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Poly(2-vinylnaphthalene-*alt*-maleic acid)-*graft*-polystyrene as a Photoactive Polymer Micelle and Stabilizer for Polystyrene Latexes

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ABSTRACT: Polymerization of maleic anhydride and 2-vinylnaphthalene produces alternating polymers. Imidization of the polymer with amino-terminated polystyrene yields different loadings of an alternating polymer with polystyrene "combs". Upon rigorous hydrolysis one obtains poly(2-vinylnaphthalene-*alt*-maleic acid)-*graft*-polystyrene (P2VNMA−PS), which is a fluorescent polymer with unusual solution properties and with significant surface activity. P2VNMA−PS forms a small micelle structure in solution or can be used as a surfactant for an emulsion polymerization of polystyrene (no cosurfactant is required), producing monodisperse latex particles which are stable for pH > 3.9. Centrifugation shows that >90% of the P2VNMA−PS is associated with the latex particles. Fluorescence quenching studies of the naphthalene excimer with Tl^+ indicate that approximately 84% and 77% of the naphthalene groups remain exposed to the aqueous phase when this polymer is micellized or incorporated onto a latex particle, respectively. These data imply that the P2VNMA−PS polymer is permanently associated with the exterior of the latex particle, as one would expect given the amphiphilic nature of this polymer.

Introduction

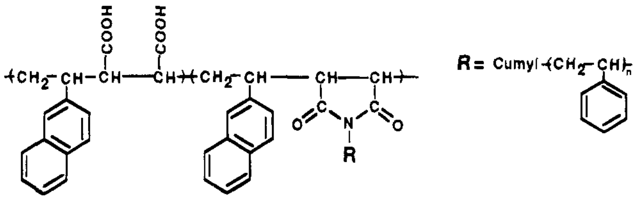
The use of polymers as surface modifiers is well-known and is being actively pursued by a variety of theoretical and experimental groups.[1] The usual motivation for this work is in polymer adhesion, modification of the wetting properties of a polymer film, colloid stabilization, emulsifying agents, etc. Another group of researchers has been actively working in the area of polymer photophysics and photochemistry, which has been the subject of a variety of symposia or monographs over the last decade.[2] Finally, there has been a huge literature generated in the general field of photochemistry in "microheterogeneous" or "self-assembling" systems which offers mimicry of biological systems.[3]

The present paper describes our efforts to produce a photoactive polymer that can be used to modify a polymer film surface, with the objective of enhancing the efficiency of excited-state redox quenching:

$$^{2S+1}D^*(\text{film}) + A(\text{aq}) \rightarrow D^{\bullet+}(\text{film}) + A^{\bullet-}(\text{aq}) \quad (1)$$

Polymer films are obviously an attractive medium for such reactions in the sense that they can be easily fabricated, are often quite rugged, and may be chemically modified in many different ways. In a related study we have adsorbed small amphiphilic chromophores onto water-soluble latexes.[4] In the present study we use a photoactive alternating-comb copolymer, poly(2-vinylnaphthalene-*alt*-maleic acid)-*graft*-polystyrene, abbreviated P2VNMA−PS (see Chart 1) hereafter, to produce photoactive polystyrene latex surfaces. We have exploited photophysics to elucidate the location of the chromophore in this system and have established that the naphthalene chromoophores are bound to the surface of a polystyrene latex particle and can be quenched by an aqueous phase species. While the use of various surfactants to modify polystyrene latexes has a long history,[5] it continues to be an area of active research.[6]

Chart 1



Experimental Section

1. Fluorescence and Light Scattering. All steady-state fluorescence measurements were carried out on a SPEX Fluorolog 2 with a 450-W Xe lamp, double monochromators for excitation and emission, and a Hamamatsu R928 photomultiplier tube for emission over the 190−900-nm range with ±0.4-nm accuracy. Fluorescence lifetimes were measured using the time-correlated single photon method, with 293-nm excitation and with a time resolution of ca. 100 ps with standard reconvolution techniques.[7] Quasi-elastic light scattering (QELS) was carried out with a Brookhaven 2020-AT system at a 90° collection angle and at 25 °C. The hydrodynamic diameter (d_h) is estimated from the measured diffusion constant (D) using Stokes law

$$D = kT/3\pi\eta d_h \quad (2)$$

where η is the solvent viscosity (the concentration of particles is sufficiently small that η is unaffected). The polydispersity is estimated from the relation

$$P_D = \mu_2(q)/\Gamma(q)^2 \quad (3)$$

where μ_2 is the second cumulant in the analysis of the decay of the QELS signal,

$$g^{(1)}(q,t) = \exp\{-\Gamma(q)\,t + 0.5\mu_2(q)\,t^2 + ...\} \quad (4)$$

The polydispersity is an important indicator that aggregation of a sample has occurred, and we will refer to a sample as "monodisperse" if $P_D < 0.1$, although for a perfectly monodisperse sample $P_D = 0$. Because the latex particles we will

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describe later are very strong scatterers, it is possible to obtain very high quality light scattering data.

2. NMR, TEM, and ESEM Experiments. All NMR spectra were taken of the esterified polymer on a GN-500 General Electric instrument at 500 MHz (11.75 T) using deuterated tetrachloroethane as a solvent. For proton and C^{13} NMR the concentrations were 10 and 50 mg/mL, respectively. For ESEM images of the latexes 1 drop of aqueous solution was placed on a polished copper surface and the solvent was removed by freeze-drying. The specimen was coated with ca. 100 Å of gold before imaging. The instrument used was an Electroscan Model E-3 with a beam energy of 20 kV. SEM micrographs taken at a 60° tilt were taken on a Philips Model 515 at 28 kV at the Cell Research Institute, The University of Texas at Austin. For these SEM samples the aqueous solution of latex was sprayed onto a polished aluminum platform and the solvent was removed by freeze-drying. The specimen was coated with ca. 100 Å of Au–Pd (60:40). TEM samples were prepared by spreading a ca. 1 μL of aqueous solution on a 200-Å-thick carbon film with a copper grid (400 mesh). After freeze-drying the specimen was stained by exposure to a RuO_4 vapor for 30 min. The TEM images were obtained on a JEM-100CX electron microscope at 80 kV at the Cell Research Institute, The University of Texas at Austin.

3. Polymer Preparation. Preparation of Basic Alternating Polymer. To prepare the basic alternating polymer, 4.27 g of maleic anhydride (Aldrich; sublimed twice in vacuum), 6.64 g of freshly sublimed 2-vinylnaphthalene (Aldrich), and 100 mg of AIBN is dissolved in 70 mL of distilled benzene. The solution was transferred into a glass ampule and degassed by four cycles of freeze–pump–thaw at 2×10^{-2} Torr and sealed. Polymerization was carried out at 65 °C for 18 h. The polymer precipitate was separated from the solution by filtration. Reprecipitation was carried out from THF into benzene two times and from THF into ether two more times. The last precipitate was dried under vacuum. The yield of alternating polymer was 78%. The mole ratio of naphthalene to maleic anhydride is 1:1 according to UV absorption spectroscopy. NMR could not be used to verify this composition (see later discussion). This polymer is denoted P2VN-*alt*-MAn. The hydrolyzed ungrafted polymer is denoted P2VNMA.

Grafting and Hydrolysis Reactions. The grafting reaction was carried out with 0.5 g of P2VN-*alt*-MAn and 0.4 g of monoamino-terminated polystyrene ($PS-NH_2$) mixed with 0.025 g of sodium acetate as a catalyst and 15 mL of pyridine. The $PS-NH_2$ was a gift from Dr. C. Ramireddy and was prepared by anionic polymerization techniques (the molecular weight of the polystyrene block was ca. 3000 by GPC).[8] The solution was transferred into a glass ampule, degassed by four freeze–pump–thaw cycles, and sealed. Imidization was carried out at 130 °C for 15 days. The hydrolysis of the product was accomplished by mixing the contents of the ampule with 0.2 g of NaOH and 4 mL of water. This mixture was degassed by two freeze–pump–thaw cycles to prevent oxidation during long exposure to elevated temperatures, sealed, and heated at 110 °C for 10 days. The IR spectrum showed that the hydrolysis was not complete, so the pyridine was removed by dialysis of the mixture against water. Further hydrolysis was carried out as follows: 0.2 g of NaOH and 20 mL of THF are added to the mixture containing water and refluxed under nitrogen for 3 days. We then added 0.2 g of SDS, which experience has shown can break up hydrophobically associated aggregates, with 10 mL of water and refluxed for another 3 days under nitrogen. This mixture was filtered to remove unreacted amino-terminated polystyrene. The solution was dialyzed against water with a pH that was diminished from ca. 11 to 7.5 over 10 days using Spectra/Por molecular porous membrane tubing MWCO6-8000 in order to remove any small molecule species (SDS, NaOH, THF). Water was removed from the sample by freeze-drying, and IR spectra of the solid did not contain the 1779 and 1856 cm^{-1} peaks attributed to the unhydrolyzed anhydride. While we have not established if all these steps are required to effect complete hydrolysis of this material, it is clear that one has to be very careful to verify the completeness of hydrolysis. We assume that part of the difficulty in hydrolysis is the presence of the extremely hydrophobic polystyrene grafts. The overall yield of hydrolyzed polymer is approximately 67%. The hydrolyzed grafted polymer is denoted P2VNMA–PS.

The hydrolysis of P2VN-*alt*-MAn was much easier. A total of 4.5 g of P2VN-*alt*-MAn was mixed with 150 mL of water and 1 g of KOH and heated under argon at 50–60 °C with continuous stirring for 24 h. The solution was acidified to pH 6 and dialyzed against water at 40 °C for 60 h. The final powderlike material was obtained by freeze-drying.

A sample of P2VNMA was esterified by reaction with diazomethane in order to render it easily soluble in dry THF and to eliminate specific interactions with the GPC column material. The GPC elution curve showed the molecular weight distribution to be broad ($M_w/M_n \approx 3$) with M_w ca. 45 000, based on polystyrene standards and using THF as an elutant. The analogous graft esterified polymer had an almost identical elution curve but shifted to a slightly higher apparent molecular weight. Obviously the GPC provides only qualitative information about the MW of these samples. From UV–vis spectroscopy the mole ratio of naphthalene groups to PS combs was calculated to be ca. 11:1.

The proton NMR of P2VNMA and P2VNMA–PS was obtained at 100 °C in tetrachloroethane-d_2. Unfortunately, the spectrum was too broad for a meaningful integration of proton intensities to provide an independent check of the composition, although a strong new contribution in the aromatic region is found in going from P2VNMA to P2VNMA–PS. ^{13}C NMR also clearly demonstrates the presence of the PS side chain, but this NMR method cannot be used to obtain composition information.

Aqueous solutions of P2VNMA–PS have to be prepared with care. First, the polymer is dissolved in a small amount of concentrated (ca. 3 N) NaOH solution, warmed slightly, and vortexed for approximately 30 min. This solution is diluted with water to achieve a pH of approximately 12 with a typical concentration of ca. 20 mg of polymer in 5 mL of water. Lower pH solutions are prepared by adding this stock solution to acidified water. Direct addition of acid to the basic P2VNMA–PS solution can result in precipitation.

4. Preparation of Polystyrene Latex. A total of 7 mg of AIBN was dissolved in 1 g of styrene. A total of 0.103 g of P2VNMA–PS was dissolved in 10 mL of water containing NaOH and diluted with water to 40 mL (final pH = 12.3). Both solutions were mixed and then vortexed for a few minutes followed by rapid stirring with a magnetic stirrer for 16 h. The milky emulsion was bubbled with styrene-saturated nitrogen, while being stirred for 30 min, and then heated to 65 °C for 72 h while stirring continuously. The emulsion was then dialyzed against basic water (pH 11–12) for 1 week to remove any unreacted monomer. Note that the emulsion remains milky after the reaction even though small particles are formed (see below).

Results

1. Characterization of the Polymer and Latexes by QELS and Electron Microscopy. The solubility properties of P2VNMA–PS are quite different than those of the ungrafted polymer. For example, P2VNMA–PS cannot dissolve in dry THF but does dissolve in 49:1 v/v THF/H_2O. The hydrodynamic diameter of P2VNMA–PS in 49:1 v/v THF/H_2O is ca. 8 nm. The polymer can also be dissolved in water and the pH lowered carefully following the procedure described earlier. Under these conditions d_h was on the order of 30 nm with a polydispersity of 0.25 down to pH ≈ 4.4, at which point aggregation occurred, with the formation of very large particles (see Figure 1). The relatively high polydispersity at higher pH is the result of a small component of ca. 200-nm particles that could not be removed by normal filtration procedures. Given the difference in d_h between H_2O and 49:1 v/v THF/H_2O, it seems likely that in pure H_2O at pH > 4.4 an "associated state" is formed which we ascribe to a polymer micelle. TEM

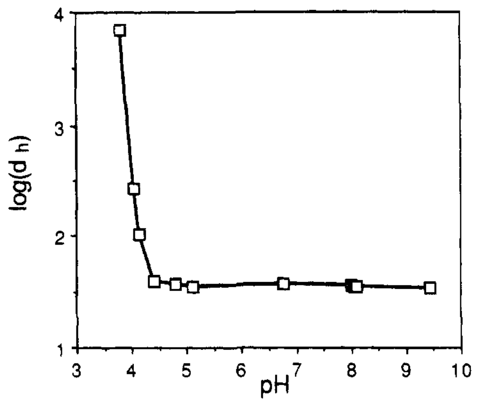


Figure 1. Plot of log d_h vs pH for P2VNMA–PS showing the onset of micelle aggregation for pH < 4.

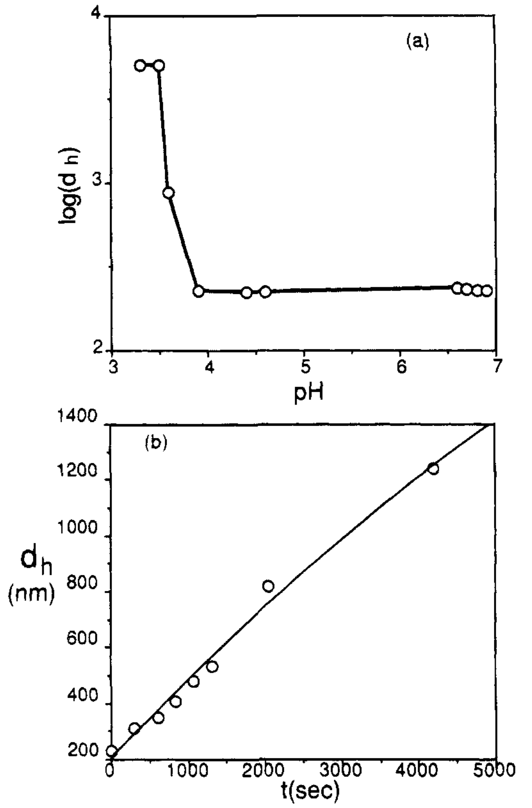


Figure 2. (a) Plot of log d_h vs pH for latexes prepared with P2VNMA–PS. (b) Plot of d_h vs time (at early time) for latexes upon lowering to pH 3.3.

images to be discussed below confirm the presence of small spherical particles. This is hardly a surprise given the presence of the highly hydrophobic polystyrene graft. These micelles could not be broken up by the addition of SDS up to 0.1 M, unlike the ungrafted P2VNMA polymer, which forms large aggregates at low pH that are readily broken up by SDS.

The polystyrene latexes prepared in the presence of P2VNMA–PS contained approximately 17 wt % of large particles (>450 nm) that could be removed by a 0.45-μm Gelman poly(vinylidene fluoride) filter. The remaining material had a hydrodynamic diameter of ca. 200 nm with a polydispersity of ca. 0.08, which is only slightly higher than found for commercial light scattering standards. These particles maintain a constant d_h down to pH ≈ 3.9, at which point formation of large, polydisperse particles occurs. The formation of these particles is slow (see Figure 2a), requiring days to complete. It seems clear that protonation of the surface P2VNMA–PS has destabilized the particle. A similar effect can be observed at pH 4.7 with the addition of KNO_3 (7×10^{-2} M). Above pH 5.5 no aggregation could be induced by KNO_3 up to 0.5 M.

Samples of the latex solution could be removed and deposited on either a copper grid and stained by $(UO_2)(OAc)_2$ or RuO_4 for TEM or onto a polished copper surface and gold coated and imaged by ESEM or SEM. When regions with a low density of latex particles are examined, we find well-defined individual spherical particles with an average diameter of 143 ± 15 nm by TEM and 155 ± 17 nm by ESEM. In the ESEM images we find approximately half the aggregates are composed of 2–4 individual latex particles. The aggregates must be formed during sample preparation because such large aggregates in solution would have produced a very different d_h and polydispersity from QELS. The smaller diameters obtained by electron imaging compared to QELS (cf. 200 nm) are expected since the latter includes the solvated polyelectrolyte corona and associated counterions. For SEM at 60 °C tilt or TEM smaller particles can be seen near or associated with the latex particles (Figure 3a–c). These smaller particles appear to be the P2VNMA–PS micelles described next.

If P2VNMA–PS solutions are deposited onto a carbon film with a copper grid and imaged by TEM, structures are observed that can be seen to be aggregates of smaller spherical particles with a clear boundary between them (Figure 3d). These large aggregates must have been formed during the TEM sample preparation stage but may also account for the ca. 200-nm component observed in QELS that increased the polydispersity. The average diameter of the small particles is 17.8 ± 0.7 nm, in reasonable agreement with the 30-nm hydrodynamic diameter.

Centrifugation of a pH 9.3 solution of the latex solution on a Sorvall RC-5B refrigerated centrifuge at 17 000 cps (22 000 *g*) for 90 min permitted a spectroscopic examination of the clear supernatant (the microspheres form a precipitate on the bottom of the tube, which can be redispersed) which contains <10% of the total naphthalene chromophore. This is consistent with the simultaneous presence of the latex and the smaller P2VNPM–PS micelles. We conclude that at least 90% of the naphthalene groups remain with the latex. This may be an underestimate because some of the naphthalene-containing polymer could be displaced during the centrifugation and a very small amount of latex remains in solution.

Thus this particular type of "polysoap" can be used to produce monodisperse polystyrene latexes that are stable over a wide pH range. The next question is, where are the naphthalene groups? Are they buried inside the latex or accessible to an aqueous phase quencher? We turn to fluorescence techniques to answer this question.

2. Fluorescence Studies. (a) Fluorescence Spectra. The fluorescence of naphthalene-containing polymers is often dominated by excimers. We have previously studied the effect of attenuation of excimer fluorescence in alternating polymers such as poly(2-vinylnaphthalene-*alt*-methacrylic acid)[9] or P2VNMA[10] as a function of pH. In general, as the polymer collapses the excimer fluorescence is enhanced, presumably because the naphthalene groups are brought into closer proximity. It is interesting to note the effect of the polystyrene grafts on the fluorescence in a homogeneous (micelle) solution at pH ≈ 11 (Figure 4). The polystyrene graft greatly increases the naphthalene excimer

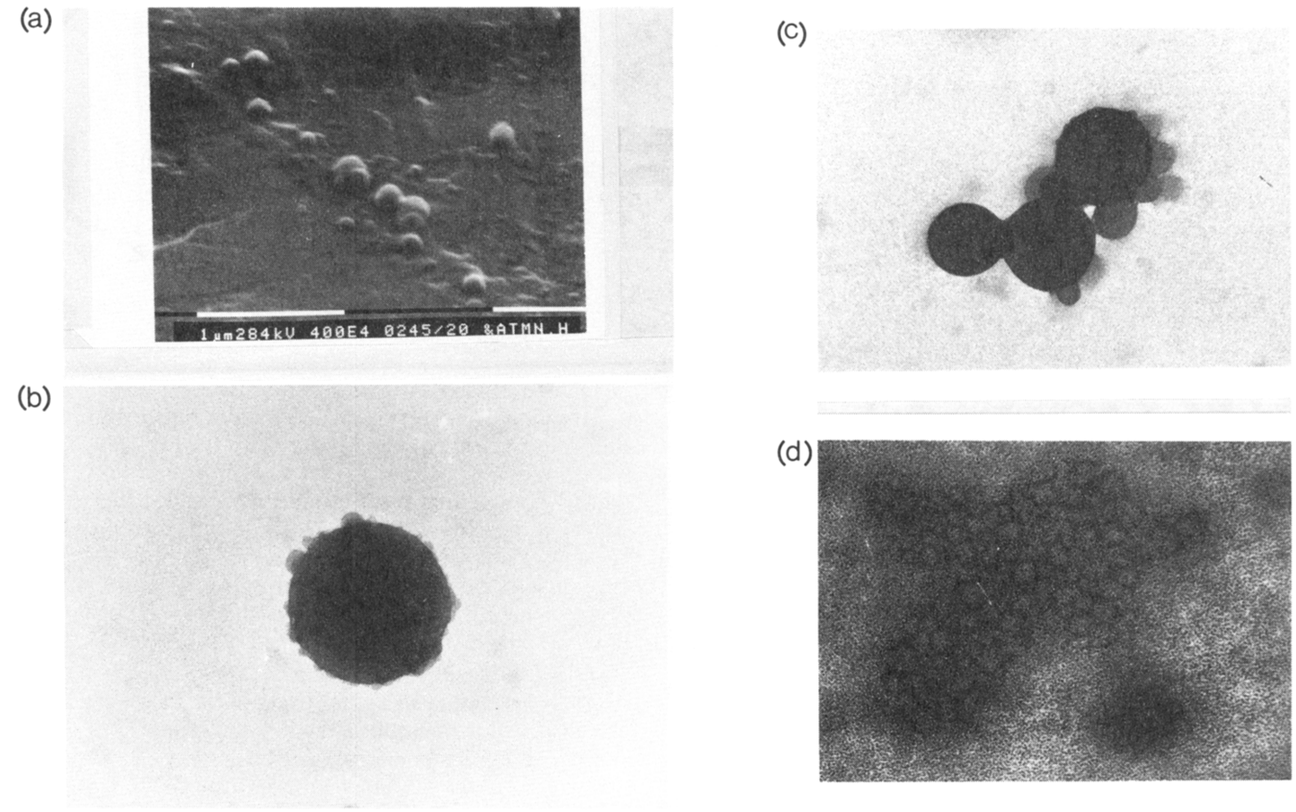


Figure 3. (a) SEM images taken at a 60° tilt; (b) TEM image of a single latex particle (diameter ca. 200 nm) with associated micelles; (c) TEM image of a group of latex particles with associated micelles and/or small latex particles; (d) TEM image of P2VNMA–PS micelles (diameter of individual micelle ca. 18 nm).

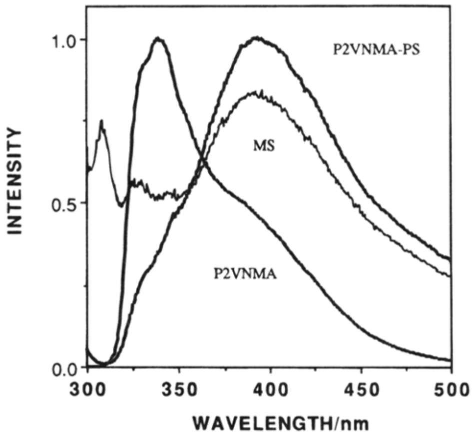


Figure 4. Comparison of the fluorescence of P2VNMA and P2VNMA–PS at pH 11 (λ_{exc} = 290 nm) and P2VNMA–PS associated with the PS latex (denoted MS) at pH 9.6.

contribution, possibly as a result of forming an associated micelle structure (as implied by QELS and the TEM images) with enhanced naphthalene–naphthalene interaction.

The fluorescence spectra of P2VNMA–PS associated with the latexes are difficult to obtain because of strong light scattering which yields a Raman peak near 300 nm that interferes with the naphthalene monomer emission. Shifting the excitation wavelength to shorter wavelengths results in direct excitation of the polystyrene groups. As it is, dimer states of the polystyrene may be excited at 290 nm, yielding excimer fluorescence in the 330-nm region. Nevertheless, from the spectrum (Figure 4) it is obvious that the excimer is still dominant, although perhaps less so than for a homogeneous solution.

(b) Fluorescence Quenching. In these studies we use Tl^+ (from $TlNO_3$) as a quencher with the assumption that this species will be able to quench only those naphthalene groups that are exposed to the aqueous phase. Tl^+ is presumed to quench by a short-range mechanism (e.g., an external heavy atom effect or electron transfer) because it does not have lower lying excited states with a strong absorption, as required for the Förster mechanism.[11] All of our studies are carried out at high pH (>9) such that the acid groups will be deprotonated. Consequently, the Tl^+ will be concentrated in the vicinity of the polyanion. This is illustrated by the Stern–Volmer plot in Figure 5a for P2VNMA (I_0/I is the ratio of fluorescence without and with quencher). The quenching of the excimer (defined as emission in the range 400–415 nm) is slightly faster than that for the monomer (315–345 nm), which is normally the case if the monomer excited state is the precursor to the excimer.[12] An upward curvature is expected if the quencher can "condense" onto the polyelectrolyte, eventually saturating the sites next to the chromophore.[13] The apparent Stern–Volmer quenching constant is very large in this case because of the electrostatic attraction ($K_{SV} = 7.8 \times 10^4\ M^{-1}$, which with a fluorescence lifetime of ca. 28 ns yields $k_q = 2.8 \times 10^{12}\ M^{-1}\ s^{-1}$). This contrasts sharply with the P2VNMA–PS comb polymer in which the quenching becomes totally ineffective for I_0/I above 4–6 for the monomer and excimer, respectively (see Figure 5b). This is a typical example of a "protected chromophore" that cannot be reached by the quencher.[14] The Stern–Volmer data can be plotted according to the equation[15]

$$\frac{I_0}{I_0 - I} = \frac{1}{f_a} + \frac{1}{f_a K_{SV}[Q]} \qquad (5)$$

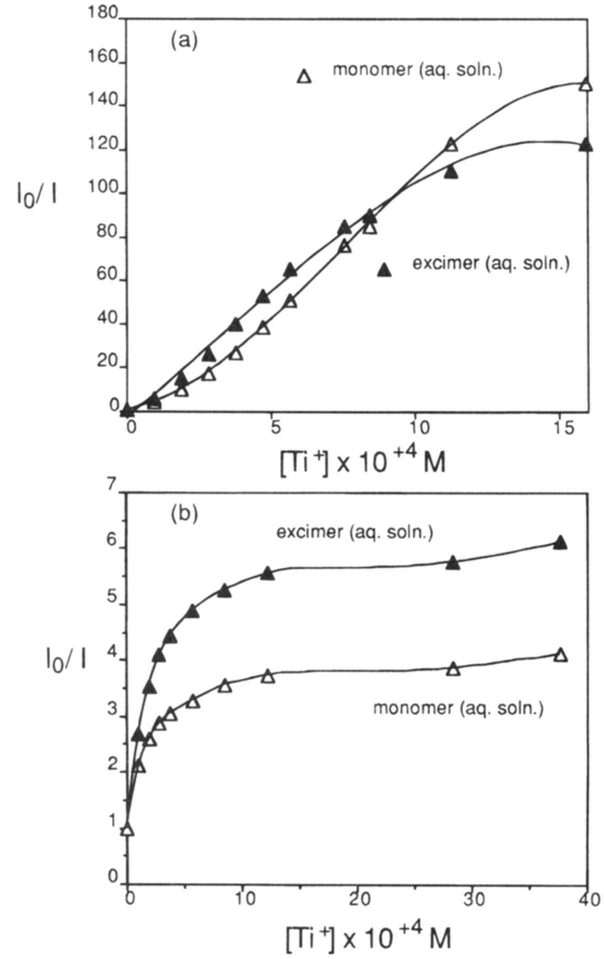


Figure 5. (a) Monomer (315–345 nm; open symbols) and excimer (400–465 nm; filled symbols) fluorescence quenching for P2VNMA by Tl$^+$ at pH 10–11. (b) Monomer and excimer fluorescence quenching for P2VNMA–PS (same wavelength range and pH as a).

In this equation f_a is the fraction of accessible chromophores and K_{SV} is the Stern–Volmer constant for the accessible chromophores. The monomer and excimer quenching curves fit eq 5 well with the values $f_a = 0.75$ and 0.84 and $K_{SV} = 2.4 \times 10^3$ and 3.2×10^3 M^{-1} for monomer and excimer, respectively. It is futile to carry out any detailed analysis of the difference in monomer and excimer fluorescence quenching since some fraction of excimers will have monomeric precursor states (i.e., dynamic formation of excimers either through physical motion of chromophores or energy transfer to excimer-forming sites) while other excimers will be directly excited at preformed excimer sites and have to be treated as a fluorophore which is kinetically independent of the monomer state. However, these results are consistent with the idea that the polystyrene grafts and/or micelle formation produces hydrophobic pockets for the pendent naphthalene groups such that approximately 25% have no contact with the aqueous phase.[16]

For P2VNMA–PS associated with latexes, the quenching curve also shows a strong negative curvature and there is slightly less quenching than for a homogeneous solution (see Figure 6). The fit of the quenching data to eq 5 yields values that are similar to those for a homogeneous solution, with $f_a = 0.47$ and 0.77 and $K_{SV} = 1.6 \times 10^3$ and 2.5×10^3 M^{-1} for monomer and excimer, respectively. These quenching results demonstrate the existence of protected naphthalenes for the comb polymers whether associated with latexes or in a homogeneous solution. However, since there is significant error in obtaining the monomer fluorescence because of Raman contamination and/or a possible contribution from directly excited polystyrene, a comparison of the excimer quenching is more meaningful. The f_a and K_{SV} values for the excimer are essentially identical for P2VNMA–PS on latexes or for micelles in a homogeneous solution.

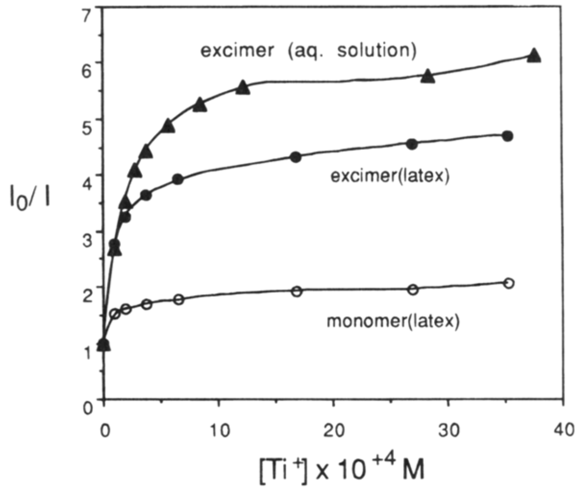
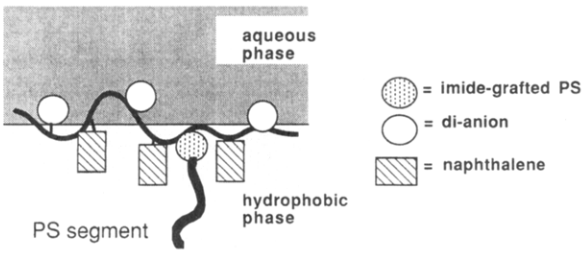


Figure 6. Monomer (330–345 nm) and excimer (400–500 nm) quenching of P2VNMA–PS associated with a latex (pH 9.6). The quenching of the excimer in a homogeneous solution (presumably micelles) from Figure 5b is shown for comparison.

Chart 2



Summary

We have described an alternating polymer of 2-vinylnaphthalene and maleic acid with polystyrene grafts (P2VNMA–PS) that is able to support a microemulsion of polystyrene with no cosurfactant, thereby producing a photophysically active latex. These latexes are monodisperse according to QELS or electron microscopy for pH > 4.4. The grafted polymer P2VNMA–PS forms a self-assembling micelle structure in an aqueous solution.

We have used fluorescence techniques to characterize the behavior of the naphthalene groups. What we found may be summarized as follows:

(1) The ratio of monomer to excimer fluorescence is strongly influenced by the presence of the grafted polystyrene or by incorporation onto a latex particle.

(2) Fluorescence quenching by Tl$^+$ yields some qualitative insight as to the exposure of the naphthalene groups to the aqueous environment. We find that the quenching mechanism is quite different from that of the ungrafted polymer (P2VNMA) and P2VNMA–PS or P2VNMA–PS/latex. In the latter two cases the monomer or excimer quenching is very inefficient, implying a significant degree of hydrophobic protection for the product naphthalene group.

These photophysical observations are consistent with Chart 2 in which ca. 20% of the naphthalene groups are buried inside the PS interface but still able to form excimers. In a related paper[17] we have presented studies of amphiphilic block polymers in which similar hydrophobic protection by a PS film and micelle core is obtained.

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(11) Lakowicz, J. R. *Principles of Fluorescence Spectroscopy*; Plenum Press: New York, 1983.

(12) In fact, this effect is not so extreme here, implying that there are many preformed excimers. This may be compared to the case in which the monomer state is the sole precursor to the excimer (Webber, S. E.; Avots-Avotins, P. E.; Deumié, M. *Macromolecules* **1981**, *14*, 105).

(13) This has been observed before with Cu^{2+} ions quenching anthracene covalently bound to poly(styrene sulfonate) (Webber, S. E. *Macromolecules* **1986**, *19*, 1658) but is much less important for monovalent ions (Morrison, M. E.; Dorfman, R. C.; Clandening, W. D.; Kiserow, D. J.; Rossky, P. J.; Webber, S. E. *J. Phys. Chem.* **1994**, *98*, 5534).

(14) For a recent review of polymer-modified reactions, including the protection of polymer-bound chromophores, see: Morishima, Y. *Prog. Polym. Sci.* **1990**, *15*, 949.

(15) See reference 11, p 281.

(16) If electronic energy transfer enhances the efficiency of quenching, then a smaller fraction of naphthalene groups may be directly exposed to the aqueous phase, but energy can migrate to these exposed sites.

(17) Cao, T.; Yin, W.; Armstrong, J. L.; Webber, S. E. *Langmuir* **1994**, *10*, 1841.