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Polymer Catalysts for Important Photoelectron Transfer Reactions

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Abstract: Photozymes are novel water-soluble polymers made by the copolymerization of mixtures of hydrophobic and hydrophilic monomers, some of which contain chromophores capable of absorbing light and transmitting the excitation energy to selected traps by means of the antenna effect. The interactions between these groups and water force the polymer to adopt a hypercoiled conformation with hydrophobic pockets similar to those in the catalytic sites of natural enzymes. Hydrophobic organic compounds in the water solution will seek out and localize themselves in these regions, where they are subjected to electronic energy transfer from the light-excited antenna chromophores. The chemical reactions which occur are often different and more specific than in the case of photoreactions in common organic solvents. In a number of cases the reactions appear to proceed by an electron transfer mechanism. This paper summarizes recent results on the dechlorination of chlorinated aromatic and aliphatic compounds, and laser studies of multiphoton processes in aromatic compounds such as 9-(acetoxymethyl)phenanthrene (AMP).

INTRODUCTION

Photozymes are constructed by copolymerization of a mixture of water-soluble and water-insoluble comonomers, some of which contain chromophores capable of absorbing light and transmitting the excitation energy by means of the "antenna effect" to selected traps within the polymer coil. The interactions between the hydrophobic and hydrophilic groups in the polymer with water cause the formation of "hypercoiled pseudomicellar" conformations of the polymer coil, leading to hydrophobic regions or "pockets" in the interior of the polymer. If the water contains hydrophobic organic

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molecules, they will locate preferentially in the center of the coil, and in the presence.of light they can be photochemically transformed into useful products, with high efficiency and selectivity.

Recently we have shown (Refs. 1, 2) that when the absorbing chromophore is a polynuclear aromatic, such as naphthalene, the chemical reactions often involve a photoelectron transfer step. Also photozymes retain their catalytic activity at very high dilution in water (there is no critical micelle concentration). For these and other reasons, we are convinced that their greatest potential may be realized in their use as biomimetic catalysts for chemical synthesis (Ref. 3). They also share many of the properties of biological enzymes. Both are macromolecules (MW = 5 to 200 kilodaltons), soluble or dispersible in water, and are constructed from mixtures of hydrophobic and hydrophilic monomers (amino acids in the case of enzymes). Biological enzymes catalyze many reactions with rate accelerations as high as 10^8, yield specific products, and show high substrate selectivity. Our synthetic polymers have displayed similar properties.

Recently, we have focused on the preparation (Refs. 4, 5), characterization (Refs. 4-6), and photocatalytic properties (Refs. 7-13) of water-soluble copolymers containing covalently attached aromatic chromophores. Typically, sodium styrenesulfonate (SSS), employed as the hydrophilic monomer, is copolymerized with hydrophobic monomers such as styrene (S), 2-vinylnaphthalene (VN), acenaphthalene (AcN), 9-vinylphenanthrene (VPh), or N-(acryloyloxyhexyl)-carbazole (AHCz). Interactions between the aromatic chromophores and water result in the formation of hydrophobic microdomains in which sparingly water-soluble organic compounds are readily solubilized. The high local concentration of aromatic chromophores found along the polymer backbone results in light-harvesting systems in which the energy of photons absorbed at sites remote from a solublized molecule can migrate through the polymer and be transferred to the solubilized molecule. The polymers have been shown to act as sensitizers for a number of different photochemical reactions in aqueous solution: (1) photooxidation of polycyclic aromatic hydrocarbons (PAH) (Refs. 7,8), (2) photodechlorination of polychlorinated biphenyls (PCB) (Refs. 9, 10), (3) photooxidation of styrene (Ref. 11), (4) photolysis of undecanone (Ref. 12), (5) photoisomerization of 7-dehydrocholesterol to previtamin D3 (Ref. 13).

This paper presents recent results concerning photochemical reactions in photozymes for which photoinduced electron transfer appears to be an essential step. Of particular interest is the photodestruction of organic pollutants such as PAHs and chlorinated aromatics.

SOLUBILIZATION

Hydrophobic compounds such as PAHs, PCBs, and other chlorinated organics are much more soluble in aqueous photozyme solutions than in water alone. In the case of perylene (P), the observation of intense perylene fluorescence and efficient energy transfer from the polymer chromophores to the substrate reveals that perylene is solubilized within the individual polymer coils.

If the aqueous polymer solution is treated as a two phase (polymer and water) system, then the partition coefficient (K_{pw}) can be defined by:

$$K_{pw} = X_p/X_w \qquad (1)$$

where X_p and X_w are the weight fractions of perylene in the polymer and water phases. The intensity of perylene fluorescence can be used to determine the perylene concentration in the polymer phase, while the concentration in water is given by the known water solubility (1.6×10^{-9} M) (Ref. 14). K_{pw} varies from 1×10^6 to 4×10^6 for PSSS-S, PSSS-VN, PSSS-VPh and PSSS-AHCz. Thus a 0.1% photozyme solution can contain at least 1000 times more perylene than the same volume of pure water.

Studies were made of the irradiation of saturated solutions of hexa- and pentachlorobenzene (HCBz and PCBz, respectively) in saturated aqueous solutions containing 200 ppm of PSSS-VN or 230 ppm PSSS-AcN using simulated solar light. In PSSS-VN the rates of decomposition for HCBz and PCBz were increased by factors of 1800 and 1200, respectively, as compared to the same compounds dissolved in acetonitrile. Even greater accelerations, 3900 and 1500 were observed with PSSS-AcN solutions, presumably because this photozyme absorbs more strongly in the near UV portion of the solar spectrum.

In each case, the isomers of the products are those expected from an electron transfer process, and appear to occur via an exciplex intermediate. Preliminary studies of 1,2,7,8 - tetrachlorodibenzo p-dioxin showed an acceleration of 17 times in the aqueous PSSS-VN solution than in methanol, showing the potential for the remediation of water contaminated with this dangerous compound. Tetrachloroethylene (TCE) also shows an accelerated rate of degradation in photozyme solution, as shown in Table 1. When TCE was irradiated in an aqueous solution of the acenaphthalene-containing photozyme, PSSS-AcN, the TCE disappeared rapidly. Irradiation for 20 min resulted in a 25% decrease in TCE concentration.

In the case of 2-methylnaphthalene, this sensitizer has little effect on the rate of photolysis. In the photozyme solution, TCE is localized within the polymer, in close proximity to the acenaphthyl groups. This higher local concentration explains why TCE is photolyzed more rapidly in PSSS-AcN than in the presence of the smallmolecule sensitizer, 2-methylnaphthalene.

Table 1. Photodegradation of tetrachloroethylene[a]

Sensitizer	Solvent	% degradation
None	CH_3CN	5
2-Methylnaphthalene (6×10^{-3} M)	CH_3CN	3
PSSS-AcN (0.20 g/L)[b]	H_20	25

[a] Irraddiation with 260-350 nm light for 20-25 min.
[b] [AcN] = 6×10^{-3} M.

POTENTIAL FOR SOLAR SYSTEMS

Does it really make sense to utilize solar systems to synthesize or destroy chemicals? The following calculations are instructive. The annual average daily solar power in temperate climates is about 300 W/m^2, of which about 9% is in the 270-400 nm range. If one is synthesizing a product like Vitamin D with a molecular weight of ca. 250 and using a collector slightly larger than a football field (100 m x 100 m), the theoretical yield would be ca. 20 tons of product per day. This is probably more than the entire world market for this compound. If you had a tailings pond contaminated with a saturated solution of perylene and the quantum yield for photochemical decomposition was 1×10^{-4} one should be able to detoxify 2×10^6 liters of water per day. The application of this technology for remediation of tailings ponds from mining and other chemical operations seems particularly promising because they are often in remote regions where conventional technology may be prohibitively expensive. From the perspective of life on earth, the most important of all chemical reactions that sustain living systems is probably natural photosynthesis. The general features of photosynthesis in green plants are now quite well understood (Refs. 15-17). Recently, a detailed crystallographic structure has been produced for the active center of a bacterial photosynthetic reaction center (Ref. 18) The primary photochemical step in photosynthesis involves a one-electron transfer from the excited singlet state of a chlorophyll species (Chl) to a quinoid group (Q) within the reaction center. In well characterized bacterial reaction centers, molecules of ubiquinone or menaquinone may also act as the electron acceptors (Ref. 19) and the photosystem of green plants also includes plastoquinone as an electron acceptor (Ref. 20). The main feature of the primary event is that electron transfer from Chl to Q leads to separation of the charged species $Chl^{+\bullet}$ and $Q^{-\bullet}$, which undergo further reactions in the photosynthetic sequence commonly known as the Calvin cycle (Ref. 21).

The net reaction in photosynthesis can be written

$$nCO_2 + nH_2O \rightarrow (CH_2O)_n + nO_2 \qquad (2)$$

where $(CH_2O)_n$ is usually a complex carbohydrate such as sugar, starch or cellulose. The energy required to balance this equation is about 90 kcal (360 kJ) per mole of CH_2O. The energy of the visible light that drives natural photosynthesis is known to be much less than this.

It is now known that the reason the process is possible is that the chloroplast in green plants contains clusters of up to 200 chlorophyll molecules associated with each photosynthetic unit. These collect the energy of solar photons and through efficient transfer and migration, transport the energy to the active sites where the chemical reactions take place.

It can easily be shown that in an efficient molecular antenna the probability of a two-photon excitation in the associated active site is proportional to n^2, where n is the number of antenna chromophores (i.e., chlorophyll). With 200 antenna units the probability increases by $(200)^2$ or 40,000 times which is just about enough to make a two photon process possible with intensities of visible solar radiation at the earth's surface.

Many organic molecules have been shown to undergo a two-step photoreaction when irradiated with short, high-intensity laser pulses. In the first step, the ground state molecule absorbs a photon, taking it to its first excited state. This state, either S_1 or T_1 depending on whether intersystem crossing occurs, can then absorb a second photon, bringing it to a very high energy state S_2 which can lead to reaction. This type of mechanism could be useful in photochemical synthesis in one of two ways: For molecules in the S_1 or T_1 state which undergo photoreaction reluctantly because of at high activity energy, the quantum yield could be greatly enhanced by bringing it to the much higher energy S_2 state. Alternatively, the reaction from S_2 could lead to a new photochemical pathway, as has been shown for two-step excitation of some amino acids (Refs. 22, 23) giving products not obtainable by one-photon absorption.

The light intensity at which the two--step mechanism become significant can be given by

$$I_{2\text{-step}} = h\nu/\sigma_1\,\tau_1 \tag{3}$$

where σ_1 is the crossection for $S_0 \rightarrow S_1$ and τ_1 is the lifetime of S_1. Equation (3) represents the intensity at which the rate of absorption for $S_0 \rightarrow S_1$ starts to exceed the rate of decay for S_1 so that the concentration of S_1 starts to increase. As mentioned above, only lasers have so far provided the intensities needed for two-step photoprocesses.

In an attempt to measure the effectiveness of our photozyme antennas, the laser photolysis of 9-(acetoxymethyl)phenanthrene (AMP) was studied both in acetonitrile solution and in aqueous solution of PSSS-VN. In this photozyme AMP will be localized in the pseudomicellar structure in water and the naphthyl chromophores will provide excitation of the AMP by Förster energy transfer. The proposed reaction mechanism is shown in Scheme 1.

In these experiments, AMP was irradiated in an aqueous solution of PSSS-VN and in acetonitrile, with laser light of λ = 308 nm at various intensities as controlled by neutral density filters. The quantum yield of photolysis was determined from the rate of disappearance of AMP estimated by liquid chromatography.

At low intensities the quantum yield should be independent of intensity. The onset of a two-photon process can be observed from. a rapid increase in quantum yield, proportional to I^2. Figure 1 shows experimental data on AMP in acetonitrile. The onset of the two-photon process is seen at $I = 1.2 \times 10^5$ watt cm^{-2}, whereas with AMP in aqueous PSSS-VN, it is 40 times lower (Fig. 2). Obviously in this case our antenna system is not working as efficiently as is theoretically possible. Energy is being collected only from the nearest six naphthalene donors. However, as far as we are aware, this is the first experimental evidence for the occurrence of two-step photo processes sensitized by a synthetic polymer antenna. We anticipate that better antenna design should lead to much higher efficiencies, leading to practical applications even at solar intensities.

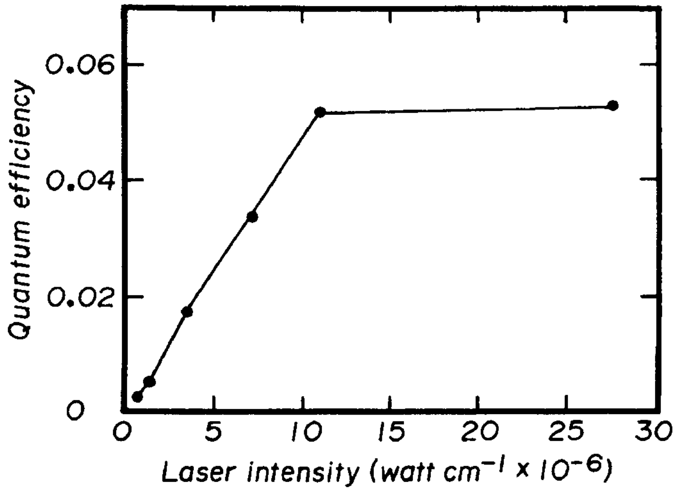


Fig. 1. Quantum efficiency vs. laser intensity (λ = 308 nm) for decomposition of AMP in CH_3CN

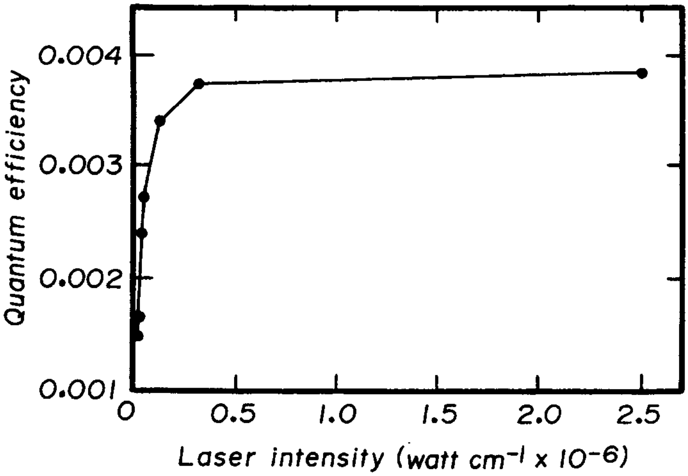
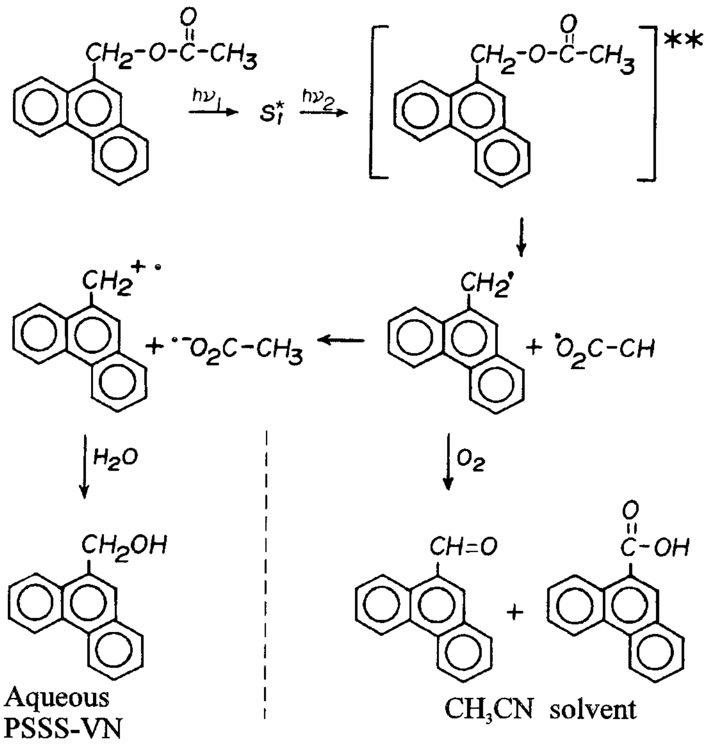


Fig. 2. Quantum efficiency vs. laser intensity (λ = 308 nm) for decomposition of AMP in PSSS-VN in aqueous solution



Scheme 1. Proposed mechanism for two-step photolysis of AMP in aqueous PSSSVN and acetonitrile.

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