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Interaction between Dyes and Polyelectrolytes. XV. Effect of Mixed Dimer Formation on the Excitation Energy Transfer between Bound Dyes

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ABSTRACT

The effect of polyanions on the formation of mixed dimers of methylene blue (MB) and trypaflavine (TF), MB and phenosafranine (PhS), and MB and pyronine G (PG) was investigated spectrophotometrically. The following polyanions were used: potassium poly(vinyl sulfate) (PVSK), potassium poly(styrenesulfonate) (PSSK), sodium poly(methacrylate) (PMANa), and sodium poly(acrylate) (PAANa). The formation of mixed dimers was dependent on the kind of polyanion and polyanion-dye ratio. MB-photosensitized isomerization of cis-p-(phenylazo)-phenyltrimethylammonium iodide (cis-PTA) to the trans-isomer was used advantageously to investigate the triplet excitation energy transfer between cationic dyes bound to polyanions. Although the efficiency of the excitation energy transfer between MB and cis-PTA was enhanced by the addition of polyanions, the formation of mixed dimer of MB with TF, PhS, or PG reduced the efficiency of the excitation energy transfer. Correlation with the formation of mixed dimer of MB with TF, PhS, or PG and the efficiency of the excitation energy transfer from MB to cis-PTA is discussed.

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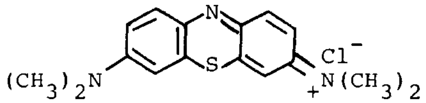
INTRODUCTION

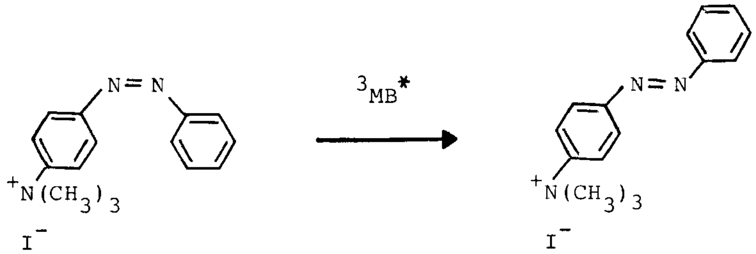
Energy transfer processes are of considerable importance in macromolecular systems. The formation of triplet ketones and the energy transfer in synthetic macromolecules have been widely investigated to understand the photodegradation of macromolecules [1-3]. Furthermore, the excitation energy transfer between bound dyes may be significant in photobleaching processes of dyestuffs in the dyeing of fibers. The triplet excited species may be much better candidate than singlet excited species in terms of reaction with, or energy transfer to, other species. The long-lived triplet excited species can migrate over longer distances than singlet excited species, thus enhancing the probability that the excitation energy reaches a reaction site. Energy transfer processes are also important in biological systems. Cilento and co-workers [4] have suggested the importance of enzyme-generated triplet species and triplet energy transfer in biological systems.

Some cationic dyes undergo a spectral change with increasing concentration. This phenomenon has been ascribed to the formation of dimers or higher aggregates of these dyes in aqueous solutions. Arvan [5] has reported that the absorbances of aqueous solutions containing both a dye of the thiazine series (thionine, methylene blue, toluidine blue) and a dye of the acridine series (trypaflavine, acridine yellow, acridine-HCl) are in disagreement with the sum of the absorbance of each dye. Lemin et al. [6] have reported a similar finding for aqueous solutions containing Durazol Red 2B and Chlorazol Sky Blue FF. They have explained this phenomenon on the basis of the formation of mixed dimers. It has been reported that the formation of the mixed dimers of some cationic dyes is enhanced by the addition of polyanions [7].

The effect of polyelectrolytes on reaction kinetics between small charged molecules has been observed and summarized in several articles [8, 9]. Large rate enhancements have been observed for chemical reactions which involve two charged reactants of the same sign and a polyelectrolyte with the opposite sign. These effects have also been observed in the fields of photochemistry and photophysics [10-12]. In previous papers [13, 14] we reported the effect of polyanions on the triplet excitation energy transfer from methylene blue (MB) to cis-p-(phenylazo)phenyltrimethylammonium iodide (cis-PTA) in aqueous media. This system was used to advantage in the study of the triplet excitation energy transfer in aqueous media: 1) the cis-trans isomerization of PTA is a unimolecular reaction without complicating reactions; 2) the isomerization of cis- to trans-PTA can be followed spectrophotometrically; 3) cis-PTA is thermally stable at room temperature even in water, differing from most of the azobenzene derivatives [15]; and 4) MB photosensitizes only the isomerization from cis- to trans-PTA, thus simplifying analyses of the processes of excitation energy transfer. It was observed that the efficiency of the triplet excitation energy transfer from MB to cis-PTA was largely influenced by such factors as the kind of polyanions added, the polymer-dye ratio, and the addition of sales [13, 14].



MB



cis-PTA

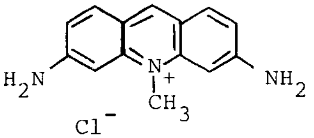
trans-PTA

In this article we report the effect of the mixed dimer formation of MB as a photosensitizer with some cationic dyes on the triplet excitation energy transfer from MB to cis-PTA in aqueous media in the presence and absence of polyanions.

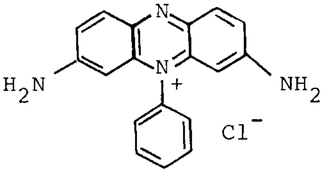
EXPERIMENTAL

Materials

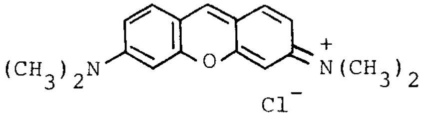
Potassium poly(vinyl sulfate) (PVSK, $P_n = 1500$), potassium poly(styrenesulfonate) (PSSK, $P_n = 700$), sodium poly(acrylate) (PAANa, $P_n = 620$), and sodium poly(methacrylate) (PMANa, $P_n = 920$) were prepared as described elsewhere [16, 17]. Methylene blue (MB) was purified by the Bergmann and O'Konski method [18]. Phenosafranine (PhS) ($\lambda_{max} = 530$ nm, $\epsilon = 2.40 \times 10^4$ $M^{-1}cm^{-1}$; Ref. 19, $\lambda_{max} = 530$ nm, $\epsilon = 3.60 \times 10^4$ $M^{-1}cm^{-1}$) and Pyronine G(PG) ($\lambda_{max} = 550$ nm, $\epsilon = 3.70 \times 10^4$ $M^{-1}cm^{-1}$; Ref. 20, $\lambda_{max} = 550$ nm, $\epsilon = 4.60 \times 10^4$ $M^{-1}cm^{-1}$) were purified by dissolving them in methanol and precipitating with ether. Trypaflavine (TF) (λ_{max} = 451 nm, $\epsilon = 3.70 \times 10^4$ $M^{-1}cm^{-1}$; Ref. 21, λ_{max} = 451, $\epsilon = 4.20 \times 10^4$ $M^{-1}cm^{-1}$), purchased, was of reagent grade and was used without further purification. p-(Phenylazo)phenyltrimethylammonium iodide (PTA) was prepared by the method of Chuang et al. [22]. Water was passed through exchange resins and distilled before use.



TF



PhS



PG

Measurements

To obtain cis-PTA, a trans-PTA solution was irradiated with a high-pressure mercury lamp filtered through a Toshiba UV-D2 filter, which allows the 360-nm line to pass with a reasonable exclusion of other light wavelengths. We obtained about 80% cis-PTA in a photostationary state by using out irradiation set-up. Although the sample solution always contained about 20% trans-PTA, separate experiments showed that trans-PTA did not affect the MB-photosensitized isomerization of cis-PTA. A sample solution (4 mL) which contained MB, cis-PTA, polyanion, and PhS, TF, or PG was placed in a qualtz cell ($1 \times 1 \times 4$ cm) and irradiated in air at 35°C with a 500-W tungsten lamp which was powered by a regulated ac power supply (Matsunaga Mfg. Co., 100 V ± 1.5%). Sample solutions were prepared in the dark before each series of experiments. A combination of two filters, Toshiba C-50S and V-R67, was used to isolate 670 nm light. The isomerization of cis-to trans-PTA was monitored at 320 nm, the absorption maximum of trans-PTA. The reported extinction coefficients of trans-PTA (2.08×10^4 $M^{-1}cm^{-1}$) [22] and cis-PTA (1.93×10^3 $M^{-1}cm^{-1}$) [22] at 320 nm were used to calculate the concentration of trans- and cis-PTA in the sample solution. A Shimadzu UV-200S recording spectrophotometer was used.

The intensity of the irradiating light was determined with a chemical actinometer, Reineck's salt, according to the method devised by Wegner and Anderson [23]. The quantum yield (Φ) for the MB-photosensitized isomerization of cis- to trans-PTA was determined as the number of moles of cis-PTA that disappeared per einstein of light absorbed by MB and/or mixed dimer of MB with PG, PhS, or TF. The conversion was always kept below 15%.

For the study of the mixed dimer formation constant, polymers and dyes were separately dissolved in water to prepare their stock solutions. Just prior to measurements of the absorption spectra, one part of the polymer stock solution. The mixture was always equilibrated for 10 min before measurement of the absorption spectrum. Spectra were measured in a quartz cell of 1 cm thickness, which was placed in a water jacket maintained at 35°C. In the presence of polyanions the association constant (K) for the mixed dimers was determined according to the method of Lang [24]. By using the equation for the association constant for 1:1 complex formation,

$$K = \frac{[D_{12}]}{([D_1] - [D_{12}])([D_2] - [D_{12}])} \quad (1)$$

and substituting the term A/ϵ_c for $[D_{12}]$, the following equation was derived:

$$[D_1][D_2]/A = ([D_1] + [D_2] - A/\epsilon_c)\cdot 1/\epsilon_c + 1/(K\epsilon_c) \quad (2)$$

where A and ϵ_c are the absorbance and molar extinction coefficient of the mixed dimer at a given wavelength, respectively, $[D_1]$ is the initial concentration of MB, and $[D_2]$ is the initial concentration of PhS, PG, or TF. For a series of solutions containing constant concentrations of D_1 (9.00×10^{-6} M) and polyanions and varying concentrations of D_2 (1.74×10^{-6} to 1.74×10^{-5} M), $[D_1][D_2]/A$ was plotted as a function of $([D_1] + [D_2] - A/\epsilon_c)$ by using a tentative value of ϵ_c. A good linear relationship was obtained. The polyanion-dye complexes were precipitated at concentrations of D_2 above 1.0×10^{-4} M. From the slope ($1/\epsilon_c$) and intercept ($1/K\epsilon_c$) of the straight line, a new value of ϵ_c was determined along with a new value of K. This procedure was repeated until a constant set of values for both ϵ_c and K was obtained from two successive plots.

In the absence of polyanions, the initial concentration of TF, PG, or PhS can be enhanced about one hundred times higher than that of MB, because no precipitate appears. In this case Eq. (2) reduces to the simple form

$$[D_1][D_2]/A = [D_2]/\epsilon_c + 1/K\epsilon_c$$

A plot of $[D_1][D_2]/A$ vs $[D_2]$ gave a straight line. The values of ϵ_c and K were obtained from the slope and intercept. No corrections for the formation of homogeneous dimers or higher aggregates for TF, PG, or PhS were made.

Determination of K and ϵ_c were carried out at 740 nm where each dye used showed a negligibly small absorption under the experimental conditions.

RESULTS AND DISCUSSION

The absorption spectrum of MB in a dilute aqueous solution is characterized by a strong and sharp peak at 664 nm. When a cationic dye such as TF, PG, or PhS was added to a dilute aqueous solution of MB, the intensity of the 664 nm band decreased with an increase in the concentration of the dye added and a new absorption band appeared around 700 nm. Arvan [5] has reported that a 1:1 complex between MB and some acridine dyes shows the new absorption band around 700 nm. Figure 1 shows the spectral change of the MB-TF system in the presence of PSSK. When TF was added, a new absorption band appeared around 700 nm. An isosbestic point was observed at 685 nm at low concentrations of TF. A deviation of the isosbestic point was observed at high concentrations of TF. This may be due to the formation of homogeneous aggregate of TF. A similar phenomenon was observed when PG or PhS was added instead of TF. Then K values were determined at the dye concentration range where an isosbestic point was observed. A separate experiment showed that cis- and trans-PTA did not form mixed dimers with MB, PG, PhS, or TF. Table 1 shows the values of K and ϵ_c for the mixed dimer of MB with TF in the presence of different concentrations of PSSK. The formation of the mixed dimers was strongly affected by addition of PSSK. The K value increased with increasing PSSK concentration, passed through a maximum, and decreased for still higher concentrations of PSSK. The value of ϵ_c in the presence of PSSK was almost the same as that in the absence of PSSK. On the other hand, K values in the presence of PSSK were 4-24 times larger than those in the absence of PSSK. The large increase in K values on addition of PSSK can be explained on the basis of a concentrating effect by which the positively charged dyes are concentrated in

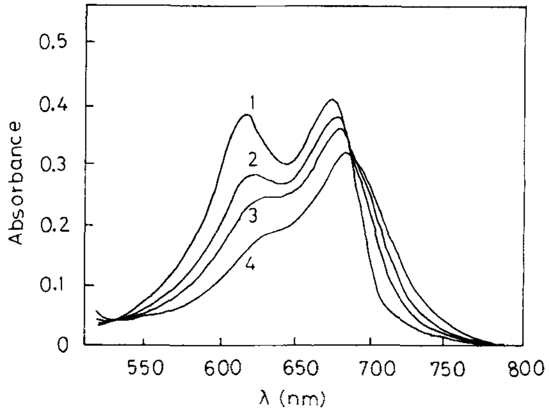


FIG. 1. Absorption spectra of MB-TF mixture in the presence of PSSK at 35°C. [MB] = 9.14×10^{-6} M; [PSSK] = 5.27×10^{-4} M. Concentration of TF: (1) 0; (2) 2.73×10^{-6} M; (3) 8.20×10^{-6} M; (4) 2.73×10^{-5} M.

TABLE 1. Association Constants (K) and Molar Extinction Coefficients (ϵ_c) at 740 nm for the Mixed Dimer of MB with TF in the Presence of PSSK at 35°C[a]

PSSK (M)	$K \times 10^{-3}$ (M^{-1})	$\epsilon_c \times 10^{-3}$ ($M^{-1} cm^{-1}$)
0	2.39	6.08
3.35×10^{-6}	22.16	2.58
3.35×10^{-5}	56.18	10.72
5.27×10^{-4}	46.52	9.03
3.35×10^{-3}	10.08	10.19
1.26×10^{-2}	9.32	5.81

[a] [MB] = 9.00×10^{-6} M; [TF] = 1.74×10^{-6} to 1.74×10^{-5} M.

the negative field of the polyanions. The decrease in K values at high PSSK concentrations may be ascribed to the redistribution of the dyes over the anionic sites of the freshly added PSSK. A similar interpretation was cited to explain the disappearance of the homogeneous dimer or higher aggregates of MB in the presence of a large excess of polyanions [16, 17, 25]. The effect of the kind of polyanions on the K and ϵ_c values for the MB-TF pair is shown in Table 2. The K value

TABLE 2. Effect of the Kind of Polyanions on the Association Constants (K) and Molar Extinction Coefficients (ϵ_c) at 740 nm for MB-TF Mixed Dimer at 35°C[a]

Polyanion	$K \times 10^{-3}$ ($\underline{M}^{-1}$)	$\epsilon_c \times 10^{-3}$ ($\underline{M}^{-1}$ cm^{-1})
None	2.39	6.08
PVSK	59.69	11.26
PSSK	46.52	9.03
PAANa	39.43	11.10
PMANa	27.68	10.23

[a] [TF] = 1.74×10^{-6} to 1.74×10^{-5} $\underline{M}$; [MB] = 9.00×10^{-6} $\underline{M}$; [polyanion] = 5.27×10^{-4} $\underline{M}$.

for the MB-TF pair decreased in the order PVSK > PSSK > PAANa > PMANa. The values of ϵ_c were almost independent on the kind of polyanions added, suggesting that the only one kind of mixed dimer was formed. PVSK and PSSK were more effective than PAANa and PMANa. This may be explained on the basis of the dye binding ability of the polyanions. It has been observed that the ability of polyanions of similar intersite spacing to bind cationic dyes such as acridine orange is $-SO_4^-$ > $-COO^-$ [26]. The same order of effectiveness was observed for the formation of aggregated MB [27]. It was reported that PAANa could more effectively induce the formation of the aggregated MB than PMANa and that PVSK could more effectively induce the aggregation of MB than PSSK [16]. Table 3 shows K and ϵ_c values for the mixed dimer of three dye pairs in the absence and presence of PSSK. K and ϵ_c values for the three dye pairs were largely enhanced on addition of PSSK. K values for three dye pairs in the presence of PSSK decreased in the order MB-TF > MB-PhS > MB-PG pair.

MB shows a strong peak at 664 nm ($\epsilon = 7.8 \times 10^4$ M^{-1} cm^{-1}) and a weak one at 290 nm ($\epsilon = 4.0 \times 10^4$ M^{-1} cm^{-1}). The absorption spectrum of an aqueous solution of cis-PTA is characterized by a strong peak at 280 nm ($\epsilon = 4.96 \times 10^3$ M^{-1} cm^{-1}) and a weak one at 430 nm ($\epsilon = 1.52 \times 10^3$ M^{-1} cm^{-1}) [22]. cis-PTA, TF, PG, and PhS have no absorption peak around 670 nm. The spectral change of a mixture of cis-PTA and MB with irradiation of 670 nm of light is shown in Fig. 2. The thermal isomerization of cis- to trans-PTA was negligibly slow in water at 35°C, differing from most azobenzene derivatives [15]. In the pattern of irradiation, no significant changes in the absorbance at 664 nm due to MB were observed. On the other hand, the absorbance at 320 nm increased with irradiation, suggesting the formation of trans-PTA. An isosbestic

TABLE 3. Association Constants (K) and Molar Extinction Coefficients (ϵ_c) at 740 nm for the Mixed Dimers of Three Dye Pairs in the Presence and Absence of PSSK at 35°C[a]

	MB-TF		MB-PhS		MB-PG	
Additive	$K \times 10^{-3}$ (M^{-1})	$\epsilon_c \times 10^{-3}$ ($M^{-1} cm^{-1}$)	$K \times 10^{-3}$ (M^{-1})	ϵ_c 10^{-3} ($M^{-1} cm^{-1}$)	$K \times 10^{-3}$ (M^{-1})	$\epsilon_c \times 10^{-3}$ ($M^{-1} cm^{-1}$)
None	2.39	6.08	0.75	5.07	1.63	4.09
PSSK	46.52	9.03	26.15	5.29	15.86	5.19

[a] [MB] = 9.00×10^{-6} M; [PSSK] = 5.27×10^{-4} M.

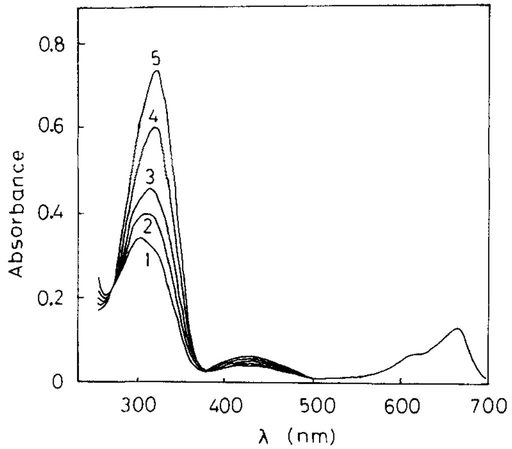


FIG. 2. Spectral changes of an aqueous solution containing MB and cis-PTA with irradiation of 670 nm of light. [MB] = 1.94 × 10^{-6} M; [cis-PTA] = 2.49 × 10^{-5} M. Irradiation time in min: (1) 0; (2) 10; (3) 20; (4) 50; (5) ∞.

point was observed at 380 nm. Prolonged irradiation caused complete isomerization of cis- to trans-PTA. No MB-photosensitized isomerization of trans- to cis-PTA was observed, and additional trans-PTA did not affect the MB-photosensitized isomerization of cis-PTA. In an earlier article [13] it was reported that MB-photosensitized isomerization of cis- to trans-PTA occurred by transfering triplet excitation energy from MB to cis-PTA.

In Fig. 3, Φ/Φ_0 values in the presence of different concentrations of PSSK are plotted against TF concentrations added, where Φ and Φ_0 are the quantum yields for the MB- photosensitized isomerization of cis- to trans-PTA in the presence and absence of TF, respectively. Irradiation was carried out with 670 nm of light by which monomeric MB (bound and free) and/or mixed dimer could be excited. The dyes TF, PhS, and PG do not absorb the 670 nm of light. Although the Φ/Φ_0 value in the absence of PSSK did not decrease on addition of TF, the Φ/Φ_0 value in the presence of PSSK decreased with increasing TF concentration. The decreasing effect on addition of TF increased with increasing PSSK concentration, passed through a maximum, and decreased for high concentrations of PSSK. In Fig. 4 the relationship between the ratio of anionic site of PSSK to dye (PSSK/D) and Φ/Φ_0 is shown along with the relationship between PSSK/D and K values for the MB-TF dye pair. The maximum decreasing effect was observed

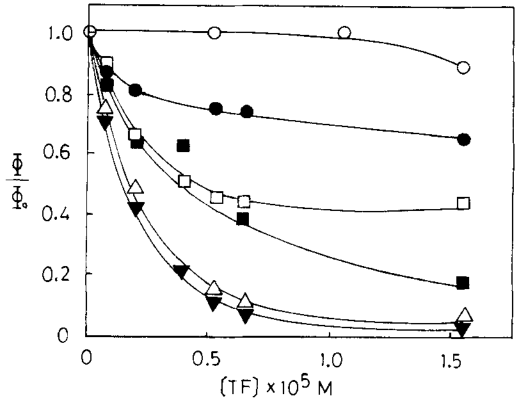


FIG. 3. Relationship between Φ/Φ_0 value and concentration of TF in the presence of PSSK at 35°C. [MB] = 1.94×10^{-6} M; [cis-PTA] = 2.49×10^{-5} M. PSSK concentration: (○) 0; (□) 3.35×10^{-6} M; (△) 1.01×10^{-5} M; (▼) 3.35×10^{-5} M; (■) 3.35×10^{-4} M; (●) 3.35×10^{-3} M.

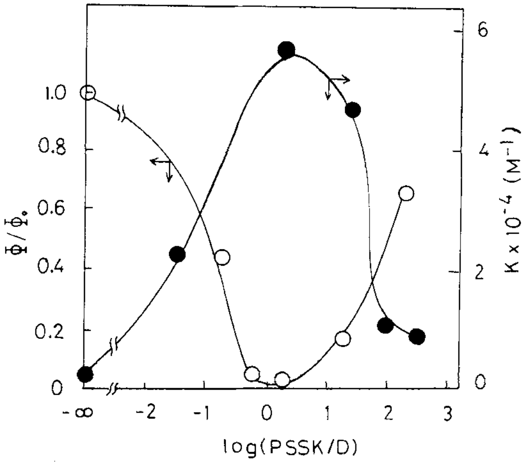


FIG. 4. Effect of PSSK/D value on (○) the Φ/Φ_0 value and (●) the K value for the mixed dimer of the MB-TF pair.

at [PSSK] = 3.35×10^{-5} M, where the excitation energy transfer from MB to cis-PTA was virtually stopped. The PSSK/D value at which the minimum Φ/Φ_0 value was observed was consistent with that at which the maximum K value for the mixed dimer formation was observed.

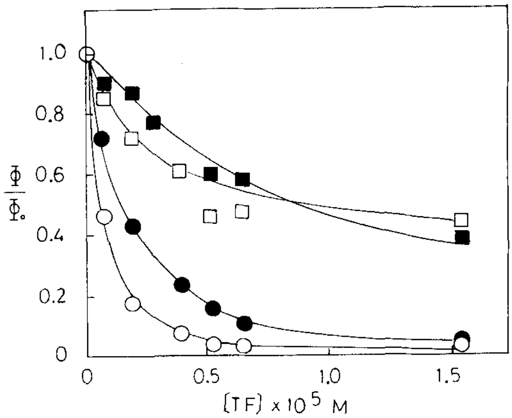


FIG. 5. Relationship between Φ/Φ_0 value and TF concentration in the presence of different kind of polyanions at 35°C. [MB] = 1.94×10^{-6} M; [cis-PTA] = 2.49×10^{-5} M; [polyanion] = 3.35×10^{-5} M. Polyanion: (○) PVSK; (●) PSSK; (■) PAANa; (□) PMANa.

Figure 5 shows the relationship between Φ/Φ_0 and TF concentration added in the presence of constant concentrations of PSSK, PVSK, PAANa, or PMANa. PSSK and PVSK reduced the Φ/Φ_0 value more effectively than PAANa and PMANa. This finding was consistent with that observed for the mixed dimer formation. This may be explained on the basis of the dye binding ability of the polyanions as described above.

Figure 6 shows the effect of the kinds of dyes added on the Φ/Φ_0 value in the presence of 3.35×10^{-5} M of PSSK. The Φ/Φ_0 value decreased with an increase of the concentration of dye added and the degree of decrease was dependent on the kind of dye added (TF > PhS > PG). The order of decreasing effect was consistent with that for K values of the mixed dimer formation of MB with TF, PhS, or PG. The polymer which gave a high K value for the mixed dimer formation caused an effective decrease in the Φ/Φ_0 value. These findings suggest that mixed dimers cannot act as effective photosensitizers for the isomerization of cis- to trans-PTA. It was reported that the formation of highly aggregated MB induced by polyanions reduced the efficiency of the excitation energy transfer between MB and cis-PTA [13, 14]. It has been reported that the lifetime of the excited state of highly aggregated MB is shorter than that of monomeric MB [28]. The shorter lifetime of the excited state of the mixed dimer than monomeric MB may play an important role in the reduction of the energy transfer efficiency.

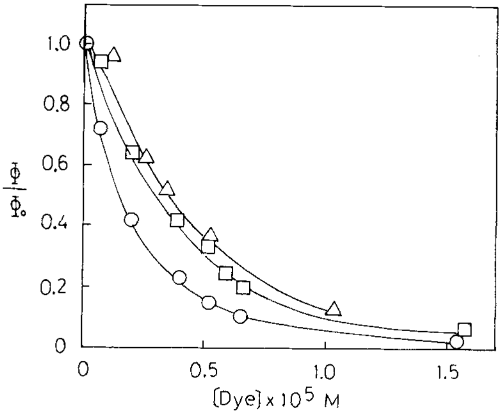


FIG. 6. Relationship between Φ/Φ_0 and dye concentration in the presence of PSSK at 35°C. [MB] = 1.96×10^{-6} M; [cis-PTA] = 2.49×10^{-6} M; [PSSK] = 3.35×10^{-5} M; Dye. (○) TF; (□) PhS; (△) PG.

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