; thus an excitation state may readily be quenched.

These polymer-dyes show the most striking features in the photoelectrochemical properties in the form of a thin film.$^{1)}$ The films of the polymer-dyes were prepared on the tin(IV) oxide optically transparent electrodes (SnO_2 OTE) from DMF solutions by spin coating technique. Photocurrents were measured at the electrode thus obtained under potentiostatic condition by using a conventional three-electrode, two-compartment cell filled with 0.1M KNO_3 and 0.1M hydroquinone.$^{1)}$ Under illumination of the light from a 500-W xenon lamp(Ushio UXL500D) combined with a monochrometer (JASCO CT-10), considerable anodic photocurrent was observed. Fig.2 shows photocurrent spectrum of the SnO_2 OTE covered with a film of PVA-Mc(35 mol%). For comparison, the absorption spectrum of the same specimen as used for the measurement of photocurrent was illustrated. The absorption band of the polymer-dye film which coincides with photocurrent spectrum is characterized by a broader spectral shape extending up to about 650 nm and an absorption maximum at longer wavelength (540 nm) as compared with the absorption spectrum of the corresponding solution (λ_{max},525 nm). Photocurrents and intrinsic current quantum efficiency obtained for the SnO_2 OTE coated with various polymer-dye films under irradiation of visible light are presented in Table II. Photocurrent was not critically dependent on the thickness of the film, whereas strikingly high quantum efficiency was observed for thinner films, although optimization has yet to be done. Because the polymer-dyes are amphiphilic in nature (backbones are hydrophilic and the dye residues hydrophobic), the films are swollen with the electrolyte solution during the measurement of photocurrent. It should be emphasized that the SnO_2 OTE coated with a Mc-blended polystyrene film, which is highly hydrophobic, gave rise to no photocurrent at all. This comparison indicates the importance of the polymer-dye film being swollen with the electrolyte solution. Although the mechanism of the photocurrent has not yet been clarified, the accessibility of the solvent, electrolyte, and hydroquinone to the reaction site in the inner volume of the film is considered to be a key factor. It is also mentioned that the photocurrent values listed in Table II were all

Table II Photocurrent at PVA-Mc(35 mol%) Film Deposited on SnO_2 OTE at 0.3 V vs. SCE with Illumination at 545 nm

OD of the film at 550 nm[a)]	Photocurrent[b)] $i_p/\mu A cm^{-2}$	η[c)]
0.01	8.0	0.6
0.03	6.4	0.2
0.17	7.2	0.04
0.19	5.4	0.03
0.23	6.8	0.03

a) As a measure of thickness. b) Steady value.
c) Intrinsic current quantum efficiency.

steady-state readings which were observed continuously for 7 hr on a recorder and there was no noticeable decrease in the photocurrent during a period of the time.

There is no doubt that the use of organic dyes is one of the most attractive approach to the improvement of the spectral response of semiconductor electrodes. However, a disadvantage lies in the fact that the quantum efficiency of the dye-sensitized photocurrent is generally very low probably because only dyes directly attached to the surface of the electrode are responsible for the photocurrent.[8-10)] A swollen polymer-dye film, where a multilayer of dye residues are constrained to a polymer matrix, may serve as a plausible candidate to overcome this problem.

References

1) Y. Morishima, M. Isono, Y. Itoh, and S. Nozakura, Chem. Lett., 1981, 1149.
2) T. Saegusa, H. Ikeda, and H. Fujii, Polym. J., 3, 35 (1972).
3) A. K. Ghosh and T. Feng, J. Appl. Phys., 49, 5982 (1978).
4) F. Mizutani, M. Yoshida, and K. Iriyama, J. C. S. Chem. Comm., 1980, 393.
5) K. Iriyama, F. Mizutani, and M. Yoshiura, Chem. Lett., 1980, 1399.
6) Y. Morishima, M. Isono, and S. Nozakura, in preparation.
7) L. G. S. Brooker, G. H. Keyes, R. H. Spragne, R. H. VanDyke, E. VanLare, G. VanZandt, F. L. White, H. W. J. Cressman, and S. G. Dent, Jr., J. Am. Chem. Soc., 73, 5332 (1951).
8) H. Gerischer, Photochem. Photobiol., 16, 243 (1972).
9) H. Tsubomura, M. Matsumura, Y. Nomura, and T. Amamiya, Nature(London) 261, 402 (1976).
10) C. K. Jaeger, F-R. F. Fan, and A. J. Bard, J. Am. Chem. Soc., 102, 2595 (1980).

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