Overview:

The underlying concept of this research is depicted in reactions 1-6 in the following which is taken with some modification from publication no. 7 of the DoE-sponsored publication list, page 8.

The transduction of light into chemical potential has been actively studied via a variety of mechanisms. Perhaps the most actively pursued approach is via photoredox chemistry, which may be generically represented by the following:

\[
D + hv \rightarrow 2S+1D^* \tag{1}
\]

\[
2S+1D^* \xrightarrow{k_0} D + \text{heat} \tag{2a}
\]

\[
2S+1D^* + A \xrightarrow{k_q} 2S+1[D^{**}, A^{-*}] \tag{2b}
\]

\[
2S+1[D^{**}, A^{-*}] \xrightarrow{k_{cs}} D^{**} + A^{-*} \tag{3a}
\]

\[
\xrightarrow{k_b} D + A + \text{heat} \tag{3b}
\]

with a quantum yield of charge separation given by

\[
\phi_{cs} = \frac{k_{cs}}{k_{cs} + k_b}. \tag{4}
\]

The fraction of excited states quenched in step (2) is given by

\[
f_q = \frac{k_q[A]}{k_0 + k_q[A]} \tag{5}
\]

In step (2b) a geminate pair of ion-radicals is formed, and in (3a) they diffuse apart to form uncorrelated ion pairs that can participate in some useful redox chemistry. Useful chemistry must compete with the bulk recombination process

\[
D^{**} + A^{-*} \xrightarrow{k_{rec}} D + A + \text{heat} \tag{6}
\]

where \(k_{rec}\) is a typical second order rate constant. If \(D^{**}\) and \(A^{-*}\) remain in the same bulk phase then this process is expected to be facile. Step (6) should be distinguished from the geminate recombination in step (3b).

Optimization of this transduction requires the following:
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(1) Efficient production of the desired excited state $2S+1D^*$ at the wavelength(s) of interest, which is determined by the extinction coefficient, concentration of D, formation yield and lifetime of $2S+1D^*$. This obviously can be controlled only by the choice of chromophore, and to a lesser extent, the solvent and/or other environmental features.

(2) The excited state $2S+1D^*$ must be efficiently quenched, which depends on the excited state properties (through $k_0$ and the excited state redox potential) and the quencher (through the product $k_q[A]$), as expressed in eq.(5). Of course, the concentration $[A]$ represents the local concentration around the D moiety in the case of heterogeneous systems, such as studied in this project.

(3) The quantum yield of charge separation ($\phi_{cs}$ in eq.(4)) is perhaps the most critical bottleneck in light energy transduction, and is the step that has played a central role in our research. $\phi_{cs}$ depends on many properties such as the strength of interaction between $2S+1D^*$ and A, the energetics of the electron-transfer step, and solvation of the $2S+1[D^{+\bullet}, A^{-\bullet}]$ geminate pair or $D^{+\bullet} + A^{-\bullet}$ bulk solvent pair.

(4) A high $\phi_{cs}$ is not of any practical utility unless the $D^{+\bullet}$ and $A^{-\bullet}$ species live long enough to carry out useful chemistry. In our work (and that of many others) the species persist for long periods of time by chemical standards (i.e. milliseconds), but this is often because of the low overall bulk concentration of the ion-pairs, since $k_{rec}$ (eq.(6)) is usually diffusion limited. Therefore if one achieved a high density of ion-pairs it would be difficult to compete with the wasteful back reactions. Many investigators have approached this problem by phase separation of the ion-pair via membranes, vesicles, or surfactant micelles. In our research we have used hydrophobic polymer-water interfaces to accomplish this goal. This is illustrated in Scheme 1.
In all the work reviewed in the following the zwitterionic viologen, abbreviated SPV, was used as the quencher and electron acceptor (A in reactions 2-3).

\[
\text{SPV} = \begin{array}{c}
\text{O}_8\text{S}^+ \text{C}^+ \text{N}^+ \text{N}^+ \text{C}^- \text{SO}_3^- \\
\end{array}
\]

It is appropriate to review how this research has evolved over time. While a variety of aromatic chromophores has been studied, we summarize the results for various derivatives of anthracene, which have been most broadly investigated by us and which illustrates the major results.

Our first work used polymethacrylic acid (PMA) with a small mole fraction of copolymerized anthracene derivative (PMA-A). It was found that for the singlet state charge separation could be observed only for rather low pH ($< 3$), where PMA is known to be "hypercoiled". This led to the idea that some sort of "hydrophobic protection" of the chromophore is required for effective singlet state charge separation. While the precise nature of "hydrophobic protection" remains vague, we have always found that if there is appreciable static quenching $\phi_{cs}$ is low. For the triplet state charge separation is observed at high and low pH, consistent with the idea that geminate recombination to the ground state is spin-forbidden (see eq. (3b)). At high pH the negative charge density of the polyelectrolyte further encourages charge separation.

The next set of experiments was to adsorb these PMA-A polymers onto polystyrene (PS) latex particles (referred to as microspheres, abbreviated $\mu S$). Surprisingly, ca. 1 mol % of a covalently-bonded hydrophobic species to PMA greatly enhances adsorption. The charge separation in the singlet state was appreciable even at high pH, which was interpreted as the result of adsorption of the chromophore or the polystyrene surface, thereby providing the required hydrophobic protection. $\phi_{cs}$ for the triplet state was comparable to homogenous solution.

The PMA-A polymer has a random distribution of chromophores, and the next approach was to place the chromophore precisely at the end of a water soluble polymer. Polyethylene oxide was used (PEO-A), and this polymer also adsorbed onto PS latexes, with good singlet state charge separation. However this polymer also exhibited excellent singlet state charge separation in
homogenous solution. Thus it would seem that PEO mimics PMA at low pH with respect to hydrophobic protection (PEO is a well-known solubilizing agent for hydrophobic materials).

Our most recent work involves diblock polymers of polystyrene and polymethacrylic acid with either a single anthracene or a short anthracene block inserted between the blocks (denoted PS-A-PMA). These materials spontaneously self-assemble into micelles. It is expected that the anthracene moieties are located near the PS-H₂O interface, seems as though it should be an ideal morphology for hydrophobic protection. However it would seem that the hydrophobic protection is too good, such that it is difficult to quench these fluorophores. The pH effects on quenching are much smaller than for linear polymers and the charge separation quantum yield is disappointing (ca. 0.05, see Table 1). However, the lifetime of the ion pair is remarkable, longer than we can measure with the standard transient absorption apparatus (> 10 ms) and in fact steady-state irradiation can be used to build up a significant concentration of SPV⁻ anion radical. Furthermore the SPV⁻ is quenched by O₂ to a much smaller extent than in homogenous solution, presumably because it resides in the micelle corona region. This implies that the PMA corona is not deprotonated near the interface, even at pH 9. A great deal more remains to be done with these materials.² In all our current work we are emphasizing the interface between a hydrophobic polymer and water. The reasons for this may be summarized:

(1) A solar energy scheme based on thin polymer films in contact with an aqueous solution of reactant would have tremendous advantages for device construction and a very large range of polymers can be explored.

(2) We believe that the photophysical experiments and classical characterization we will carry out will provide unique insights to the behavior of polymers at solid and liquid interfaces, which is a very important scientific and technological problem in its own right.

All the information discussed above is compiled in Table 1 (p. 9) which provides a broad overview of our research on photoredox processes in polymers for the specific case of anthracene chromophores.

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Summary of Results

In the interest of space, we have not included a detailed discussion of the experimental results that was part of the publication used as the basis of the preceding material but we summarize these results here:

(1) Effect of Adsorbing Polymers onto Latex Particles: In general this permits the formation of charge separated pairs with a yield that is similar to a collapsed polyacid in homogeneous solution. This results was important because it represented the first example of using a polymer interface to provide "hydrophobic protection" for the chromophore.

(2) Use of Diblock Amphiphilic Polymers with Interfacial Chromophores

The polymers that were studied had anthracene as a chromophore (Scheme 2) and self-assemble into polymer micelles. The positioning of these chromophores is expected to be very close to the ideal structures in Scheme 1 and the yield of charge-separated ion-pairs was very good. However this system illustrated some of the complications that can arise in the use of interfacially-localized chromophores. First, relatively high concentrations of viologen were required to quench the excited singlet state. This is a result of the dense "polymer brush" that surrounds the polystyrene core (Scheme 3). Additionally the anthracene cation radical was not observed accompanying the formation of the viologen anion radical, except on the ps time scale. While there is loss of anthracene to photooxidation, the turnover number per anthracene is estimated to ca. 17. We have suggested that the acid groups located near the anthracene moiety were acting like a sacrificial reagent (e.g. irreversibly oxidized by the anthracene cation radical) but this was not proved. This work suggested that one would have to consider carefully the design of a polymer-water interface with respect to the chemical nature of charge bearing and protective groups. In previous work we have found that methacrylic acid groups in linear polyacids did not react with the anthracene cation radicals, while we suggest that this does happen in polymer micelle systems. This is one of the surprising results of this research project.
Evaluation of this Project from the Point of View of Solar Energy Conversion

This project clearly demonstrated that polymers and polymer interfaces can be designed to enhance photoredox reactions that can be used in light energy transduction. The chromophores used in these studies are not suitable for solar energy conversion because they absorb in the ultraviolet part of the spectrum. Furthermore most organic chromophores are not sufficiently rugged to undergo the large number of photoredox cycles (ca. $10^8$) that one might wish for a practical system. This comment can be made for most chromophores studied in solar energy research. Organic materials have a huge advantage over transition metal systems such as Ru or Os with respect to toxicity and cost, not to mention the range of synthetic schemes that can be applied. We believe that the lessons learned from our work will be applicable to more suitable chromophores, which will certainly be larger if their absorption is to extend into the visible (an

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exception are the fullerenes, discussed below). Larger chromophores may disturb the polymer chain in their immediate vicinity and this factor may have to be taken into account in designing appropriate polymer-water interfaces.

In our research we did not attempt to close the photoredox cycle by using the "hole" (D**+) and "electron" (A**) to carry out a secondary chemical reaction. In principle this is straightforward but in practice it is quite demanding because one must avoid competing reactions that destroy these reactive intermediates. The use of "relay compounds" to accomplish this has been active pursued by other researchers and is a very difficult problem to solve satisfactorily.

A Fortuitous Discovery: Copolymerization of C_{60} and C_{70}

As part of a project involving a summer high school student, Dr. T. Cao discovered that C_{60} or C_{70} could be copolymerized with standard monomers such as styrene or methyl methacrylate. The adsorption spectrum of the attached fullerene was strongly modified, with a stronger absorption extending into the visible than for the parent fullerene itself. Preliminary studies of polystyrene-1,3C_{60}* indicated the lifetime of the excited state to be very short for both multiplicities, which is not favorable for charge separation. In one of these interesting coincidences that one sometimes encounters, two other groups observed similar copolymerizations about the same time. Over the past few years quite a few different approaches have been reported to incorporate fullerenes into polymers via free-radical polymerization.

As this project was being wrapped up at the time of this discover it was not considered appropriate to have a graduate student examine the photophysics of PS-C_{60} in any detail. This is know to be a complex system that depends on the number of substitutions on C_{60} and their proximity on the C_{60} surface.
Publications Based on DoE-Sponsored Research:
8.) "Free Radical Copolymerization of Styrene and C60", T. Cao and S. E. Webber Macromolecules 29, 3826 (1996)

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Table 1: Charge separation yields ($\phi_{cs}$) (±10% est. error) (using SPV as acceptor)

<table>
<thead>
<tr>
<th>system</th>
<th>pH</th>
<th>$\phi_{cs}$</th>
<th>comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMA-1A*(aq.soln)$^a$</td>
<td>2.8</td>
<td>0.21</td>
<td>original polyelectrolyte work, illustrates effect of &quot;hydrophobic protection&quot;</td>
</tr>
<tr>
<td>ditto</td>
<td>11</td>
<td>ca.0.05</td>
<td></td>
</tr>
<tr>
<td>PMA-3A*(aq.soln)$^b$</td>
<td>4</td>
<td>0.30</td>
<td>illustrates that the effect of spin on the back reaction can overcome lack of &quot;hydrophobic protection&quot;</td>
</tr>
<tr>
<td>ditto</td>
<td>11</td>
<td>0.89</td>
<td></td>
</tr>
<tr>
<td>PMA-1A*(µS)$^c$</td>
<td>4</td>
<td>0.64</td>
<td>illustrates that the µS provides &quot;hydrophobic protection&quot; even at high pH</td>
</tr>
<tr>
<td>ditto</td>
<td>11</td>
<td>0.39</td>
<td></td>
</tr>
<tr>
<td>PMA-3A*(µS)$^c$</td>
<td>4</td>
<td>0.24</td>
<td>combined &quot;hydrophobic protection&quot; and effect of spin</td>
</tr>
<tr>
<td>ditto</td>
<td>11</td>
<td>0.95</td>
<td></td>
</tr>
<tr>
<td>PEO-1A*(µS)$^d$</td>
<td>NA</td>
<td>0.32</td>
<td>another example of using latexes, only</td>
</tr>
<tr>
<td>PEO-3A*(µS)$^d$</td>
<td></td>
<td>0.60</td>
<td>now with end-tagged polymer</td>
</tr>
<tr>
<td>PEO-1A*(aq. soln)$^d$</td>
<td></td>
<td>0.29</td>
<td>PEO as hydrophobic protector in homogeneous solution</td>
</tr>
<tr>
<td>PS-1A*-PMA(micelle)$^e$</td>
<td>4-11</td>
<td>0.3-0.7+</td>
<td>first example of using polymer micelle as photoredox medium; only slight pH dependence; exceptionally long ion-pair lifetime</td>
</tr>
</tbody>
</table>


+ The precise yield depends on anthracene derivative and pH. The 2-anthryl chromophore had a consistently higher yield than 9,10 diphenyl anthracene and the best yield was usually near pH 6.
References


2 Publication no. 9 in the list of papers that resulted from DoE sponsored research, p. xx.


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