The mechanism of perylene photo-oxidation in a water-soluble polymeric photocatalyst

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Abstract

The photo-oxidation of perylene in aqueous solutions of a polymeric photocatalyst was investigated to probe the mechanism of polycyclic aromatic hydrocarbon degradation. Perylene and other hydrophobic molecules are efficiently solubilized in aqueous polymer solutions with distribution coefficients as high as 4×10^6. The rate of perylene photo-oxidation was much more rapid in aqueous polymer solutions than in organic solvents. In organic solvents, $^1O_2$ sensitizers (rose bengal) had little effect on the reaction, but electron acceptors, such as dicyanobenzene, caused an acceleration in rate. Naphthoquinone was suggested as a potential electron acceptor in the naphthalene-containing polymer, and it was shown to be formed in small concentrations by polymer oxidation. It was concluded that the polymer plays several key functions in perylene photo-oxidation: (1) solubilization of the hydrophobic molecule; (2) energy migration through the polymer coil and energy transfer, providing additional photochemical energy to the reactants; (3) the enhancement of oxidation by photoinduced electron transfer via provision of an electron acceptor and facilitation of charge separation.

Keywords: Perylene; Photo-oxidation; Polymeric photocatalyst

1. Introduction

Recent studies carried out in this laboratory have focused on the preparation [1,2], characterization [1–3] and photocatalytic properties [4–9] of water-soluble copolymers bearing covalently attached aromatic chromophores. Hydrophobic interactions between the aromatic chromophores and water result in the formation of hydrophobic microdomains. Sparingly water-soluble organic compounds are readily solubilized within these microdomains. The high local concentration of aromatic chromophore found along the polymer backbone results in efficient light-harvesting systems in which the energy of photons absorbed at sites remote from the solubilized molecule may 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) photo-oxidation of polycyclic aromatic hydrocarbons (PAHs) [4,5]; (2) photodechlorination of polychlorinated biphenyls (PCBs) [6]; (3) photo-oxidation of styrene [7]; (4) photolysis of undecanone [8]; (5) photoisomerization of 7-dehydrocholesterol to previtamin D_3 [9]. The term
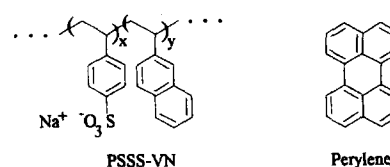
Scheme 1.

"photozyme", short for photochemical enzyme, is used to describe polymers with the properties given above.

As part of an ongoing investigation of the potential of photozymes for wastewater clean-up, the photo-oxidation of perylene in photozymes bearing phenyl, naphthyl, phenanthryl or carbazolyl groups was investigated. In particular, the mechanism of perylene photo-oxidation in the naphthyl-containing photozyme was probed. The structures of perylene and PSSS–VN, a copolymer of p-styrenesulfonate and 2-vinylnaphthalene, are shown in Scheme 1.

The ready availability and high reactivity of oxygen make photo-oxidation one of the more important reactions of electron-rich PAHs in the environment. In general, the photo-oxidation of PAHs with oxygen occurs by reaction with photochemically generated singlet oxygen ($^1O_2$) or by photoinduced electron transfer to produce radical ions followed by reaction with an oxygen species (O_2, $^1O_2$ or O_2^-) [10]. A photocatalyst may function by enhancing either of these

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reactions. For instance, a $^1O_2$ sensitizer, such as rose bengal, can greatly enhance the rate of photo-oxidation of molecules which react with $^1O_2$. An electron acceptor, such as chloranil, can speed up the photoreaction of many electron-rich molecules with oxygen [11,12]. In a previous publication [4] from this laboratory, it was suggested that perylene photo-oxidation occurs via reaction with $^1O_2$, although this is at odds with the observation that perylene is relatively unreactive with $^1O_2$ compared with other PAHs [13]. In this paper, evidence is provided that perylene oxidation in photozyme solution is mediated by photoinduced electron transfer.

2. Experimental details

2.1. Materials

The preparation and purification of poly(sodium p-styrenesulfonate-co-2-vinylnaphthalene) [1] and poly(sodium p-styrenesulfonate-co-N-(6-acryloyloxyhexyl)carbazole) [2] have been described previously. Poly(sodium p-styrenesulfonate-co-styrene) [14] and poly(sodium p-styrenesulfonate-co-9-vinylphenanthrene) [15] were prepared in a similar fashion. Solutions of sodium styrenesulfonate, hydrophobic monomer and AIBN (0.5–1 mol.%) were dissolved in dimethylsulfoxide (DMSO), degassed during three freeze–pump–thaw cycles and heated at 60 °C for 24 h. The polymers were precipitated in acetone, purified by exhaustive dialysis (12 000–14 000 MW cut-off) with deionized water and freeze dried. The composition of the polymers was determined by UV spectroscopy and/or elemental analysis.

Perylene, 1,4-dicyanobenzene and dimethyl terephthalate were purchased from Aldrich Chemical Company and were used as received. Deionized water from a Millipore Milli-Q water purification system was used to prepare polymer solutions. Methanol, tetrahydrofuran (THF), benzene and acetonitrile (CH_3CN) (Spectrograde, Caledon Laboratories) were used for the preparation of solutions for solubilization, fluorescence and photochemical experiments.

2.2. Solubilization of probes

Perylene was solubilized by injecting microliter quantities (10^{-3} M in THF or CH_3CN) into milliliter quantities of water or aqueous photozyme solution. The resulting solutions were shaken for several minutes and then left to equilibrate overnight. The extent of solubilization of perylene was monitored by fluorescence spectroscopy and the concentration of perylene was determined by comparison with a calibration curve.

2.3. Spectroscopic measurements

The steady state emission spectra were measured with an SLM 4800S spectrofluorometer. Absorption spectra were measured with a Hewlett-Packard 8451A spectrophotometer. Gas chromatography (GC) analysis was performed using a

Hewlett-Packard 5890 gas chromatograph equipped with a J and W Scientific DB-1 capillary column (dimethylsiloxane packing, 25 m × 0.25 mm (inside diameter) × 0.25 μm (film thickness)) and a flame ionization detector (FID).

2.4. Photochemical reactions

Irradiation at 280 nm was performed with a deep-UV irradiation system (Optical Associates Inc., model 780) equipped with a 280 nm interference filter. The incident light intensity was measured with a radiometer which had been calibrated against ferrioxalate. Direct irradiation of perylene at 428 or 439 nm was achieved with an SLM 4800S spectrofluorometer. Light from the 450 W xenon lamp was passed through a grating monochromator such that a 16 nm wide band of light centered at 428 or 439 nm impinged on the sample. Irradiation with solar-simulated light was performed with a "home-built" apparatus with a 275 W sunlamp and a 500 W mercury discharge/tungsten filament industrial lamp [16] or a Sciencetech 5511-01 solar simulator with a 1000 W xenon lamp equipped with air mass 1.5 (AM 1.5) filters. Solutions were bubbled with oxygen prior to or during irradiation. The rate of photo-oxidation was determined by monitoring changes in the UV, fluorescence or GC of the solution.

2.5. Product analysis [4,17]

The products of perylene photo-oxidation were purified by thin layer chromatography (TLC) or column chromatography (silica with $CHCl_3$–acetone (19 : 1) (A) or $CHCl_3$–hexanes–acetone (6 : 3 : 1) (B)). The reaction mixture from the irradiation of perylene–dicyanobenzene in CH_3CN contained several products. Two major products were isolated and identified on the basis of their UV and mass spectral data [4,17]. 1,2-Perylenequinone ($R_f = 0.71$ (solvent A) or 0.63 (solvent B) exhibited the following spectral data: UV (λ (nm) in methanol): 320 (shoulder), 334, 360, 440; mass spectrum (electron impact (EI)): 282 (M^+), 254 ($M^+ - CO$), 226 ($M^+ - 2CO$). 3,10-Perylenequinone ($R_f = 0.52$ (solvent A) or 0.50 (solvent B)) exhibited the following spectral data: UV (λ (nm) in methanol): 306, 318, 335 (shoulder), 350; mass spectrum (EI): 282 (M^+), 254 ($M^+ - CO$), 226 ($M^+ - 2CO$).

3. Results and discussion

3.1. Solubilization

Perylene was dissolved in aqueous solutions of phenyl- (PSSS–S), naphthyl- (PSSS–VN), phenanthryl- (PSSS–VPh) or carbazolyl-containing (PSSS–AHCz) polymers. The observation of intense perylene fluorescence and efficient energy transfer from the polymer chromophores to perylene revealed that perylene was solubilized within the polymer [4,5]. If the aqueous polymer solution is treated as two phases

Table 1

Partition coefficients for PSSS–VN–water and octanol–water systems

Compound	log K_{ow}^a	log K_{pw}
Anthracene	4.54	4.99
9-Me-anthracene	5.07	4.68
9,10-diMe-anthracene	5.25	4.90
Perylene	6.50	6.56
Hexachlorobenzene	5.50	5.3

[a]Refs. [18,24].

(polymer–water), the partition coefficient can be defined as shown in Eq. (1)

$$K_{pw} = \frac{\chi_p}{\chi_w} \tag{1}$$

where χ_p and χ_w are the weight fractions of perylene in the polymer and water phases respectively. 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) [18]. The partition coefficient K_{pw} was found to vary in the range (1–4) $\times 10^6$ for the four polymers.

A strong relationship between the partition coefficient for surfactant–water systems and the octanol–water partition coefficient has been noted [19–22]. Solubilization data previously measured for PAHs [5] and hexachlorobenzene [23] in PSSS–VN are compared with K_{ow} in Table 1. A good correlation between K_{pw} and K_{ow} is seen for these compounds. Thus the K_{ow} values found in the literature [18,24] may serve as good indicators of K_{pw} for other hydrophobic compounds.

3.2. Photo-oxidation

The aqueous perylene–polymer solutions were saturated with oxygen and then irradiated with simulated sunlight (intensity of approximately one sun [16]). The rate of reaction was determined by measuring the changes in the intensity of perylene fluorescence with irradiation time (Table 2). The products of perylene oxidation are non-fluorescent. The decay of perylene fluorescence was found to obey first-order kinetics.

Although perylene photo-oxidation occurs in photozyme solution, no reaction was detected during irradiation in benzene. Perylene photo-oxidation in photozyme solution has been proposed to occur by reaction with $^1O_2$, with $^1O_2$ production sensitized by the polymer chromophores [4]. In this case, it might be expected that perylene photo-oxidation would be slowest in PSSS–S, since there is little or no overlap between its absorption spectrum and the solar spectrum or that of the lamps. However, perylene photo-oxidation occurs at similar rates in all four photozymes (Table 2).

The photocatalytic efficiencies of perylene photo-oxidation in the four photozyme polymers were measured. With irradiation at 280 nm, most of the light is absorbed by the polymer chromophores. The concentrations of perylene

Table 2

Photo-oxidation of perylene with artificial sunlight[a]

Photozyme[b]	Relative rate
PSSS–(77% VPh)	2.2
PSSS–(60% VN)	1
PSSS–(44% AHCz)	1.3
PSSS–(60% S)	1
Benzene	Not detected

[a]Solar simulator [16] with intensity approximately equal to one sun. [Perylene] $= 10^{-6}$ M. [b]0.1 g l^{-1} polymer in water.

Table 3

Photo-oxidation: comparison of photozymes[a]

Photozyme	Polymer concentration (g l^{-1})	Perylene concentration (M)	Quantum efficiency
PSSS–(77% VPh)	0.01	4.0×10^{-8}	1.0×10^{-4}
PSSS–(60% VN)	0.03	1.2×10^{-7}	1.4×10^{-4}
PSSS–(44% AHCz)	0.03	3.2×10^{-8}	1.4×10^{-4}
PSSS–(60% S)	0.10	2.3×10^{-7}	2.5×10^{-3}

[a]Irradiation at 280 nm.

before and during irradiation were determined by monitoring the intensity of perylene fluorescence. In each case, the rate of disappearance of perylene fluorescence was found to be first order in perylene. The apparent quantum efficiencies of perylene photo-oxidation in the four photozymes are summarized in Table 3.

The quantum efficiency of polymer-sensitized perylene photo-oxidation is a combination of the efficiencies of several steps: (1) energy migration in the polymer; (2) energy transfer from the polymer chromophore to perylene or oxygen producing a reactive intermediate; (3) diffusion of the reactants; (4) reaction of the PAH with oxygen, where one or both exist as reactive intermediates (i.e. excited state, radical ion). Although the efficiency is low, the number of photons absorbed is high, such that the overall rate of photo-oxidation is rapid.

All four photozymes are efficient photocatalysts for the oxidation of perylene at 280 nm. The most surprising result is that, once again, PSSS–S displays better photocatalysis than expected.

3.3. Mechanism of perylene photo-oxidation

White and coworkers [4,5] have shown that perylene is oxidized when irradiated in aqueous PSSS–VN solution. The major products of photo-oxidation are perylenequinones (Scheme 2), which are difficult to produce by conventional synthetic routes [17].

White and coworkers proposed that the quenching of excited naphthalene by oxygen produces singlet oxygen ($^1O_2$) which then reacts with perylene. Reaction with $^1O_2$ was postulated, since naphthalene is known to sensitize the formation of $^1O_2$ and products typical of $^1O_2$ reactions are
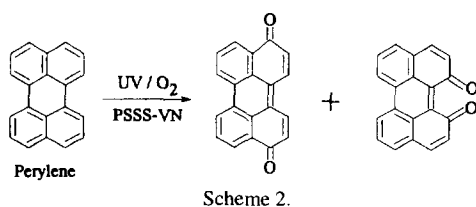
Scheme 2.

Table 4
Rate of perylene photo-oxidation on irradiation with simulated sunlight[a,b]

Sensitizer (concentration)	Conditions	Relative rate
None	Sunlight, CH_3CN	1
Rose bengal (10^{-4} M)	Sunlight, CH_3CN	0.6
Phenanthrene (10^{-4} M)	Sunlight, CH_3CN	1
Dicyanobenzene (10^{-4} M)	Sunlight, CH_3CN	4

[a]Irradiation with 1000 W Xe lamp (AM 1.5 filters).
[b][Perylene] $= 3 \times 10^{-5}$ M.

observed when substrates such as anthryl compounds [5] or 1,3-diphenylisobenzofuran [25] are oxidized in photozyme solution. However, perylene is also a $^1O_2$ sensitizer [13], and thus a significant degree of photo-oxidation may be expected on direct irradiation if reaction with $^1O_2$ is important. Thus the mechanism of the photo-oxidation remains uncertain. Identification of the mechanism may allow the design of more efficient photocatalysts for the photodegradation of this and other PAHs.

UV spectroscopy was used to monitor the rate of disappearance of perylene when irradiated in the presence of several potential sensitizers (Table 4). Irradiation of an acetonitrile solution of perylene with simulated sunlight caused very slow oxidation. When rose bengal, a $^1O_2$ sensitizer, was added to the solution, the rate of photo-oxidation decreased. Indeed, the UV spectrum revealed that rose bengal was consumed more quickly than perylene during irradiation. Phenanthrene, a model chromophore for the PSSS–VPh photozyme, had no effect on the rate of perylene photo-oxidation. However, in the presence of dicyanobenzene, an electron acceptor, the rate of perylene photo-oxidation increased. It should be noted that dicyanobenzene is not a true sensitizer since it absorbs little or no light during irradiation. Thus the energy used to drive perylene oxidation in this case was absorbed by perylene.

A similar observation was made by Kitamura and Tazuke [26,27] during photoinduced charge transfer studies. Perylene was used as a cosensitizer to mediate electron transfer from dicyanobenzene to a leuco derivative or vinylcarbazole. In the absence of the leuco derivative or vinylcarbazole, perylene was consumed during irradiation. They also found that the rate of perylene disappearance was solvent sensitive, i.e. rapid in acetone, moderate in N,N-dimethylformamide (DMF) and DMSO, but slow in THF [26].

If dicyanobenzene acts as a catalyst and mediates electron transfer between perylene and oxygen leading to oxidation, the concentration of dicyanobenzene should not change during irradiation. An acetonitrile solution of perylene and dicy-
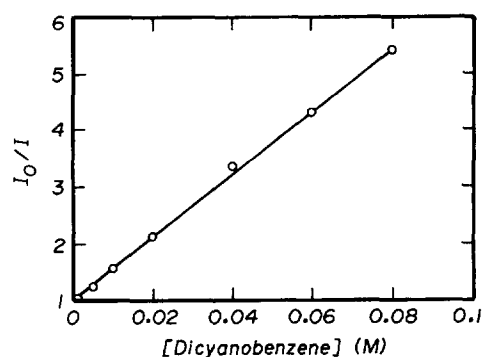
Fig. 1. Stern–Volmer plot for quenching of perylene fluorescence by dicyanobenzene. [Perylene] $= 1 \times 10^{-6}$ M.

anobenzene (2×10^{-4} M in both) was analyzed by GC and TLC after irradiation for 1 h with 350–450 nm light from a 1 kW Xe lamp. Although about 80% of the perylene was consumed, the concentration of dicyanobenzene remained unchanged. TLC analysis revealed the same principal photoproducts as obtained by photo-oxidation in the photozyme solutions [4]. Thus dicyanobenzene acts as a catalyst, and product analysis indicates that a similar process may be occurring in both perylene–dicyanobenzene and perylene–photozyme systems.

A fluorescence quenching experiment confirmed that dicyanobenzene interacts with excited perylene. Perylene fluorescence was effectively quenched by dicyanobenzene. These results are displayed in the form of a Stern–Volmer plot (Fig. 1). The plot is based on the Stern–Volmer equation (Eq. (2)) for quenching kinetics

$$\frac{I_0}{I} = 1 + k_q \tau_f [Q] \qquad (2)$$

where I_0 is the fluorescence intensity in the absence of quencher, k_q is the bimolecular rate constant for quenching, τ_f is the fluorescence lifetime of perylene and [Q] is the concentration of the quencher. Since the plot has a slope of $k_q \tau_f = 55.5$ M^{-1} and $\tau_f = 6$ ns for perylene [28], the rate constant for quenching is $k_q = 9 \times 10^9$ M^{-1} s^{-1}. This value is about half the diffusion-controlled rate for bimolecular reactions in acetonitrile ($k_{dif} = 2 \times 10^{10}$ M^{-1} s^{-1} at 25 °C), and means that half of the encounters between excited perylene and dicyanobenzene lead to quenching. With the dicyanobenzene concentration used in the earlier experiment (Table 4), less than 1% of the excited perylene molecules will encounter dicyanobenzene during their lifetime. This explains the rather moderate rate enhancement.

If a similar process occurs during photo-oxidation in photozyme solution, it may be possible to drive the reaction with light which excites perylene and not the chromophores of the polymer. A reaction of this type might explain the anomalous results for perylene photo-oxidation in PSSS–S: perylene photo-oxidation is equally rapid in this photozyme as in the photozymes with a much stronger overlap with simulated sunlight. If direct excitation of perylene is an important path-
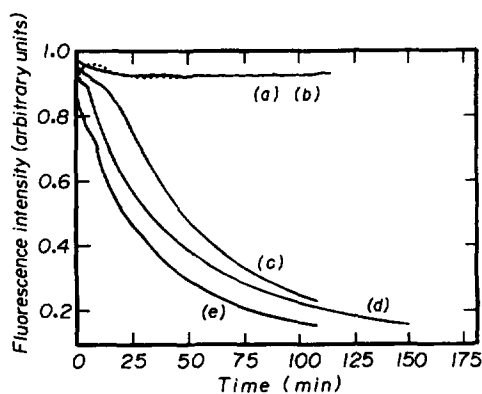
Fig. 2. Intensity of perylene fluorescence vs. irradiation time in CH_3CN (a), benzene with dimethyl terephthalate (0.012 M) (b), CH_3CN with dicyanobenzene (0.010 M) (c), CH_3CN with dimethyl terephthalate (0.012 M) (d) and H_2O with PSSS–VN (1.02 g l^{-1}) (e). Irradiation with 16 nm wide band centered at 428 nm for (a)–(d) and 439 nm for (e).

Table 5

Rate of perylene photo-oxidation in the presence of electron acceptors on direct irradiation of perylene[a,b]

Acceptor (concentration)	Conditions	Relative rate
None	428 nm, CH_3CN	≤ 1
Terephthalate (10^{-2} M)	428 nm, benzene	≤ 1
Terephthalate (10^{-2} M)	428 nm, CH_3CN	637
Dicyanobenzene (10^{-2} M)	428 nm, CH_3CN	550
PSSS–VN (1.02 g l^{-1})[c]	439 nm, H_2O	858

[a]Irradiation in spectrofluorometer with 16 nm wide band of light centered at wavelength noted.
[b][Perylene] = 1.2×10^{-6} M.
[c]The concentrations of naphthyl and benzenesulfonate groups are 3×10^{-3} M and 2×10^{-3} M respectively.

way for photo-oxidation, similar rates of reaction may be expected for the different photozymes.

The grating monochromator of a spectrofluorometer was used to achieve a narrow band of light which was absorbed only by perylene. Irradiations were carried out in the presence of electron acceptors and the naphthalene-containing photozyme PSSS–VN. The changes in perylene fluorescence are displayed in Fig. 2 and summarized in Table 5. In the presence of dimethyl terephthalate, dicyanobenzene and PSSS–VN, the rate of photo-oxidation is at least 550 times faster than that observed during irradiation of perylene alone. It should be noted that the concentration of the small-molecule sensitizers is 100 times higher than for the experiments in Table 4 and the rate acceleration is also much higher.

As expected, the efficiency of the reaction is sensitive to the polarity of the solvent. Photo-oxidation in the perylene–terephthalate system is rapid in acetonitrile ($\epsilon = 38$) but undetected in benzene ($\epsilon = 2.3$). Non-polar solvents, such as benzene, are poor solvents for radical ions. Thus ion pairs, if formed at all, are likely to remain in close contact and back electron transfer will be the principal reaction.

It is possible to calculate the energetics of photoinduced electron transfer and determine in which systems perylene

photo-oxidation will be observed [11,29]. The reaction of interest is the electron transfer between excited perylene and an acceptor

$$P^* + A \rightarrow P^{\cdot +} + A^{\cdot -}$$
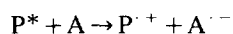
The free energy of this reaction is given by Eq. (3)

$$\Delta G_{eT} = -E(P^{\cdot +}/P^*) + E(A/A^{\cdot -}) \tag{3}$$

where $E(P^{\cdot +}/P^*)$ is the oxidation potential of excited perylene and $E(A/A^{\cdot -})$ is the reduction potential of the acceptor. The oxidation potential of excited perylene can be expressed in the more easily obtained values of E^*, the excited state energy, and $E(P^{\cdot +}/P)$, the oxidation potential of ground state perylene

$$E(P^{\cdot +}/P^*) = E^* - E(P^{\cdot +}/P)$$

Substitution in Eq. (3) leads to the Rehm–Weller equation (Eq. (4))

$$\Delta G_{eT} = -E^* + E(P^{\cdot +}/P) - E(A/A^{\cdot -}) - C \tag{4}$$

where C, an electrostatic term, is typically 0.1 eV or less in polar solvents.

The Rehm–Weller equation was used to calculate the energetics of electron transfer from excited perylene ($E^* = 2.85$ eV; $E(P^{\cdot +}/P) = 0.85$ eV) [11] to a variety of acceptors. The polymer will provide mainly naphthalene and benzenesulfonate groups as possible acceptors; however, neither of these groups can be considered as a strong electron acceptor. In addition to these groups, there may be smaller concentrations of naphthoquinone, as a result of naphthalene oxidation, and benzenesulfonic acid. As presented in Table 6, electron transfer from perylene to dicyanobenzene, terephthalate, naphthoquinone and toluenesulfonic acid is calculated to be exothermic.

Toluenesulfonic acid was used as a model compound to test whether the benzenesulfonic acid groups of the photozyme might act as electron acceptors during perylene photo-oxidation. Conditions similar to those described in Table 5 were used. In the presence of toluenesulfonic acid (0.01 M), irradiation at 429 nm caused no detectable perylene photo-oxidation in either methanol or acetonitrile.

The styrenesulfonic acid groups of the polymer may play a role during perylene photo-oxidation in photozyme solu-

Table 6

Energetics for electron transfer from perylene to various acceptors as calculated by the Rehm–Weller equation (Eq. (4))[a]

Acceptor	$E(A/A^{\cdot -})$ (eV)[b]	ΔG_{eT} (eV)
Dicyanobenzene	-1.60	-0.5
Dimethyl terephthalate	-1.74	-0.36
Naphthalene	-2.29	$+0.2$
1,4-Naphthoquinone	-0.69	-1.3
Toluenesulfonic acid	-0.9	-1.2

[a]For perylene, $E^* = 2.85$ eV and $E(P^{\cdot +}/P) = 0.85$ eV [11].
[b]From Refs. [11,30].

tions. Investigations of electron transfer reactions in polymers have revealed several important effects exerted by polymers on these reactions. Neighboring groups on a polymer backbone can have a pronounced stabilizing effect on radical ions bound to the polymer [31–33]. Electron transfer reactions which do not occur for small molecules in solution are observed if either the acceptor or donor is bound to the polymer. It has been postulated that sandwich complexes between the radical ion and neighboring group(s) are responsible for the stabilizing effect. The formation of the complex, analogous to an excimer or exciplex, leads to a sharing of the charge between two or more groups and to stabilizations of 10 kcal mol^{-1} or more [31–33]. Thus electron transfer to the styrenesulfonic acid group may occur in polymer solutions, but not in the small-molecule model experiments.

Charged polymers (polyelectrolytes) can have a pronounced effect on electron transfer reactions. Electrostatic forces between the charges on the polymer and the radical ions can cause efficient separation of the ion pair [34–36]. If the ions are well separated, back electron transfer, an energy wasting process, is less likely. Thus perylene oxidation by a photoinduced electron transfer mechanism may be facilitated by both stabilization of one of the radical ions and efficient charge separation.

Functional groups introduced as a result of polymer oxidation are another potential source of electron acceptors in the polymer. This possibility was evaluated for the naphthyl-containing polymer PSSS–VN. If polymer oxidation results in the formation of naphthoquinone groups, it may be possible to detect these groups. Indeed, during the irradiation of an oxygenated aqueous PSSS–VN solution, the intensity of naphthyl fluorescence decreased rapidly (Fig. 3). The oxidized polymer proved difficult to analyze for the presence of naphthoquinone groups. Although the intensity of polymer fluorescence decreased by 70% following 3 min of irradiation, the UV spectrum was essentially unchanged (Fig. 4). Similarly, no change was detected in the IR spectrum of the photo-oxidized polymer. This indicates that oxidation causes a minor structural change, perhaps as little as one new group per chain, but a change that efficiently quenches the naphthyl fluorescence of PSSS–VN. This is not surprising since a sin-
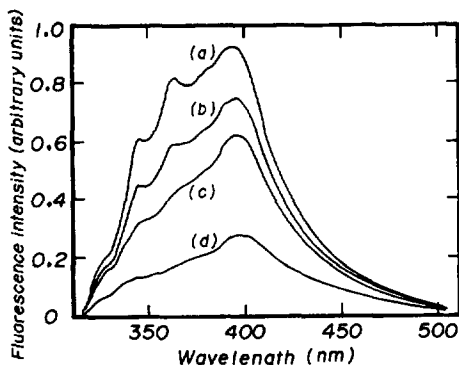

Fig. 4. UV spectrum of PSSS–VN (0.21 g l^{-1}) before (———) and after (· · ·) irradiation in a Rayonet photoreactor (300 nm lamps) for 3 min.
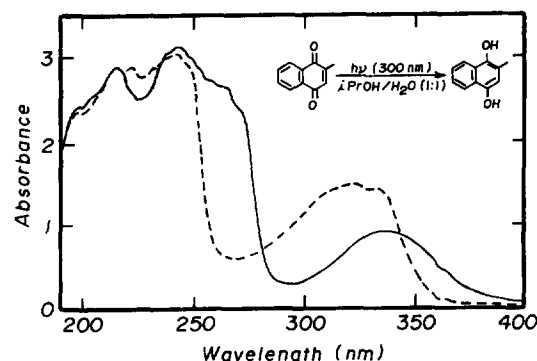
Fig. 5. UV spectrum of 2-methylnaphthoquinone (3 × 10^{-4} M) in degassed 50% isopropanol before (———) and after (– – –) irradiation in a Rayonet photoreactor (300 nm lamps).

gle energy trap on the polymer backbone can efficiently quench naphthalene fluorescence because of energy migration [37–40].

Fluorescence techniques can be used to confirm the presence of naphthoquinone if the quinone is first converted to its hydroquinone, which is fluorescent. Naphthoquinone may be reduced to naphthohydroquinone by either chemical or photochemical means. The behavior of a model compound, 2-methylnaphthoquinone, was investigated. Irradiation of an isopropanol–water solution of naphthoquinone, in the absence of oxygen, resulted in the formation of naphthohydroquinone (Fig. 5). Naphthohydroquinone proved to be fluorescent with a maximum emission at approximately 410 nm (Fig. 6).

Following the photoreduction of oxidized PSSS–VN in oxygen-free isopropanol–water, a strong emission spectrum ($\lambda_{max} = 400$ nm) was observed (Fig. 6). With $\lambda_{ex} = 346$ nm, the naphthyl groups of PSSS–VN do not absorb light, and the fluorescence stems from another species, presumably naphthohydroquinone. It appears that photo-oxidized PSSS–VN contains naphthoquinone groups, and it may be these groups which serve as electron acceptors during perylene oxidation by photoinduced electron transfer.

The experiments described in this section have led us to propose the reaction mechanism shown in Scheme 3 to explain perylene photo-oxidation in the photozymes. Excited perylene may be produced by direct excitation or by energy

Fig. 3. Naphthyl fluorescence from PSSS–VN (0.21 g l^{-1}) following irradiation in a Rayonet photoreactor (300 nm lamps) for zero time (a), 15 s (b), 1 min (c) and 3 min (d). $\lambda_{ex} = 300$ nm.
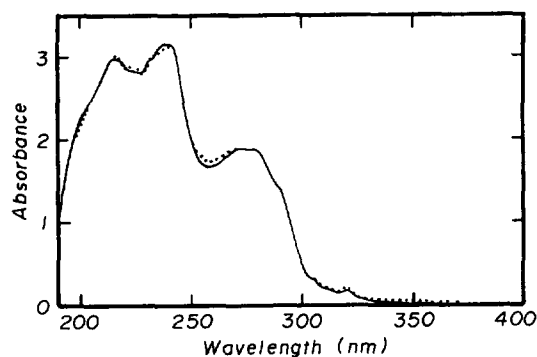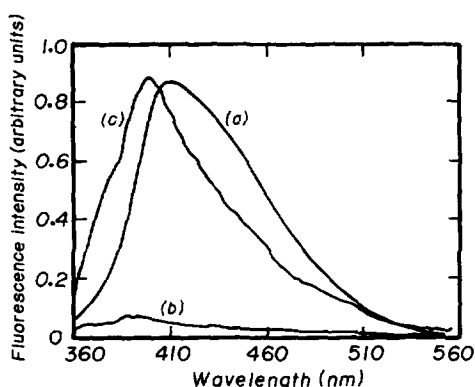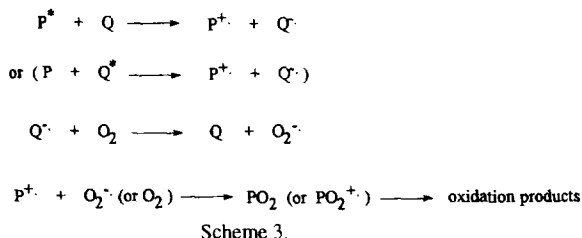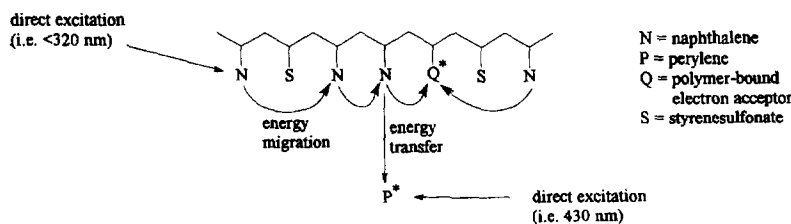
Scheme 3.

Fig. 6. Fluorescence spectra in 50% isopropanol: (a) 2-methylnaphthohy-droquinone; (b) oxidized PSSS–VN $(0.1\ g\ l^{-1})$ before photoreduction; (c) oxidized PSSS–VN $(0.1\ g\ l^{-1})$ after photoreduction. $\lambda_{ex} = 346$ nm.

transfer from the chromophores of the photozyme. Electron transfer from excited perylene to an acceptor within the polymer produces the perylene radical cation. The radical cation may react with ground state oxygen or a superoxide anion produced by the reaction of oxygen with the radical anion.

If this is the mechanism for perylene, and perhaps other, oxidations, it may be possible to design polymers which are more suited to this task. Copolymerization of a small concentration of electron acceptor with the regular photozyme monomers may produce polymers which exhibit better photocatalysis.

Acknowledgements

References

[1] M. Nowakowska, B. White and J.E. Guillet, Macromolecules, 22 (1989) 3903.

[2] M. Nowakowska, B. White, S. Vogt and J.E. Guillet, J. Polym. Sci., Polym. Chem., 30 (1992) 271.

[3] M. Nowakowska, B. White and J.E. Guillet, Macromolecules, 23 (1990) 3375.

[4] B. White, M. Nowakowska and J.E. Guillet, J. Photochem. Photobiol. A: Chem., 50 (1989) 147.

[5] M. Nowakowska, B. White and J.E. Guillet, Macromolecules, 22 (1989) 2317.

[6] E. Sustar, M. Nowakowska and J.E. Guillet, J. Photochem. Photobiol. A: Chem., 53 (1990) 233. M. Nowakowska, E. Sustar and J.E. Guillet, J. Am. Chem. Soc., 113 (1991) 253.

[7] M. Nowakowska and J.E. Guillet, Macromolecules, 24 (1991) 474.

[8] M. Nowakowska, B. White and J.E. Guillet, Macromolecules, 21 (1988) 3430.

[9] M. Nowakowska, V.P. Foyle and J.E. Guillet, J. Am. Chem. Soc., 115 (1993) 5975.

[10] A. Gilbert and J. Baggott, Essentials of Molecular Photochemistry, Blackwell Scientific, London, 1991, Chapter 11.

[11] G.J. Kavarnos and N.J. Turro, Chem. Rev., 86 (1986) 401.

[12] M. Julliard, A. Galadi and M. Chanon, J. Photochem. Photobiol. A: Chem., 54 (1990) 79.

[13] B. Stevens and J.A. Ors, U.S. Natl. Bur. Stand., Spec. Publ., 526 (1978) 66.

[14] J. Moselhy and J.E. Guillet, unpublished results, 1990.

[15] A. Linde and J.E. Guillet, unpublished results, 1990.

[16] V.P. Foyle and J.E. Guillet, Rev. Sci. Instrum., 61 (1990) 3421.

[17] A.J. Fatiadi, J. Res. Natl. Bur. Stand., Sect. A, 72 (1968) 39.

[18] M.M. Miller, S.P. Wasik, G.-L. Huang, W.Y. Shiu and D. Mackay, Environ. Sci. Technol., 19 (1985) 522.

[19] W.R. Haulbrook, J.L. Feerer, T.A. Hatton, J.W. Tester, Environ. Sci. Technol., 27 (1993) 2783.

[20] D.A. Edwards, R.G. Luthy and Z. Liu, Environ. Sci. Technol., 25 (1991) 127.

[21] P.N. Hurter and T.A. Hatton, Langmuir, 8 (1992) 1291.

[22] X. Wang and M.L. Brusseau, Environ. Sci. Technol., 27 (1993) 2821.

[23] N.A.D. Burke and J.E. Guillet, unpublished results, 1992.

[24] C.T. Chiou, Environ. Sci. Technol., 19 (1985) 57.

[25] M. Nowakowska and J.E. Guillet, Acta Chim. Univ. Jagiellon, 34 (1991) 37.

[26] N. Kitamura and S. Tazuke, Bull. Chem. Soc. Jpn., 53 (1980) 2594.

[27] N. Kitamura and S. Tazuke, Bull. Chem. Soc. Jpn., 53 (1980) 2598.

[28] S.L. Murov, I. Carmichael and G.L. Hug, Handbook of Photochemistry, Marcel Dekker, New York, 2nd edn., 1993, p. 37.

[29] D. Rehm and A. Weller, Isr. J. Chem., 8 (1970) 259.

[30] L. Meites and P. Zuman, Electrochemical Data, Wiley, Toronto, 1974.

[31] Y. Tsujii, A. Tsuchida, S. Ito and M. Yamamoto, *Macromolecules, 24* (1991) 4061.

[32] A. Tsuchida, N. Masuda, M. Yamamoto and Y. Nishijima, *Macromolecules, 19* (1986) 1299.

[33] Y. Tsujii, A. Tsuchida, M. Yamamoto and Y. Nishijima, *Macromolecules, 21* (1988) 665.

[34] Y. Morishima, *Adv. Polym. Sci., 104* (1992) 51.

[35] Y. Morishima, *Prog. Polym. Sci., 15* (1990) 949.

[36] Y. Morishima and S. Nozakura, *J. Polym. Sci., Polym. Symp., 74* (1986) 1.

[37] J.E. Guillet, *Polymer Photophysics and Photochemistry*, Cambridge University Press, Cambridge, 1985, Chapter 9.

[38] J.S. Aspler, C.E. Hoyle and J.E. Guillet, *Macromolecules, 11* (1978) 925.

[39] D.A. Holden and J.E. Guillet, *Macromolecules, 13* (1980) 289.

[40] D. Ng and J.E. Guillet, *Macromolecules, 15* (1982) 724.