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POLYMER EFFECTS ON ELECTRON TRANSPORT SENSITIZATION: A KINETIC ATTEMPT TO MIMIC THE PRIMARY ACTION OF CHLOROPHYLL.

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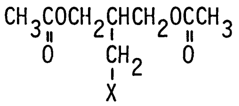
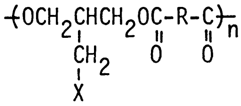
Photooxidation of Leuco Crystal Violet to the dye cation using polymer bound anthryl and pyrenyl groups as electron transport sensitizers showed that all of anthryl polymers were more efficient than their monomer model compound whereas pyrenyl polymers were not. The positive polymer effect was attributed to energy migration along polymer chain to increase the energy utilization efficiency.

This is a kinetic attempt to approach the high efficiency of chlorophyll in transporting electrons while the actual reactions involved in photosynthesis are yet far beyond the ability of chemists. The structure and actions of chlorophyll have been well studied and the information is as follows[1]. The absorbed photoenergy by antena chlorophyll is transferred to reaction center(P) which drives the linked electron transport system to couple oxidation of water with reduction of NADP to NADPH. This elaborated principle informs us that the kinetic mimicry may be possible on the condition that i) electron transport sensitization instead of conventional energy transfer sensitization and ii) aggregation of sensitizer molecules to induce energy transfer between sensitizers are achieved. The first condition has been already solved by the recent studies[2-7] in which aromatic hydrocarbon recycles as an electron carrier between D and A via singlet excited state. It is also possible to couple photoreduction of carbon dioxide to carboxylic acids with oxidation of water[7]. We can think of several approaches to the second condition. Here we look at the polymer effects expected when sensitizer components are bound to a polymer as side groups with appropriate intervals so as to induce energy migration. Enhanced utilization efficiency of absorbed energy is consequently expected for the polymeric electron transport sensitizer although the efficiency increase due to random energy migration in polymer will be much smaller than in the case of chlorophyll where energy transfer is oriented to P as shown in Figure 1.

In practice, we prepared the following polymers[8]. As an electron transfer reaction to be





1: X = 9-anthryl
3: X = 3-pyrenyl

	X	R		X	R
2a:	9-anthryl	$-(CH_2)_2-$	4a:	3-pyrenyl	$-(CH_2)_2-$
2b:	"	$-(CH_2)_4-$	4b:	"	$-(CH_2)_4-$
2c:	"	$-(CH_2)_8-$	4c:	"	$-(CH_2)_8-$
			4d:	"	$-(CH_2)_{10}-$

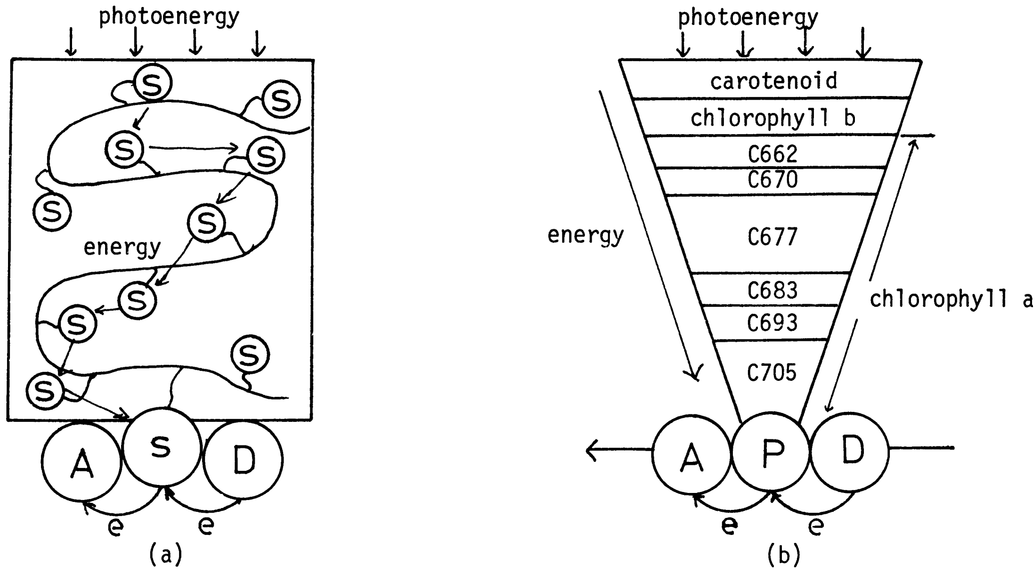


Figure 1. Similarity between polymer bound electron transport sensitizer(a) and the initial stage of photosynthesis(b).
a : Energy migration is random and unoriented. b : Energy transfer is oriented to P(from ref. 1)

driven, photooxidation of Leuco Crystal Violet(LCV) was chosen. The reaction has been shown to proceed via electron transfer process giving Crystal Violet(CV^+) absorbing at around 596nm[9]. Our experiments proved aromatic hydrocarbons such as perylene(5), pyrene(6), and anthracene(7) to be good sensitizers acting as follows, A being an acceptor[10].

$$\mathrm{Sens}(5,\ 6,\ \text{or}\ 7) \xrightarrow{h\nu} \mathrm{Sens}^{*1}$$

$$\mathrm{Sens}^{*1} + \mathrm{A} \longrightarrow \mathrm{Sens}^{+\cdot} + \mathrm{A}^{-\cdot}$$

$$(\text{or } \mathrm{Sens}^{*1} + \mathrm{LCV} \longrightarrow \mathrm{Sens}^{-\cdot} + \mathrm{LCV}^{+\cdot})$$

$$\mathrm{Sens}^{+\cdot} + \mathrm{LCV} \longrightarrow \mathrm{Sen} + \mathrm{LCV}^{+\cdot}$$

$$(\text{or } \mathrm{Sens}^{-\cdot} + \mathrm{A} \longrightarrow \mathrm{Sens} + \mathrm{A}^{-\cdot})$$

$$\mathrm{LCV}^{+\cdot} \rightleftharpoons \mathrm{CV}\cdot + \mathrm{H}^+$$

$$\mathrm{CV}\cdot + \mathrm{LCV}^{+\cdot} \longrightarrow \mathrm{CV}^+ + \mathrm{LCV}$$

Relevant properties and relative efficiency of the sensitizers are shown in Table 1 and Figure 2, respectively. Under the condition that all molecular motions are frozen and no excimer is observed, fluorescence from diluted polymer solution is strongly depolarized in comparison with the monomer model compounds(Table 1) indicating the participation of efficient intrapolymer singlet energy migration. We assume the participation of energy migration in fluid solution as well. Since singlet energy migration occurs via long range interaction, no clear dependence of the degree of depolarization on polymer structure is not observed. However, the excimer intensity(F_e/F_m) reflects polymer structure sharply. In particular, the pyrenyl polymers show strong excimer emission, which would be the major reason for the low sensitizer efficiency of the polymers, the excimer acting as energy traps. The short emission lifetime of anthryl group($\tau_f < 10$ns)

Table 1. Properties of Polymer Bound Sensitizers and Their Monomer Model Compounds.

Sample	MW	$\overline{DP}$	$(F_e/F_m)_{c\to 0}$*	P**
1	350.4		0.0	0.233
2a	4,200	12	0.22	0.096
2b	2,500	6-7	0.08	0.073
2c	11,000	25	0.09	0.061
3	374.4		0.0	0.097
4a	5,100	13	5.55	0.046
4b	13,000	32	5.60	0.040
4c	46,000	100	4.05	0.037
4d	11,000	22	1.90	0.091

* F_e : Excimer emission intensity determined at 500nm(shoulder) for 2 and at 475nm(broad peak) for 4.

F_m : Monomer emission intensity determined at 415nm for 2 and at 376nm for 4.

Measurements in THF at room temperature under nitrogen atmosphere. The intensity ratio was extrapolated to infinite dilution.

**Fluorescence depolarization($(I_{/\!/} - I_{\perp})/(I_{/\!/} + I_{\perp})$) measured in frozen 2-methyltetrahydrofuran matrix at 77 K.

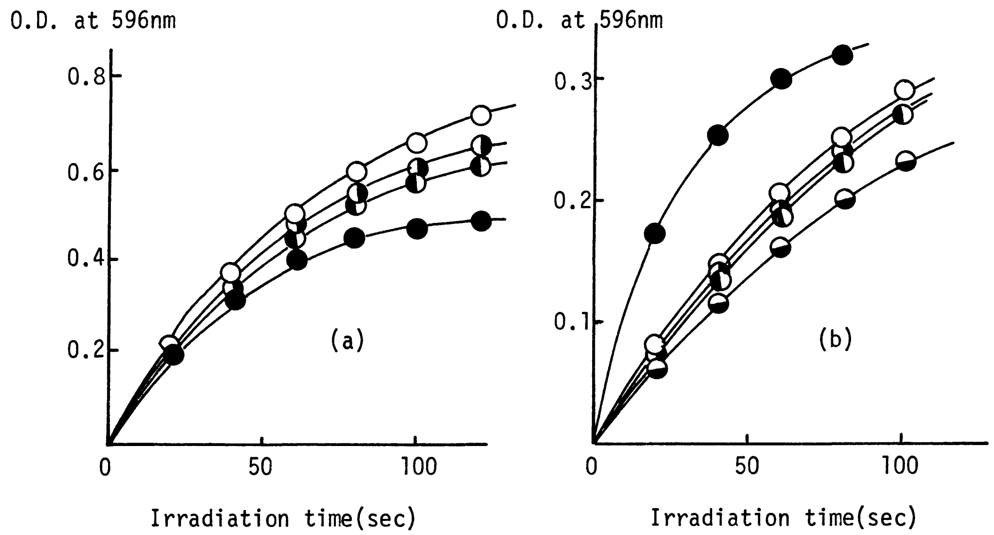


Figure 2. Photo-oxidation of Leuco Crystal Violet in the presence of polymer bound electron transport sensitizers.

[LCV] = 1×10^{-3}M, [sensitizer] = 2×10^{-4}M in DMF, acceptor: oxygen.

a : Sensitization by anthryl group. Irradiation at 390nm. Since $O.D._{390}>1.5$, complete photo-absorption was assumed. ●: 1, ◑: 2a, ○: 2b, ◐: 2c.

b : Sensitization by pyrenyl group. Irradiation at 377nm(^1L_a forbidden band). The absorbance at 377nm was constant at 0.1. ●: 3, ◐: 4a, ⊖: 4b, ○: 4c, ◑: 4d.

will be an important factor favoring energy migration over excimer formation since energy migration probability is proportional to the reciprocal of τ_f according to the Förster mechanism[11] whereas face-to-face approach of chromophores to a distance of 3-4Å within τ_f is necessary for excimer formation[12].

Besides the positive polymer effect brought about by energy migration, reduced diffusion constant in polymeric systems and energy traps caused by excimer formation[11,13] would result in reduced sensitizer efficiency. Furthermore, the enhanced photodimerizability of anthryl groups in 2a, 2b, and 2c would further reduce the sensitizer efficiency[14]. The finding that the anthracene polymers are better sensitizers than 1 (Figure 2a) indicates that the positive polymer effect overcomes unequivocally the demerits mentioned above. Further improvement of electron transport efficiency is consequently anticipated if the choice of chromophore and polymer structure is adequately made to avoid excimer formation and side reactions and to facilitate energy migration along polymer chain.

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14) The rate of photodimerization of anthryl groups in 2a, 2b, and 2c are ~3, ~7, and ~10 times faster than that of 1, respectively. The stationary concentration of the singlet state in 2a, 2b, and 2c is therefore much smaller than that in 1. See S.Tazuke and F.Banba, ref. 7.

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