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POLYMERS AT LIQUID-LIQUID INTERFACES:
PHOTOPHYSICS AND PHOTOREDOX CHEMISTRY

Progress Report

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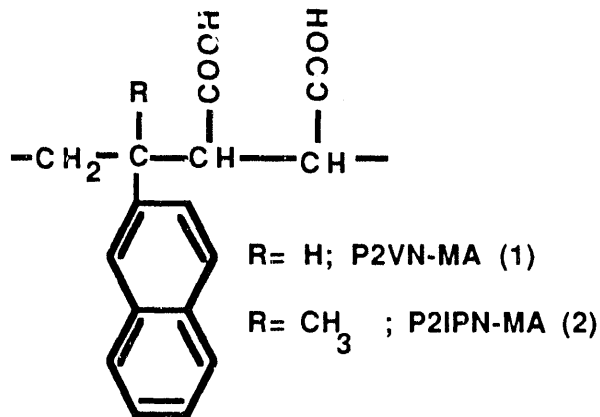
Accomplishments during past year:

1. Preparation of poly(styrene-alt-maleic acid-co-chromophore) polymers

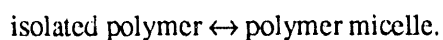
The original polymer types proposed for these studies, such as poly(2-vinylnaphthalene-alt-maleic acid), have proved to have complex photophysical and solution behavior (see next section). In order to simplify the polymer system a set of ternary copolymers were prepared. A feed of maleic anhydride and styrene was used that has been shown to yield a nearly perfectly alternating poly(styrene-maleic anhydride) polymer ¹. A small mole fraction of vinylphenanthrene, vinylpyrene, or vinyl-diphenylanthracene was added with the ultimate incorporation of ca. 0.1 - 0.05 mole %. These polymers were hydrolyzed to yield the maleic acid species and dialyzed. The molecular weights of these polymers turned out to be fairly high, ca. 100,000 according to GPC. The absorption and fluorescence properties of the chromophore were typical of the particular species. However it was found that the incorporation of these small mole fraction of hydrophobic pendent groups had a profound effect on the aqueous solution properties. In analogy to other amphiphilic polymer systems ², it seems like that these polymers tend to aggregate because of the inter- and intra-hydrophobic attraction. This suggests that it will be necessary to use surfactants to disperse such polymers before attempting to adsorb them at an organic-water liquid interface. A similar situation exists for the alternating vinylnaphthalene-maleic acid polymers, described next.

2. Studies of Vinylnaphthalene-maleic acid Polymers

The polymers studied are poly(2-isopropenylnaphthalene-alt-maleic acid) (P2IPN-MA, 1) and poly(2-vinylnaphthalene-alt-maleic acid) (P2VN-MA, 2).



These two polymers displayed significant aggregation in aqueous solution, which became more serious as the pH was lowered. This can be understood as the result of protonation of the acid groups with subsequent coiling of the polymer. Inelastic light scattering demonstrated a hydrodynamic radius of ca. 300-400 nm while classical light scattering yields a slightly smaller diameter of gyration. These sizes were similar at all pHs but the scattering intensity increases rapidly as the pH is lowered, implying that there exists an equilibrium



These results are consistent with the measurement of octane:H₂O interfacial surface tension (γ)³. While these measurements demonstrated that both P2VN-MA and P2IPN-MA are surface active, the concentration dependence of γ was consistent with that expected for a surfactant above its critical micelle concentration. Furthermore the value of γ depended slightly on the shear at the oil:water interface and was slow to respond to a change of shear. This suggests that the surface active species is a polymer micelle and that the surface activity can be modified by the rheology of the adsorbed polymer. As seems to be the case for the PS-alt-MA-co-chromophore polymers, it seems likely that some surfactant will be required to break up these aggregates in order to encourage adsorption at the organic:H₂O liquid-liquid interface. We regard understanding and modifying these polymer solution properties as one of the most important next steps of this research project.

In order to carry out some initial photophysical studies we studied the properties of these polymers as emulsifying agents for water:octane. In general fairly stable emulsions could be made. These emulsions usually consisted of three phases, a lower aqueous phase (from which polymer had been partially extracted), a middle macroemulsion with a water continuous phase, and an upper octane phase (the polymer is completely insoluble in octane). In some cases these emulsions are stable to storage at room temperature for weeks. Surprisingly the emulsifying ability of P2VN-MA and P2IPN-MA were quite different at high pH, where the latter did not form stable emulsions. We presume that this is the effect of the extra -CH₃ group (cf. **1** and **2**) since these two polymers have similar molecular weights, according to GPC measurements. At low pH most of the polymer resides in the middle macroemulsion phase.

Fluorescence studies revealed that the naphthalene fluorescence could be partially quenched by Cu^{+2} but was not quenched efficiently by CCl_4 . Since CCl_4 is expected to reside preferentially in the octane phase, this implies that a relatively small fraction of naphthalenes extend inside the octane. However the emulsions are difficult to work with and probably are not of practical interest to this project, so we are concentrating on polymer solution properties, as discussed in earlier paragraphs.

3. Assembly of Optical Fiber Reticon-based Transient Absorption System

As part of the permanent equipment of this grant a 1420 gated reticon system was purchased, upgrading our optical multichannel analyzer system. This system provides enhanced sensitivity in the red (see attached Xe spectrum) and ca. 100 ns time resolution from 350-850 nm in a single shot, although signal averaging is required for improved signal-to-noise ratio. An example spectrum is included. We hope that this extended spectral range will be particularly useful in detecting anion and cation radical formation.

A useful feature of this system is the use of an optical fiber bundle to collect the interrogation beam. This permits the interrogation beam to be attached to either the spectrograph-reticon system for spectral analysis, or to a monochromator for kinetic analysis of the OD at a single wavelength.

References

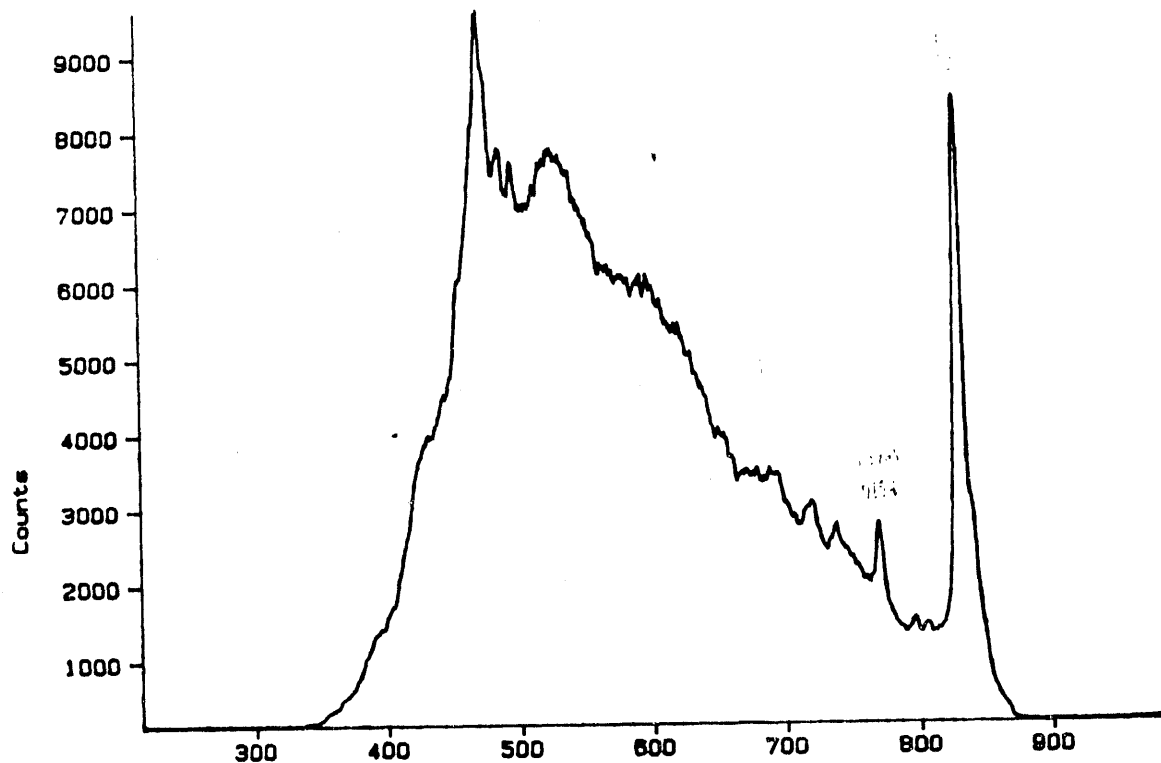
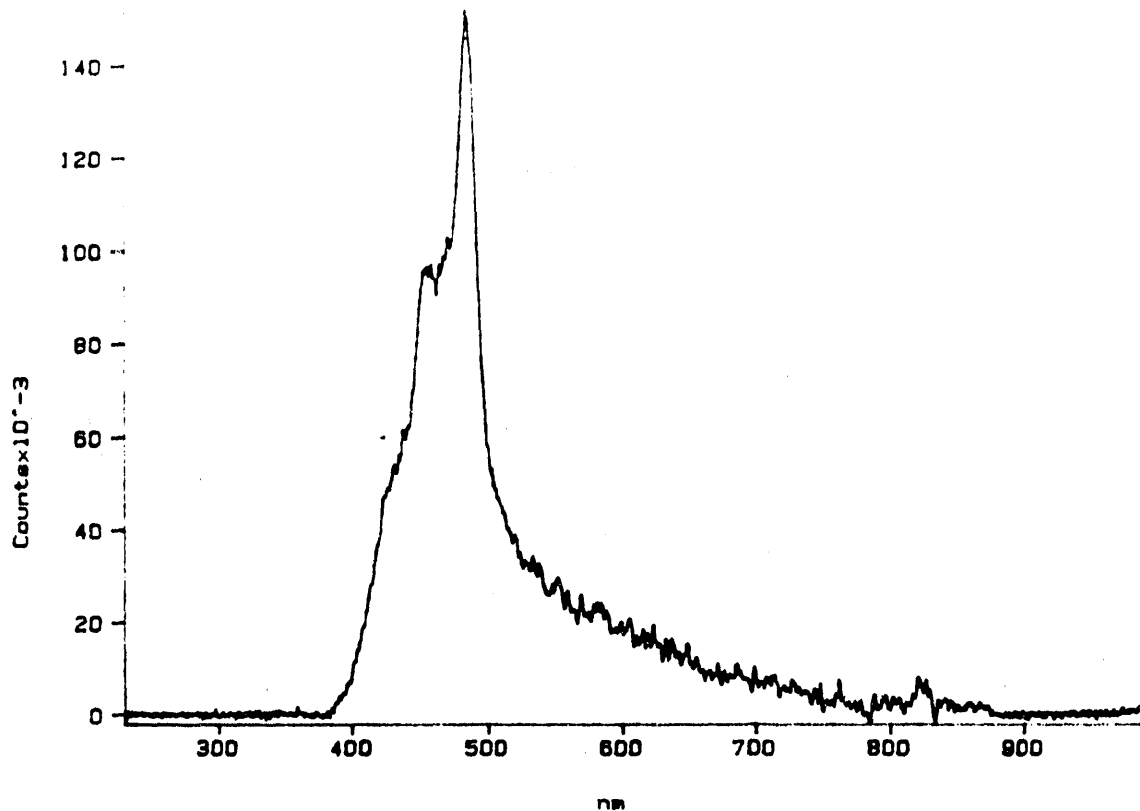
- ¹ Zeng, W.; Shirota, Y. *Macromolecules* **1985**, *22* 4204.
- ² Clark, M.D.; Schott, T.A.; McCormick, C.L. *Polym. Preprints* **1989**, *30* 375.
- ³ These experiments were carried out in the laboratory of Prof. W.H. Wade of this Department using the spinning-drop method (described in Cayias, J.L.; Schechter, R.S.; Wade, W.H. ACS Symposium Series No. 8, "Adsorption and Interfaces" **1975**, 234). In this method a drop of the less dense phase is rotated in the dense phase and γ is determined by the shape of the drop at a given rotation speed.

Publications Listing

1. "Triplet State Electron Transfer in Poly(methacrylic acid) with Covalently Bound Pheranthracene and Naphthalene", *J. Phys. Chem.* (in press).

Preprint Removed.

TA for Phenanthrene gating time at 14 micro second delay
Pulse width: 1 micro sec, Detector temp: 10 C, Laser power: 190 J/pulse



Xe lamp spectra. Note that because of Reticon size valid data collected from 350 - 870 nm.

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