

Graft Polymerization of Methyl Methacrylate on Flavin Mononucleotide by Tetravalent Cerium Ion and an Application of Obtained Polymer to Dye Transfer Printing

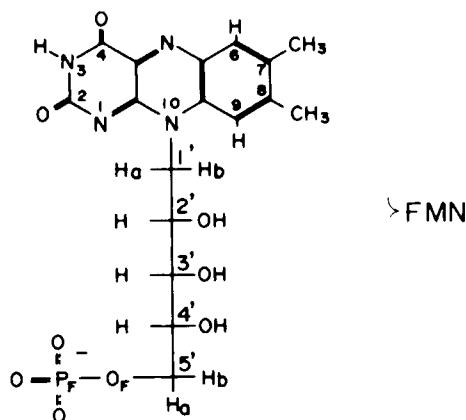
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Synopsis

The polymerization mechanism of methyl methacrylate (MMA) with flavin mononucleotide (FMN) and cerium nitrate was investigated. The effect of the polymer grafted to FMN on the color fastness to light of some dyes were also investigated. Poly(methyl methacrylate) (PMMA) was produced with FMN, cerium nitrate, and MMA in the presence of water above 40°C. The conversion of PMMA is proportional to the reaction time up to 2 h in this system. It is also proportional to the first order of concentration of FMN and Ce(IV). Activation energy of the polymerization reaction was estimated to be 29.3 kJ mol⁻¹ by the investigation of the temperature dependence of conversion. Purified polymer in acetone has the absorption peak at the same wavelength as FMN aqueous solution. The color fastness to light of Methylene Blue and anthraquinone dye were improved in the presence of the obtained polymer. Heat stability of the printed image which is made by transferring anthraquinone dye did not decrease by use of obtained polymer to recording layer of the medium in dye transfer printing system.

INTRODUCTION

Currently, the demands for color hard copy has been increased. Especially thermal transfer printing process has been used for television printer as its noiseless, pollutionless driving and its conventional structure.¹ There are two kinds of thermal transfer printing: One is an ink transfer printing and the other is a dye transfer printing. The dye-transfer process is desirable for tone tuning printing, but the sublimation dyes which are used for this process have the problem for the color fastness to light.² It has been found that addition of nucleic acid, i.e., caffeine, flavin mononucleotide (FMN) (Scheme 1), adenosine-5'-monophosphate (5'-AMP) to such a solution as Methylene Blue aqueous solution made the color fastness to light of dyes increase.³ Further, it was shown that the color fastness to light of anthraquinone dye which is used in the dye transfer printing process can be increased by dispersing caffeine or FMN to poly(vinyl alcohol) (PVA), which is a binder of the recording medium.² Because the interaction between the anthraquinone dye and the nucleic acid is weak, the storage property of the sublimation dye was too low in the printed recording medium which is composed with PVA dispersed with 5'-AMP or FMN.² Therefore, the process that can improve both the color fastness to light and the storage property has been desired. The author would expect that the color fastness to light can be improved by the interaction between the dye



Scheme 1

and the nucleic acid moiety and that the storage property can be improved by the interaction between the methyl ester moiety of the side chain and the dye, if poly(methyl methacrylate) (PMMA) which contains nucleic acid in the chain branch was used for the recording layer of the medium. The oxidation polymerization of MMA with Ce(IV) ion was considered as the method for grafting nucleic acid to vinyl polymer. FMN, one kind of nucleic acid, was used instead of silk in the literature,⁴ and the mechanism of the polymerization reaction and the data for the improvement of the color fastness to light of Methylene Blue or anthraquinone dye by the obtained polymer will be reported. The storage stability of the printed image will also be reported.

EXPERIMENTAL

Materials. FMN and cerium nitrate(IV) were purchased from Nakarai Chemical Co. and used without purification. MMA (Nakarai Chemical Co. reagent grade) was purified by vacuum distillation. Water was deionized and redistilled. Methylene Blue was purchased from Nakarai Chemical Co. and SOT-Blue 2 was obtained from Hodogaya Chemical Co.

Methods. A certain amount of FMN and cerium nitrate(IV) was taken in the four-neck flasks and kept in the water bath with water added, which is adjusted at pH 6.0 by the phosphate buffer (0.01 mol dm^{-3}), substituted with nitrogen, MMA added, and stirred by a stirrer. After certain hours, the content was thrown into the excess amount of methanol, the performed precipitant was filtered, washed several times with methanol and water for removing free monomer, cerium nitrate(IV), and FMN.

We will indicate the proportion of the graft polymer to the entire amount of the polymer by the next equation from the yield after the homopolymer is extracted by toluene:

$$GP = \frac{(G_t - G_h) \times 100(\%)}{G_t} \quad (1)$$

Here GP is the ratio of graft polymer to all of the polymer, G_t is the yield of

the total polymer produced and G_h is the yield of homopolymer extracted by toluene.

A recording medium was produced by the following procedure: Acetone solution of obtained graft polymer which contains 20% polymer by weight was coated on the plain paper by wire bar to 10 μm as final thickness and dried at room temperature.

The heat stability of the printed recording medium was judged with the following procedure: The transfer sheet described in Ref. 5 was superimposed on the obtained recording medium and they were printed with the thermal head (400 Ω) the added voltage of which was 16 V and the pulse width of which was 3 ms. If the vapor pressure of the sublimation dye at room temperature is proportional to that at 170°C, the storage property at room temperature can be assumed by that at 170°C. The printed recording medium was heated in oven at 170°C. The ratios of reflection density of the sample to the initial reflection density were plotted vs. heating time.

The color fastness to light of printed recording medium was measured according to JISL0841 by use of fademeter purchased from Mitsubishi Electric Co.⁶ The color fastness to light of Methylene Blue was judged by the following procedure: The light of super-high-pressure mercury lamp (Ushio 500) equipped with a VY-51 filter which cuts the light under 510 nm (100 mw cm^{-2}) was irradiated to the acetone solution of Methylene Blue (5.16×10^{-5} mol dm^{-3}) and the ratio of optical density at 658 nm to initial optical density was plotted vs. irradiated time.

RESULTS AND DISCUSSION

The effects of various factors on the polymerization rate, the time dependence of polymer yield at the condition of MMA (20 g), water (100 mL), FMN

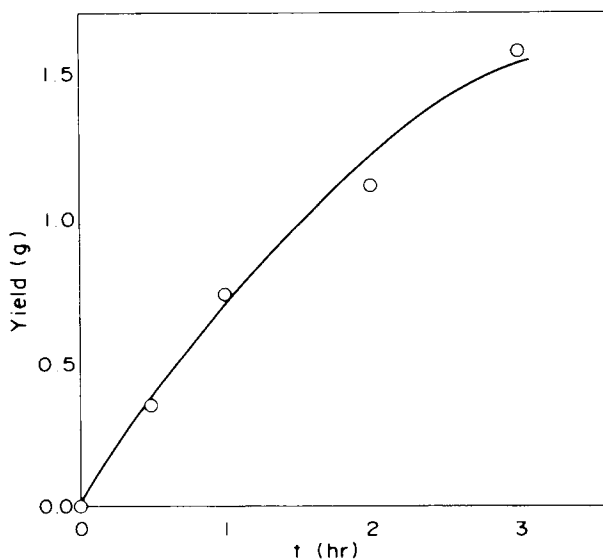


Fig. 1. Reaction time dependence of polymer yield of polymerization induced with FMN and Ce(IV) ion: MMA, 20 g; water, 100 cm^3 ; [FMN], 1.95 mmol dm^{-3} ; [Ce(IV)], 9.12 mmol dm^{-3} ; temperature, 60°C.

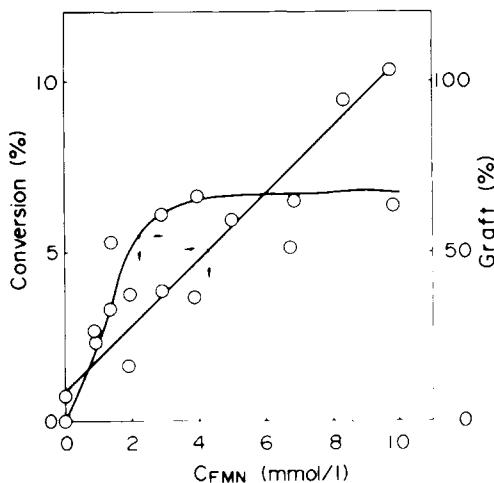


Fig. 2. Dependence of conversion of polymerization induced with FMN and Ce(IV) ion on FMN concentration: MMA, 20 g; water, 100 cm³; [Ce(IV)], 9.12 mmol dm⁻³; temperature, 60°C; reaction time, 2 h.

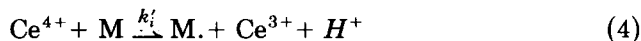
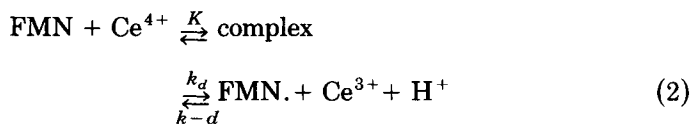
(0.195 mmol), cerium nitrate(IV) (0.912 mmol), pH (6.), and reaction temperature (60°C), are shown in Figure 1. The reaction rate can be estimated easily by measuring the yield for 2 h after initiation of the reaction to analyze the reaction mechanism, because the yield was linearly increased against the reaction time up to 2 h, as can be seen in Figure 1.

The polymer yield and graft ratio are shown in Figure 2, where Ce(IV) concentration is constant and FMN concentration varied. As can be seen in Figure 2, it was found that the polymer yield was proportional to the first order of FMN concentration. The graft ratio was proportional to FMN concentration initially but lately saturated with FMN concentration. This phenomenon is interpreted by the theory that the homopolymerization was inferior to graft polymerization at the high FMN concentration.

The polymer yield and graft ratio are shown in Figure 3, where FMN concentration is constant and Ce(IV) concentration varied. It was also found that the yield of the entire polymer was increased in proportion to the first order of Ce(IV) concentration. But the graft ratios with FMN concentration slowly decreased. This phenomenon can be interpreted by the theory that oxidation of monomer by Ce⁴⁺ ion increased at higher Ce⁴⁺ concentration.

The reaction mechanism of this polymerization would be presumed to be the following equation from the literature⁴:

Initiation:



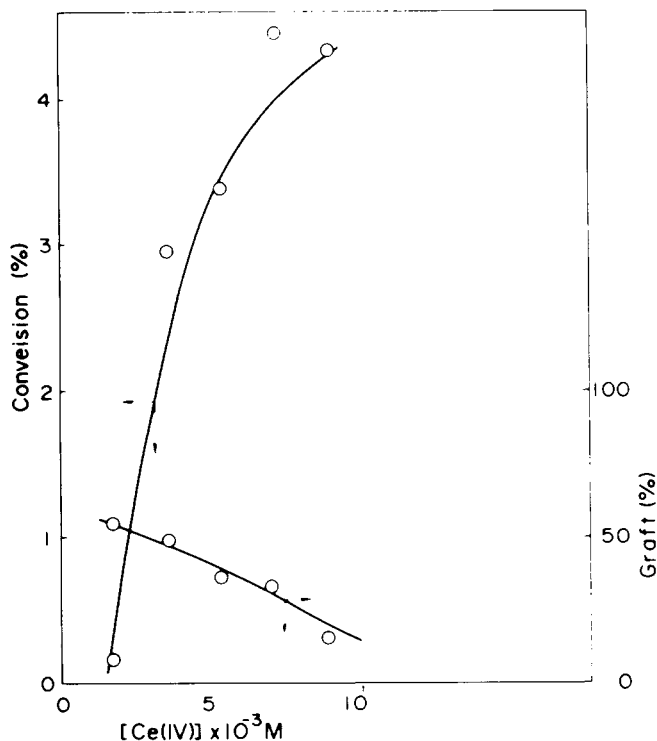
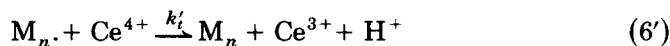
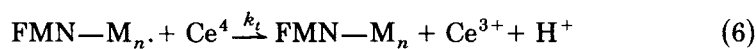


Fig. 3. Dependence of conversion of polymerization induced with FMN and Ce(IV) ion on Ce(IV) ion concentration: MMA, 20 g; water, 100 cm³; [FMN], 1.95 mmol dm⁻³; temperature, 60°C; reaction time, 2 h.

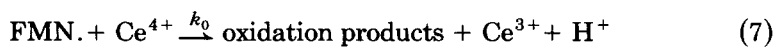
Propagation:



Termination:



Oxidation:



Equation (8) was obtained by the upper reaction equation:

$$R_p = k_p k_i [\text{M}]^2 \left[\frac{k_d [\text{Ce}^{4+}] [\text{FMN}]}{k_{-d} [\text{Ce}^{3+}] [\text{H}^+] + k_i [\text{M}]} \right] \quad (8)$$

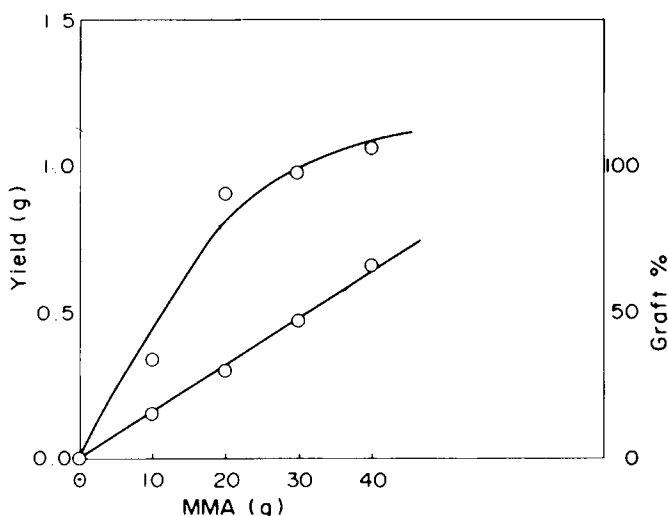


Fig. 4. Dependence of polymer yield of polymerization induced with FMN and Ce(IV) ion: water, 100 cm³; [FMN], 1.95 mmol dm⁻³; [Ce(IV)], 9.12 mmol dm⁻³; temperature, 60°C; reaction time, 2 h.

It was found that the theory agreed with the experimental results as the reaction rate was proportional to the first order of Ce(IV) and FMN concentration from eq. (8).

The yield is plotted vs. monomer amount holding FMN and Ce(IV) concentration constant in Figure 4. As can be seen in this figure, the yield and graft ratio increased with monomer amount. If $k_i[M] \gg k_{-d}[Ce^{3+}][H^+]$ holds, this result does not conflict with eq. (8). The activating energy of polymerization reaction can be estimated by the Arrhenius equation

$$\frac{dR_p}{dT} = \frac{E_a}{RT} \quad (9)$$

Here E_a is the activation energy of the polymerization reaction. The temperature dependence of polymer yield is shown in Figure 5. The activation energy E_a is found to be 29.3 kJ mol⁻¹ from Figure 5 and eq. (9). This value is close to the activation energy of photopolymerization of MMA with α -tocopherol (33.9 kJ mol⁻¹).⁷

The visible absorption spectrum of PMMA grafted with FMN which was made by this method is shown in Figure 6(a). As can be seen in this figure, because the spectrum has maxima at 325 nm and 450 nm and these peaks lie in the same position as those of the FMN aqueous solution [Fig. 6(b)], the existence of FMN in polymer chain is assured. Because the absorption peak of FMN at 450 nm was reduced a little (Fig. 7) by adding Ce(IV), and a large part of the absorption was preserved, the isoalloxazine ring which causes the visible absorption may not be oxidized, but the ribose chain which does not cause the visible absorption may be oxidized. The concept of oxidation of ribose is the same mechanism as that in the grafting of acrylonitrile with glucose⁸ or of MMA with starch.⁹

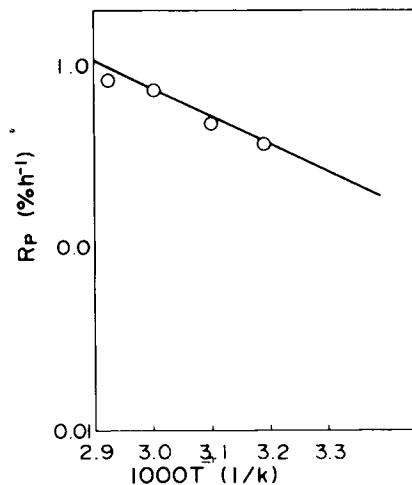


Fig. 5. Temperature dependence of conversion of polymerization induced with FMN and Ce(IV) ion: MMA, 20 g; water, 100 cm³; [FMN], 1.95 mmol dm⁻³; [Ce(IV)], 9.12 mmol dm⁻³; reaction time, 1 h.

The IR spectra of FMN (a), PMMA (b) and the polymer obtained by this method (c) are shown in Figure 8. As can be seen in this figure, the polymer obtained has the absorption peak at 1590 cm⁻¹ which is returned to C=O stretching of FMN by comparing the (b) spectrum with the (c) spectrum. This shows that the polymer obtained has the FMN moiety, that is to say, FMN grafts with PMMA.

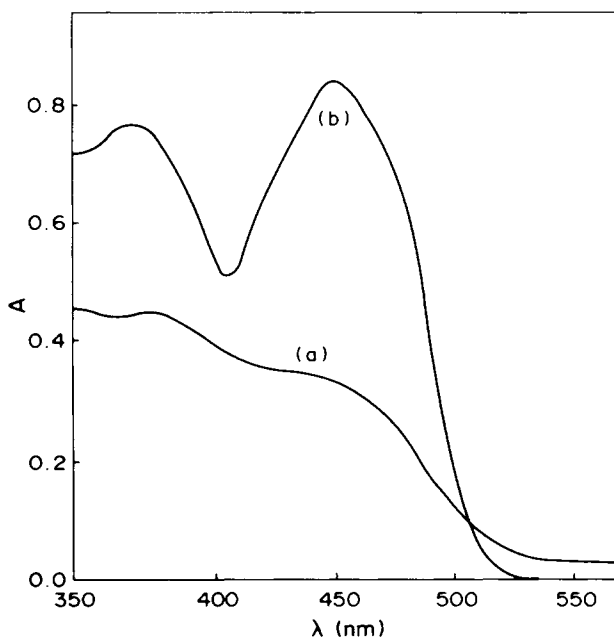


Fig. 6. Electronic spectra of FMN and the polymer obtained by this method: (a) polymer obtained by this method (1 mmol dm⁻³); (b) FMN aqueous solution (10⁻⁵ mol dm⁻³).

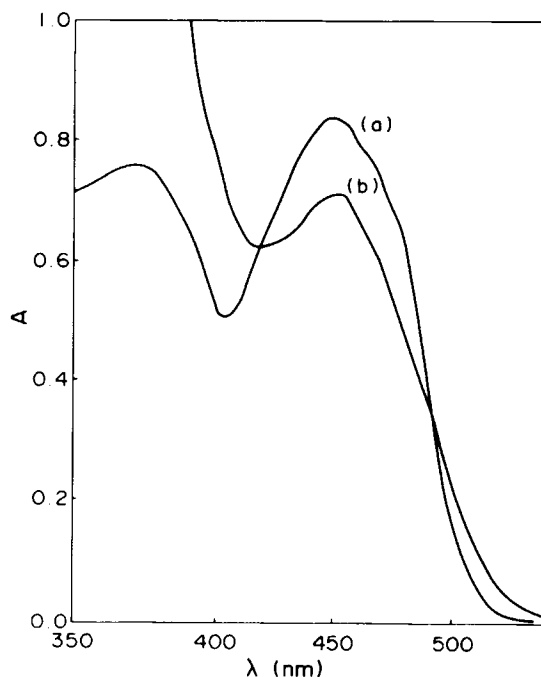
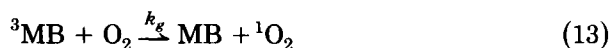


Fig. 7. Electronic spectra of FMN and FMN in the presence of Ce(IV) ion: (a) FMN (10^{-5} mol dm^{-3}); (b) FMN (10^{-5} mol dm^{-3}) in the presence of Ce(IV) (1.95 mmol dm^{-3}).

The Effect of PMMA Grafted to FMN on the Fading of the Dyes

The ratio of optical density at 658 nm to initial OD after irradiation of light in the system of Methylene Blue only (a), Methylene Blue in the presence of PMMA (1 mmol dm^{-3}) (b), and Methylene Blue in the presence of PMMA grafted to FMN (1 mmole dm^{-3}) (c) in acetone are shown in Figure 9. As can be seen in this figure, the effect of PMMA only on the photofading rate of Methylene Blue was not found but that of PMMA grafted to FMN on the photofading rate of Methylene Blue was found.

The mechanism of photofading of Methylene Blue in the presence of oxygen can be expressed by following equations:¹⁰



Here, MB, ${}^1\text{MB}$, and ${}^3\text{MB}$ represent the ground state, the singlet excited

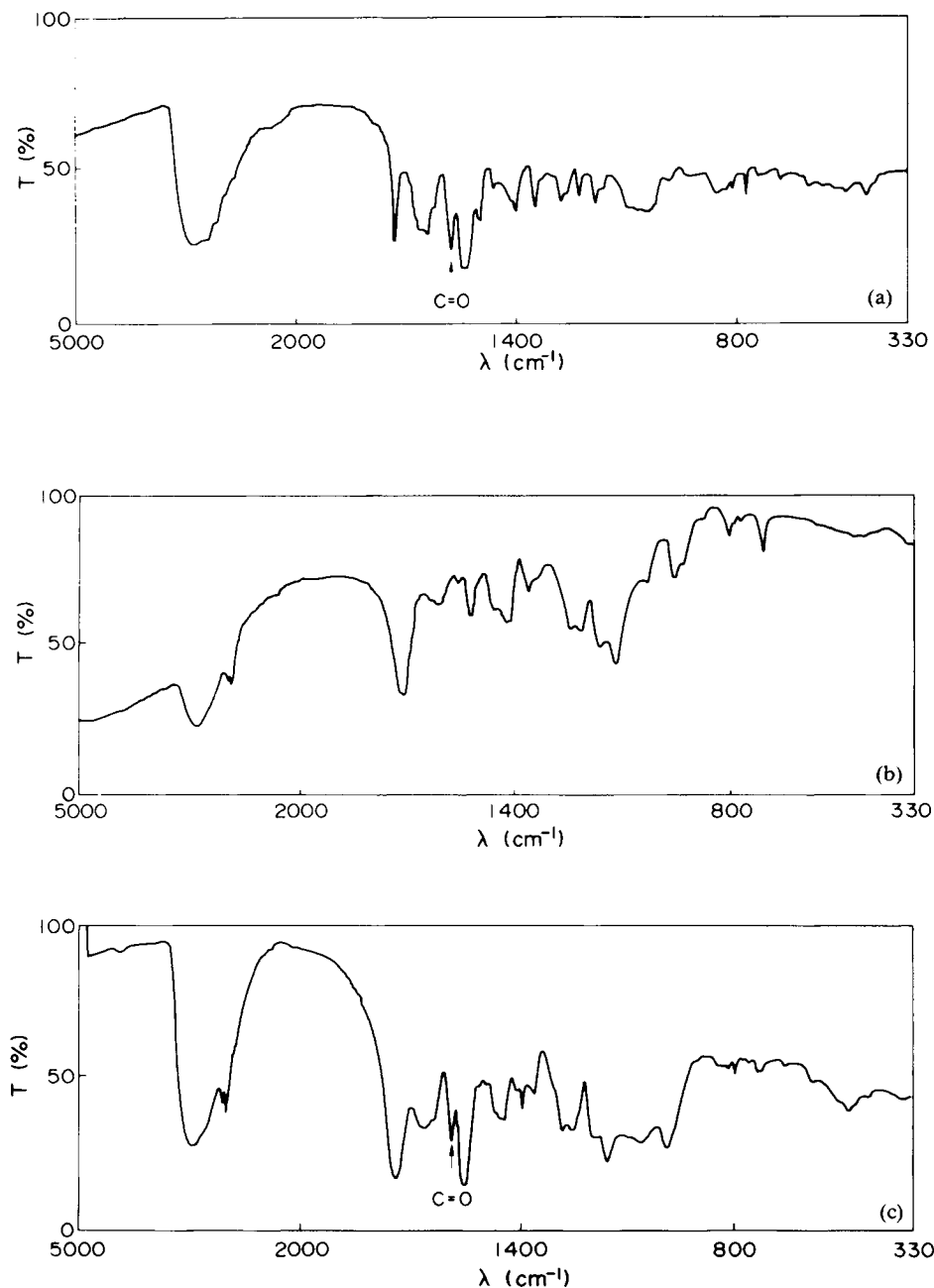


Fig. 8. IR spectra: (a) FMN, (b) poly(methyl methacrylate), (c) polymer obtained by this method.

state, and the triplet excited state of Methylene Blue. It was found that the photofading rate of MB aqueous solution was inhibited by the addition of FMN.

The FMN monomer and the polymer obtained which is grafted to the FMN may make a complex with MB as eq. (15) and it is proposed that FMN blocks

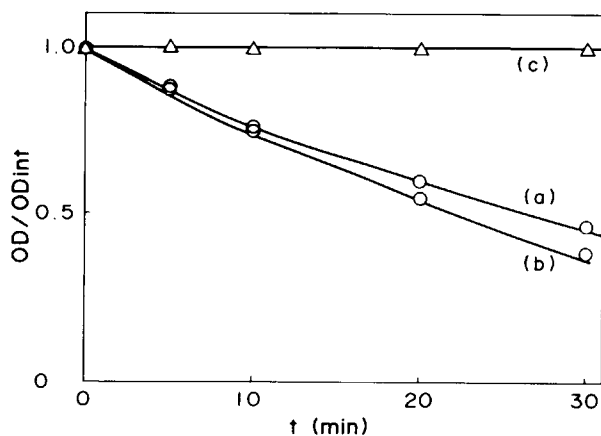


Fig. 9. Photodecoloration of Methylene Blue in the presence of the polymer obtained: (a) MB, 5×10^{-5} mol dm $^{-3}$; (b) MB, 5×10^{-5} mol dm $^{-3}$; PMMA, 10^{-3} mol dm $^{-3}$; (c) MB, 5×10^{-5} mol dm $^{-3}$, polymer obtained, 10^{-3} mol dm $^{-3}$.

the reaction point of the singlet oxygen produced in eq. (13). Therefore, MMA moiety was thought to exist free from any obstacle by forming the complex formation between FMN and MB:



For investigating the interaction between FMN and MB in the solution, the difference spectra of MB between in the presence of and in the absence of FMN were measured. The spectra had a maximum at 686 nm. The Hildebrand plot between MB and FMN was measured. For the straight line of this plot it is assumed that MB makes a 1:1 complex with FMN, and the equilibrium constant was estimated to be 6740 mol $^{-1}$ dm 3 . Assigning by the same procedure, the equilibrium constant between MB, SOT-Blue 2-anthraquinone dye, which is used for dye transfer thermal printing system, and FMN, PMMA, FMN-grafted PMMA polymer, and PVA are shown in Table I. As shown in the table, the equilibrium constant between dye and FMN is large, but those

TABLE I
The Equilibrium Constant between Dyes and FMN

Dye	Polymer	FMN	Solvent	K (M^{-1})
Methylene Blue	—	○	Water	6740
Methylene Blue	PMMA	—	Acetone	0.13
Methylene Blue	PMMA ^a	○ ^a	Acetone	1320
SOT-Blue 2	—	○	Acetone-water	5310
SOT-Blue 2	PMMA	—	Acetone	0.04
SOT-Blue 2	PMMA ^a	○ ^a	Acetone	964
SOT-Blue 2	PVA	—	Acetone	—

^aGraft polymer.

TABLE II
Difference of Color Fastness to Light among Binders

Binder	FMN	Color fastness to light
(a) PVA	20%	5
(b) PVA	—	3
PMMA	—	3
(c) PMMA	Graft	4

between the dye and PMMA are small and the equilibrium constant between the dye and the grafted compound are a little smaller than that between the dye and FMN only. This phenomenon shows that the interaction between FMN and dye are inhibited a little by the PMMA chain. The difference spectrum between the dye and PVA which is used in the binder of FMN showed that SOT-Blue 2 does not interact with PVA.

The dye transfer thermal printing method is a new method for color printing, which consists of the transfer sheet and the recording medium. The transfer sheet is made of the binder containing sublimation dye upon poly(ethylene terephthalate) films. The recording medium consists of thin polymer layer coated on base paper. The transfer sheet and the recording medium are piled and the thermal head heats them imagingly, which introduce the sublimation of dye. The dye migrates to the polymer layer of the recording medium and the image is fixed.

The image was recorded by the dye transfer sheet which was made by the following content: dye; SOT-Blue 2, 4 g; PVA, 1 g; DMABr; 0.05 g. This transfer sheet was put on the recording medium which was coated on plain paper to 10 μm thickness shown in Table II. They were heated by a thermal head (400 Ω thick membrane type) under the following conditions: added voltage, 16V and pulse width 3 ms. The printed image was irradiated by a mercury lamp with an 8-ranks-departed color plate of which the color fastness to light is twice as strong as the next plate. The color plates and samples were partially covered by aluminum foil and the color of the irradiated part was compared with that of the covered part. The critical point at which the color was changed between the irradiated part and the covered part of the plate shows the class of the color fastness to light of the sample. As can be seen in Table II, the color fastness to light of the sample which was coated with PVA or PMMA only or with PMMA which contains 20% dispersed FMN was of degree 3. But that of the PVA which was coated with PVA which contains 20% dispersed FMN on the plain paper to the 10 μm thickness was of degree 5. This phenomenon shows that the most of the dye may interact with FMN but some dye may not interact with FMN but with PMMA; this latter dye can decolor rapidly and the difference between the covered and uncovered parts appears and the degree of color fastness to light may be lowered. That of the sample which was printed on the medium-coated FMN-grafted PMMA was of degree 4. These data show that PMMA grafted to FMN inhibits the photofading of the anthraquinone dye.

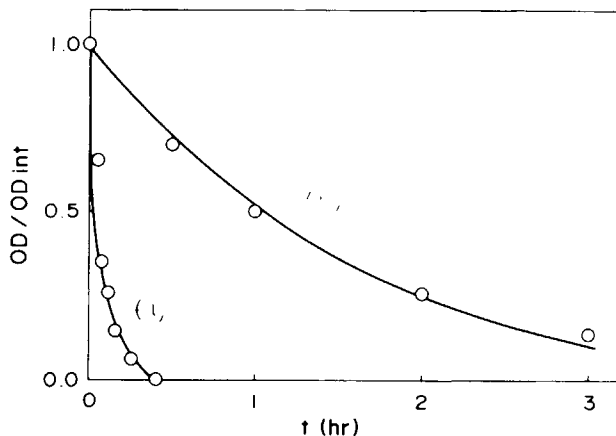
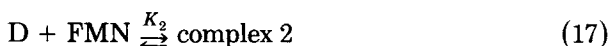


Fig. 10. Heat stability of anthraquinone dye on recording medium: (a) FMN (10%) dispersed in poly(vinyl alcohol) in a 170°C oven; (b) polymer obtained in a 170°C oven.

On the other hand, the dyes used in the dye transfer printing system have the sublimation pressure at room temperature, and the image was lost in such a long storage time. If we assume that the Arrhenius relation holds in this dye-recording medium system, the fastness of the image can be found by the measurement in high temperature. When the printed recording medium was heated in an oven at 170°C, the ratio of the reflection density to initial OD (reserved ratio) was plotted vs. the heating time in Figure 10. The reserved ratio may be proportional to the equilibrium constant between the dyes and the coated polymer:



Free dye sublimates to air and complex 1 or complex 2 stabilizes the dye from the sublimation. K_1 ($\sim 0.051/\text{mol}$) is much smaller than K_2 ($\sim 5000 \text{ l/mol}$) but if $[P] \gg [\text{FMN}]$ can be held, the amount of complex 1 will be larger than that of complex 2. The amount of complex 1 when P is PMMA is much larger than that when P is PVA. As can be seen in Figure 10, the heat resistance of the printed image of the recording medium which was measured by the above procedure was increased by the introduction of the graft polymer to the recording medium obtained by this method. It was considered that the interaction between anthraquinone dye and FMN or poly(vinyl alcohol) was too weak to inhibit the sublimation of anthraquinone dye for recording medium, but the interaction between anthraquinone dye and MMA moiety of the polymer obtained was strong enough so that the sublimation from the recording medium can be inhibited.

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