

DOE/ER/13629--5

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POLYMERS AT LIQUID-LIQUID INTERFACES:  
PHOTOPHYSICS AND PHOTOREDOX CHEMISTRY

Progress Report

JAN 15 1992

April 1, 1991 to March 31, 1992

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December 1991

PREPARED FOR THE U.S. DEPARTMENT OF ENERGY

UNDER GRANT NUMBER DE-FG05-86ER13629

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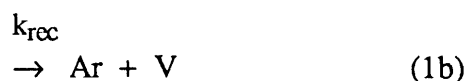
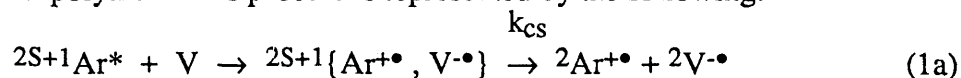
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Accomplishments during past year:

1. Study of Triplet State Electron Transfer from Polymer-Bound Anthracene and Pyrene Chromophores

Poly(methacrylic acid) polymers containing small mole fractions of anthracene and pyrene chromophores were studied during this period. The quenching of the triplet state of these species by the zwitterionic viologen 4,4'-bipyridino-1,1' bis (propane sulfonate) (referred to as SPV) leads to a quantum efficiency of charge separation ( $\phi_{ce}$ ) in the range of 0.2 to 1.0 depending on the pH and the particular polymer. This process is represented by the following:



with a charge separation quantum yield given by

$$\phi_{cs} = k_{cs} / (k_{cs} + k_{rec}). \quad (2)$$

In all cases the lifetime of the charge separated state was quite long, in excess of 2 ms. This data is briefly summarized below:

polymer	pH	$\phi_{ce}$ (est.)
PMA-Anthracene	4	0.3-0.5
	8.4	0.3-0.5
	11	0.8-1.0
PMA-Pyrene	4	0.8-0.9
	11	0.7-0.9

These two polymer systems are the same as studied previously for the singlet excited state in DoE sponsored work (J. Phys. Chem. **1988**, 92, 2934). In this earlier work the PMA-Pyrene polymers displayed no charge separation following singlet state quenching at any pH. For the PMA-Anthracene polymers  $\phi_{ce}$  was on the order of 0.3-0.4 at pH <3 but  $\phi_{ce}$  was less than .05 (the limit of detection) at higher pH values. These results were rationalized as the basis of different degrees of "hydrophobic protection" provided by the collapsed poly(methacrylic acid) coil. The recent triplet state results are consistent with that conjecture. A detailed consideration of the quenching kinetics implies that the pyrene moiety is more accessible to solution phase quenchers at low pH than anthracene. Thus relatively subtle changes in pendent chromophores evidently have a large effect on the local polymer structure.

A variety of different polymer systems containing pyrene were also examined. In general all triplet state quenching yields long-lived ion pairs with  $\phi_{ce}$  in the range 0.4 to 1.0.

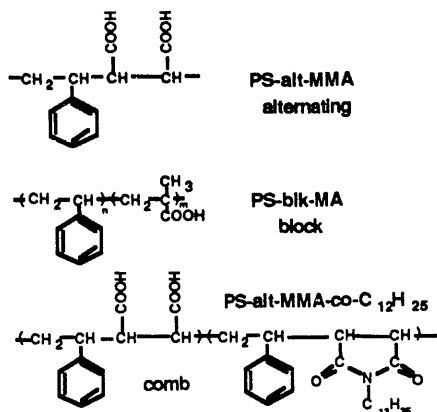
This work is described in the attached manuscript which has been accepted for publication in the Journal of Physical Chemistry.

In summary, we believe the new work, combined with our earlier DoE sponsored efforts, has demonstrated that chromophores bound to water soluble polymers provides a uniquely effective method of providing transduction of photon energy into chemical potential via reactive species that live long enough to participate in useful chemical reactions, without any "sacrificial reagents". A number of interesting polymer properties also have been elucidated by this work, especially the idea of the protection of a hydrophobic chromophore by an amphiphilic polymer and the utilization of a polyelectrolyte to enhance charge separation of ion-pairs. From the point of view of practical applications these materials suffer from the typical disadvantages of any homogeneous solution system: the concentration of reactants is fairly low, so that the converted energy density will tend to be low, although achieving reasonably high optical densities is not difficult. Follow up chemistry for the ion-pairs would have to be designed, which is compatible with the homogeneous solution phase. While this could be accomplished relatively easily for the  $SPV^{\bullet-}$  species by reaction with colloidal Pt to produce  $H_2$ , it is not so obvious what useful reactions could be accomplished with the aromatic cations radical (e.g. Anth $^{\bullet+}$  or Pyrene $^{\bullet+}$ ). We have chosen to examine self-assembling polymer-interfacial systems to accomplish these goals, but now that some of the polymer photophysical principles have been established one could equally well consider looking at different classes of polymer-bound chromophores.

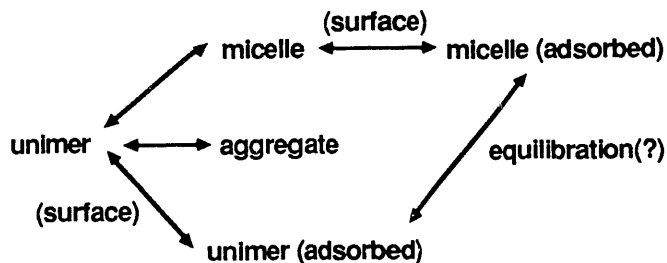
## 2. Adsorption of Alternating, Block and Comb Polymers onto Polymer Surfaces

Our new efforts center around the adsorption of amphiphilic polymers at a hydrophobic-water interface. Our first experiments centered on liquid-liquid interfaces but more recently we have examined polymer-water interfaces. Liquid-liquid interfaces are experimentally difficult to manipulate for the requisite optical experiments. Also the polymer systems we are studying tend to be good emulsifying agents, and emulsions are also difficult to work with (although see last section of this progress report). Films of polystyrene (PS), poly(methylmethacrylate) (PMMA) or polyethylene (PE) have many of the adsorption characteristics of the corresponding simple liquid and obviously are much more suitable for fabrication of devices.

Before we can carry out meaningful photophysical and photochemical experiments we must understand the adsorption properties of our polymers, and in so far as possible, the morphology of the adsorbed polymers. The types of polymers we have examined are indicated below:



In all these polymers some or all the phenyl groups may be replaced by aromatic chromophores, which is expected to modify the adsorption properties of the polymer. Likewise the molecular weight will affect the solution properties of the polymer. In all these polymer systems there is a tendency to undergo solution micellization and/or aggregation, which depends on the solvent composition as well as the molecular weight. Thus we have found the following generalized scheme to apply. (Unimer refers to a molecularly dissolved polymer and micelle refers to a micelle formed from polymers.)



Fortunately aggregates can be distinguished from micelles by light scattering and conditions can usually be found to avoid aggregation. There is no obvious way to distinguish the adsorption of micelles vs. unimers except by controlling the solvent conditions in such a way that the unimer-micelle equilibrium is shifted to favor one species. We have also found the solution pH to strongly affect the adsorption because of polymer-polymer repulsion and the effect of charge density on the average polymer conformation. In general we have found that deprotonation decreases adsorption, probably because of enhanced solubility of the polymers in the solution phase.

What we have found to date may be summarized as follows:

1) All these polymers adsorb on PS or PMMA films from H<sub>2</sub>O or H<sub>2</sub>O:dioxane solutions. The comb polymer adsorbs strongly to a PE film. The H<sub>2</sub>O contact angle ( $\theta_{H_2O}$ ) is lowered significantly, especially for the block or comb polymer. This implies that the acid groups extend away from the previously hydrophobic surface.

Polymers	Film	$\theta_{H_2O}^*$	adherence
PS-alt-MAA	PS	75-85°	poor
	PMMA	75-85°	poor
PS-blk-MA	PS	35-50°	excellent
PS-alt-MAA-co-C <sub>12</sub> H <sub>25</sub>	PE	20-30°	excellent

\* $\theta_{H_2O}$  on the unmodified film is >90°.

2) As is noted on the above Table, the adherence of the block and comb polymer to the film is excellent, with no change of  $\theta_{H_2O}$  with vigorous washing. This is not true of the alternating polymers for which  $\theta_{H_2O}$  returns to the original value for the polymer film with vigorous washing with water.

3) If vinylnaphthalene is substituted for styrene in PS-alt-MAA the adsorbed amount is decreased by ca. 30%. This could be the effect of molecular weight, since these naphthalene polymers have a lower molecular weight by a factor of ca. 3. For the PS-blk-MA polymers a small mole fraction of vinylnaphthalene can be co-polymerized at the styrene-methacrylic acid junction. It remains to be seen if a sufficiently high optical density at the surface can be achieved with this approach. In the comb polymer the "teeth" of the comb can also be polystyrene by the imidization of -NH<sub>2</sub> terminated PS, but this has not been accomplished as yet. Likewise chromophores can be added by an imidization reaction of H<sub>2</sub>N-(CH<sub>2</sub>)<sub>n</sub> chromophore.

### 3) Discussion of Transient Absorption Systems

In the previous progress report the setup of a gated 1420 PRA reticon system for transient spectroscopy was described. All the transient spectra described in the attached manuscript were obtained with this system. We have also added a new transient digitizer to this system (LeCroy 8828D, with a 5 ns/channel time resolution, and a LeCroy 6103 amplifier and trigger module). This will permit much more efficient signal averaging in addition to the elucidation of the kinetics on a faster time scale.

We have recently modified this system to permit diffuse reflectance transient spectroscopy. This is important for carrying out experiments on photoactive polymers adsorbed onto polymer beads or emulsions formed from amphiphilic polymers in octane:H<sub>2</sub>O. While the optimum operating conditions have not yet been established, we have been able to detect the triplet state of anthracene adsorbed on polystyrene microspheres from Polysciences.

#### Publications Listing

- \* 1. "Triplet State Electron Transfer in Poly(methacrylic acid) with Covalently Bound Phenanthracene and Naphthalene", J. Phys. Chem. **1991**, 95 960.
- \* 2. "Triplet State Electron Transfer from Anthracene and Pyrene Covalently Bound to Polyelectrolytes in Aqueous Solution", J. Phys. Chem. (in press).

\* removed and cycled separately -

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