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Photophysical Characterization of Water-Soluble Styrene-Grafted Poly(acrylamide) Copolymers

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ABSTRACT: Although radiation grafting of styrene to poly(acrylamide) was found to be inefficient in aqueous micellar media, however, hexadecylpyridinium chloride micelles provided a measure of control over the grafted styrene side-chain lengths. Measurements with Poisson fluorescence quenching kinetics indicated that the side chains ranged from 24 to 52 units. Fluorescence fine structure using pyrene as a probe revealed that the styrene side chains give rise to hydrophobic domains in aqueous copolymer solutions. An equilibrium constant of 4×10^{-7} M was measured for the solvation of pyrene in the hydrophobic sites compared to the aqueous phase. Fluorescence quenching was monitored to show that the copolymers isolate and screen hydrophobic guest molecules from the aqueous phase. Hydrolysis of the poly(acrylamide) backbone resulted in no significant change in the characteristics of the hydrophobic domains, in direct contrast to results reported for water-soluble block copolymers of these monomers.

Introduction

Photophysical and photochemical methods have been used increasingly in studies of microheterogeneous systems, such as micelles and vesicles, and including multiphase polymer systems.[1-4] Fundamental to this interest is their ability to organize molecular species and provide unique chemical environments for guest molecules. These systems impart a higher degree of organization compared to homogeneous systems, yielding a wide array of potential applications in fields as diverse as solar energy conversion, drug encapsulation, and catalysis.[5] In addition, multiphase characteristics can have a profound affect on the properties of polymeric systems, of interest in the development of specialty materials.

Simple polymers can often be modified to have an amphiphilic nature, imparting microheterogeneity to these systems. Radiation grafting has been accepted as a simple means of modifying polymer characteristics.[6] Amphiphilic materials may result when a hydrophobic side chain such as polystyrene is grafted to a hydrophilic polymer like poly(acrylamide). Although block copolymers of acrylamide and styrene, with polystyrene blocks incorporated into the backbone of these linear polymers, have been shown to have amphiphilic properties,[7] the hydrophobic portion of the graft copolymers branches out from the main polymer chain. The effects of configurational differences on the properties of these systems are important in the understanding of the structure-property relationships in amphiphilic polymer systems and provide insight into the nature of hydrophobic interactions in aqueous media.

It was the aim of this study to synthesize and characterize water-soluble graft copolymers of acrylamide and styrene and to monitor the resulting chemical environments of the hydrophobic domains, with particular attention paid to any microheterogeneity that might arise. A micellar medium has been shown to be an effective means of controlling polystyrene latex particle sizes[8,9] and block sizes in a copolymerization of styrene and acrylamide.[7] In this investigation, this technique is applied in the grafting of styrene to poly(acrylamide) (PAM). Differences in behavior between the graft copolymers and the chemically similar block copolymers were interpreted in terms of differences in molecular architecture. The primary goal of the present work is to regulate side-chain lengths in the grafting of styrene to acrylamide through a micellar mechanism, characterize the resulting chemical environments for solubilized probes, and contrast the characteristics with those of the block copolymer counterparts.

Experimental Section

Instrumentation. Steady-state fluorescence measurements were predominantly made on an SLM/Aminco SPF-500C spectrofluorometer. Data were transferred to a Zenith PC microcomputer for storage and analysis. Additional steady-state fluorescence measurements were made on a Perkin-Elmer MPF-44B spectrofluorometer. This instrument was preferred for excitation below 300 nm.

Time-resolved fluorescence measurements were carried out by using the configuration of instruments described elsewhere.[10] The arrangement includes a nitrogen laser excitation source, a partial reflector, focusing lenses, monochromator, PMT, digitizing transient capture device, monitor, and microcomputer for storage. Excitation sources used were PRA Nitromite LN100 and PRA LN1000 nitrogen lasers. The principal wavelength of each is 337.1 nm. Pulses of 70 μJ, 120 ps FWHM, and 2.5 μJ, 0.8 ns FWHM, are provided, respectively. Response times of 1 ns are obtainable through this arrangement.

Absorption spectra were obtained by using a Perkin-Elmer Model 552 spectrophotometer and used to determine the styrene content of the synthesized copolymers.

Materials and Preparations. Several of the reagents used for syntheses required additional treatment for purification and/or removal of inhibitors prior to use. Styrene was obtained from Aldrich Chemical Co., was washed with concentrated sodium hydroxide and then distilled water, followed by drying over anhydrous calcium chloride, and was distilled twice under vacuum to remove TBC inhibitor. Sodium hydroxide solutions for hydrolysis reactions were prepared from 50% w/w solutions purchased from Fisher. Prepurified nitrogen from Union Carbide was used for the deaeration of samples by gentle bubbling for at least 10 min. USP-grade nitrous oxide was used in solutions for radiolysis. Distilled and deionized water was used exclusively for the preparation of aqueous solutions. Poly(acrylamide) from Aldrich was used as received. Pyrene was purchased from Aldrich and purified by column chromatography prior to use. Nitromethane from Eastman Chemical was distilled under vacuum twice prior to use. Other reagents and surfactants used were reagent grade or better and used as received.

Synthesis of Graft Copolymers. A micellar polymerization method was used in the synthesis of graft copolymers of acrylamide and styrene. A surfactant, hexadecylpyridinium chloride

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Table I
Reaction Mixtures for Grafting Styrene to Poly(acrylamide)

copolymer	[Sty], mM	PAM, g/L	[CPC], mM	[Sty]/[mic][a]	% graft
G(AM/Sty)-0	0	8.81	10.4	0	N/A
G(AM/Sty)-35	6.83	8.75	16.4	35	17
G(AM/Sty)-57	6.83	8.77	10.4	57	19
G(AM/Sty)-85	6.83	8.77	7.32	85	14
G(AM/Sty)-112	6.83	8.77	5.72	112	16

[a] Calculated from cmc and *N* values reported in ref 12.

(CPC), was used to support the hydrophobic monomer, styrene, in an aqueous solution of poly(acrylamide). The function of the CPC surfactant was 2-fold: (1) to solvate the styrene in an aqueous medium and (2) to regulate the length of the hydrophobic side chains. Solutions were deaerated and saturated with nitrous oxide by gentle bubbling with the N_2O for 30 min. Upon irradiation with the γ source, hydroxyl radicals were formed:

$$H_2O \xrightarrow{\gamma} H_2O^+ + e^-(aq)$$

$$e^-(aq) + N_2O \rightarrow N_2O^-$$

$$H_2O^+ + H_2O \rightarrow {}^{\bullet}OH + H_3O^+$$

$$N_2O^- + H_3O^+ \rightarrow N_2 + {}^{\bullet}OH + H_2O$$

$$\text{net:} \qquad H_2O + N_2O \xrightarrow{\gamma} N_2 + 2({}^{\bullet}OH)$$

Hydroxyl radicals are capable of abstracting H atoms from the PAM chain, leaving free-radical sites on the polymer chain. Note that the intermediate species above, and the hydroxide radicals, are relatively short-lived compared to the more stable intermediate, PAM radical sites.[11] These latter sites can initiate polymerization of the styrene solvated in the CPC micelles, resulting in side chains of polystyrene grafted onto the main poly(acrylamide) chain.

Two side reactions of importance to the polymerization mechanism are conceivable. One, homopolymerization of the styrene, may be directly initiated by the γ irradiation or the hydroxyl radicals. The product, polystyrene, is not water-soluble and can be easily isolated from the copolymer product. Two, cross-linking of the poly(acrylamide) may occur due to radical–radical recombination between PAM radical sites. This reaction is minimized by using low PAM concentrations (<10 g/L) and short radiation exposures (90 s, 32 krad).

After irradiation, reaction mixtures were allowed to stand in darkness for 12 h. Observations showed an increase in solution viscosity upon standing due to radical–radical reactions, and thus an additional 12 h was allowed for complete reaction. Polymers were then recovered by precipitation with the addition of methanol. The polymers were repeatedly dissolved in water; insolubles were filtered, reprecipitated with methanol, and washed alternately with methanol and benzene. This procedure removed the unreacted styrene monomer, polystyrene homopolymer, and CPC surfactant from the water-soluble copolymer product. These copolymers, designated G(AM/Sty), were prepared from the reaction mixtures in Table I, and are labeled according to the calculated average occupation of the CPC micelles with styrene monomer by the hyphenated suffix. The reaction mixture G(AM/Sty)-0 contained no styrene and was used as a control. A 20 g/L solution of poly(acrylamide) was irradiated for 5 min to gauge the effects of cross-linking on the polymer.

The graft copolymers were easily converted to their poly(acrylic acid) (PAA) derivatives by hydrolysis. The G(AM/Sty) copolymers were hydrolyzed in aqueous solutions of 40 g/L copolymer and 1 M NaOH, providing nearly 2:1 excess base. These solutions were heated to 80 °C for 18 h, and the resulting hydrolyzed copolymers were precipitated and washed with methanol repeatedly. The degree of hydrolysis was estimated to be in excess of 80% hydrolyzed based on band intensities in the infrared spectra of the two polymers.

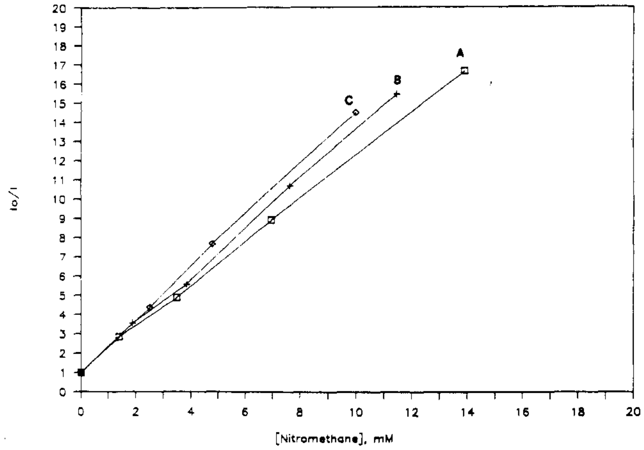

Figure 1. Quenching of pyrene steady-state emission in aqueous poly(acrylamide) solutions by nitromethane. (A) Cross-linked PAM, 20 g/L; (B) linear PAM, 20 g/L; (C) water.

Results and Discussion

Polymer Configurations. The Mark–Houwink equation for linear poly(acrylamide) (eq 1)[13] was used to gauge

$$[\eta]/100\ \mathrm{cm^3/g} = 6.8 \times 10^{-4} M_w^{0.66} \qquad (1)$$

the change in molecular weight of the polymers due to cross-linking using viscosity measurements. The starting PAM was measured to have $M_w = 2.2 \times 10^6$. G(AM/Sty)-0 was measured to have $M_w = 3.7 \times 10^6$. Although only accurate for linear polymers, the measured increase by a factor of 1.7 in the molecular weight indicates only slight cross-linking, one or two per chain, occurred during the grafting reactions.

This degree of cross-linking does not affect the amphiphilic properties of the polymer. A highly cross-linked poly(acrylamide) was prepared in concentrated PAM over long radiation times. The cross-linking was observed by the gelation of the sample. The resulting gel was equilibrated with pyrene over 4 weeks, and the ratio of the pyrene III peak to the I peak in the emission in the steady-state spectra and fluorescence lifetimes were unchanged from those in the linear PAM, indicative of similar, aqueous environments for the solubilization of pyrene.[14] The accessibility by nitromethane was also unchanged, as shown in Figure 1 by the steady-state quenching. Thus, the minor cross-linking that occurred in the grafting reactions does not appreciably alter the chemical nature of these systems and can be ignored in the investigations that follow.

Styrene Configurations. The amount of styrene in the grafted copolymers was measured by UV absorption spectroscopy. Polystyrene was measured to have an extinction coefficient of 205 L cm^{-1} mol^{-1} at 260 nm, on a monomer basis. This number was used to calculate the quantity of polystyrene incorporated into the G(AM/Sty) copolymers, which is reported in Table I. It is evident that only a small fraction (<20%) of the styrene is grafted to the PAM. The remainder is removed either as unreacted monomer or as homopolymer. The low styrene contents and the relatively high PAM molecular weight is responsible for the high water solubility of these grafted copolymers.

Each of the grafted copolymers exhibited measurable fluorescent emission from the styrene units. The proportions of excimer and monomer emission report on the relative packing of those units.[15] In each copolymer, excimer emission was observed exclusively. Figure 2 shows

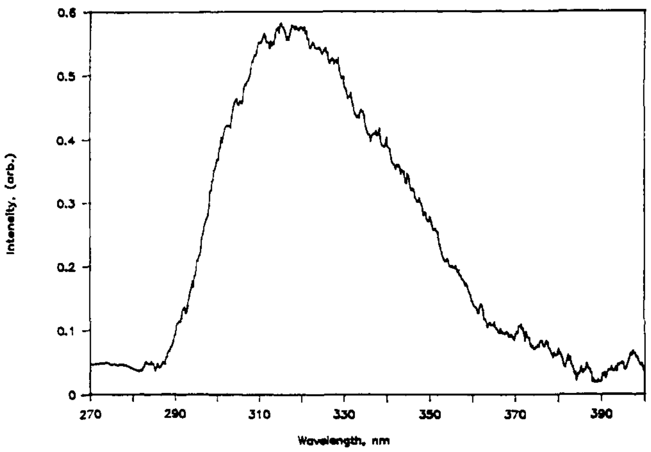

Figure 2. Styrene emission from graft copolymer G(AM/Sty)-57. 3 g/L copolymer in water; λ_{ex} = 245 nm. Only excimer emission is observed.

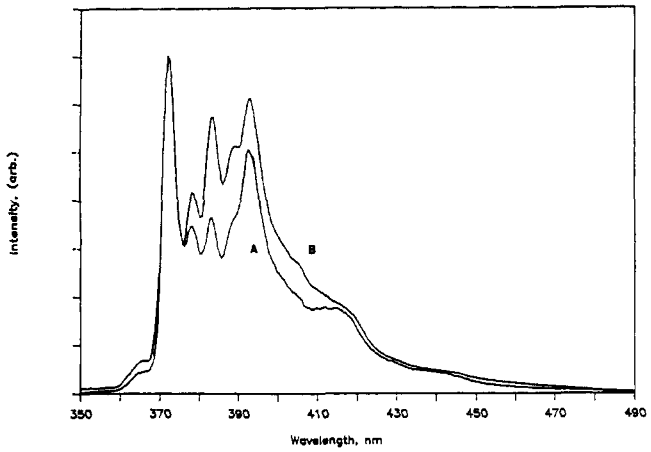

Figure 3. Comparison of pyrene vibronic band intensities in aqueous solutions of PAM and styrene-grafted PAM. (A) 3 g/L G(AM/Sty)-0, III/I = 0.52; (B) 3 g/L G(AM/Sty)-57, III/I = 0.82.

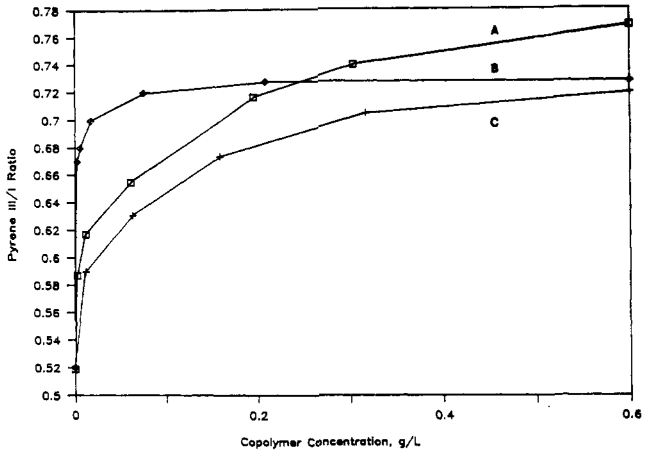

Figure 4. Dilution stability of hydrophobic sites as measured by pyrene III/I ratios. (A) G(AM/Sty)-57; (B) P(AM/Sty)-22; (C) P(AA/Sty)-22 hydrolyzed derivative at pH = 7.

Table II
Tl^+ and I^- Stern–Volmer Quenching Rate Constants of Pyrene Emission in Various Media

quencher	medium	k_q, M^{-1} s^{-1}
I^-	water	1.3×10^9
	3 g/L graft G(AM/Sty)-57	6.0×10^8
	3 g/L block P(AM/Sty)-28	4.0×10^7
Tl^+	water	6.2×10^9
	3 g/L graft G(AM/Sty)-57	4.0×10^8
	3 g/L block P(AM/Sty)-28	2.0×10^7

the broad emission band centered at 331 nm for G(AM/Sty)-57 typical of the close packing of the pendant phenyl groups. These spectra confirm the styrene incorporated in these copolymers is grafted in the form of long side chains of polystyrene on the PAM backbone.

Probe Studies. Pyrene, a well-characterized fluorescent probe,[14] was added to aqueous solutions of the graft copolymers. In Figure 3, the vibronic band intensities for pyrene in G(AM/Sty)-0 and G(AM/Sty)-57 are compared. In G(AM/Sty)-0 solutions, there are no styrene side chains, and the low III/I ratio (III/I = 0.52) corresponds to an aqueous environment for the solvation of pyrene. Conversely, in the G(AM/Sty)-57 solutions, the relatively high III/I ratio (III/I = 0.82) has been correlated with a hydrophobic environment similar to that in benzene.[15] Thus, the hydrophobic probe, pyrene, can be solvated by the styrene side chains in the graft copolymers. These grafted polystyrene side chains impart a hydrophobic nature to graft copolymer solutions.

The hydrophobic nature of the solvation sites for pyrene in aqueous solutions of the graft copolymers has a slight concentration dependence, as displayed in Figure 4. The III/I ratio for pyrene emission is constant at III/I = 0.82 above 2 g/L G(AM/Sty)-57 (not shown). However, from 0.6 to 0.1 g/L, the III/I ratio decreases by 36% of the difference between the maximum and minimum values. This decrease is in marked contrast to the behavior of block copolymers of acrylamide but is comparable to that of their hydrolyzed poly(acrylic acid-*block*-styrene) derivatives, suggesting the conformations of the polymer backbone in the graft copolymers are not important in the nature of the sites, in contrast to the behavior of the block copolymers.[7] The gradual decrease in III/I in this concentration range is indicative of an equilibrium between site-solvated and aqueous-solvated pyrene. As concentrations of the graft copolymer are decreased, the equilibrium is shifted to the aqueous medium. This analysis is substantiated by the III/I values approach to those expected in solely an aqueous environment; the equilibrium is confirmed in the quenching studies that follow.

Quenching Studies of Host Sites. Fluorescence quenching experiments were used to explore the properties of the hydrophobic sites provided by the graft copolymers of styrene and acrylamide in aqueous solutions. Quenchers possessing different chemical characteristics report on the nature of the polymer systems through their reactions with pyrene solvated within the hydrophobic microdomains.

Ionic Quenchers. The ionic quenchers I^- and Tl^+ are efficient quenchers of pyrene emission in homogeneous solutions. The quenching efficiency of these materials in aqueous solutions of the graft copolymers is significantly reduced, as determined by using the Stern–Volmer quenching rate constants, k_q, for comparison. These constants were determined at 3 g/L copolymer to eliminate effects of a possible equilibrium between the aqueous and the hydrophobic phases. The values are reported in Table II along with those calculated in aqueous block copolymer solutions. Although the quenching efficiency is decreased in the graft copolymer solutions, the graft copolymer sites are much more readily quenched than the block copolymer sites. The effective screening by the block copolymer sites was attributed to a mantle of poly(acrylamide) backbone about the hydrophobic polystyrene cores. It is concluded that the hydrophobic sites in the graft copolymers have sites that are more approachable by bulk-phase quench-

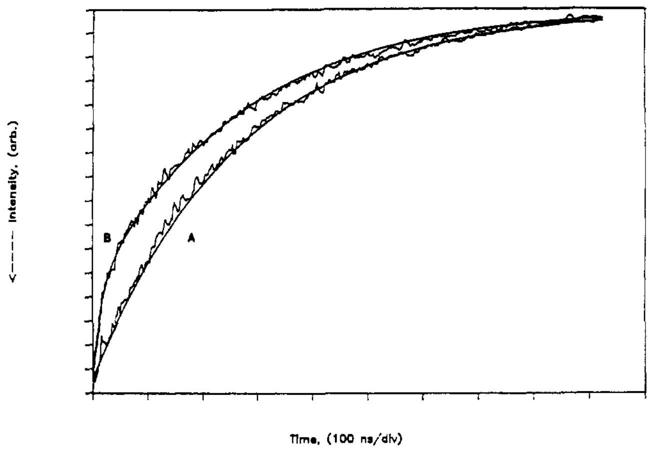

Figure 5. Time-resolved pyrene fluorescence in G(AM/Sty)-57 graft copolymer in the presence of 2 mM Tl^+: (A) 5 g/L, first-order fit; $k_{obs} = 3.76 \times 10^6$/s; (B) 0.2 g/L, biexponential fit; $k_1 = 3.76 \times 10^6$/s, $k_2 = 2.65 \times 10^7$/s, $A = 0.729$.

ers, are substantially smaller, or are less rigid than the corresponding sites in the block copolymer solutions.

Quenching by Tl^+ at low polymer concentrations exhibits more complicated decay kinetics due to a solvation equilibrium for the probe, pyrene. The proposed equilibrium between site-solvated and aqueous-solvated pyrene may be written as follows:

$$[\text{Py-site}] \overset{K_{eq}}{\rightleftarrows} [\text{Py}]_{aq} + [\text{sites}] \qquad (2)$$

The two distinct environments for pyrene should lead to biexponential behavior in the fluorescence kinetics:

$$I(t) = A \exp\{-k_1 t\} + (1 - A) \exp\{-k_2 t\} \qquad (3)$$

The parameters k_1 and k_2 describe the observed decay rates for the probe in each environment. However, only when the rate constants differ by about an order of magnitude are deviations from single-exponential behavior obvious. Quenching by Tl^+ was shown in Table II to accelerate the observed emission decay in the aqueous medium much more than in the graft copolymer sites, thus giving rise to a substantial difference in the fluorescence decays in the two environments. Figure 5 shows the fluorescence decays of pyrene in 5 and 0.2 g/L G(AM/Sty)-57 solutions containing 0.002 M Tl^+. At 5 g/L, aqueous pyrene does not provide a significant contribution to the emission; the decay is single-exponential with $k_{obs} = 3.76 \times 10^6$/s. At 0.2 g/L, however, a biexponential function is required to describe the decay; $k_1 = 3.76 \times 10^6$/s, $k_2 = 2.65 \times 10^7$/s, and $A = 0.729$. The rate constants are equivalent to those predicted from the Stern–Volmer parameters (k_0, k_q, [Tl^+]) for the two environments. The distribution parameter, A, indicates about 73% of the pyrene is associated with the hydrophobic sites at 0.2 g/L G(AM/Sty)-57 and 27% is in the aqueous phase. By comparison, the steady-state III/I ratios from Figure 4 indicate 66% hydrophobic and 34% aqueous, based on the measured maximum and minimum III/I ratios for this system. The surprisingly good agreement between those measured values confirms the establishment of an equilibrium for probe solvation as described by eq 2. The equilibrium constant can be written as follows:

$$K_{eq} = [\text{Py}]_{aq}[\text{sites}]/[\text{Py-sites}] \qquad (4)$$

where the ratio of $[\text{Py}]_{aq}/[\text{Py-sites}]$ is determined to be 0.3/0.7 based on the biexponential fits and the steady-state III/I ratio. Calculation of an equilibrium constant requires the knowledge of the number of available sites that were determined by Poisson kinetics, as discussed below. Above 2 g/L, the contribution to the emission by aqueous pyrene becomes negligible, and the quenching reactions report only on the properties of the site-solubilized probe.

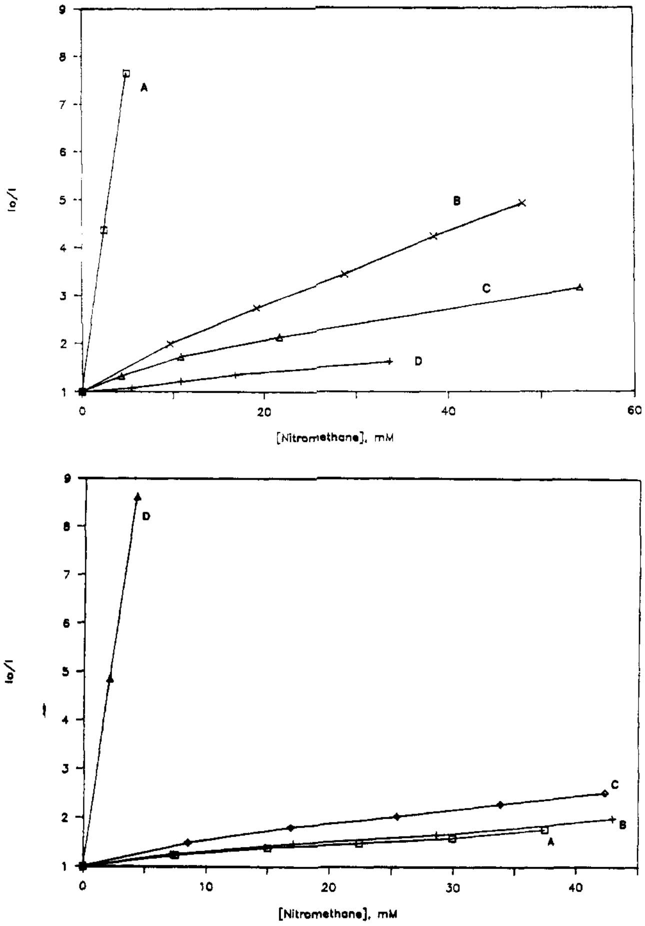

Figure 6. (a, top) Quenching of pyrene steady-state emission in aqueous graft copolymer solutions by nitromethane. (A) water; (B) 3 g/L G(AM/Sty)-35; (C) 3 g/L G(AM/Sty)-57; (D) 3 g/L G(AM/Sty)-112. (b, bottom) Quenching of pyrene by nitromethane in G(AM/Sty) block copolymers and water. Copolymers as described in ref 7. Each was 2.6 g/L copolymer and 7.7×10^{-6} M pyrene. (A) G(AM/Sty)-28, (B) G(AM/Sty)-22, (C) G(AM/Sty)-13, (D) water.

Nitromethane Quenching. The quenching efficiency of pyrene by nitromethane, a neutral aqueous-phase quencher, is also inhibited in graft copolymer solutions compared with that in water. Results of the steady-state quenching by nitromethane are presented in the form of a Stern–Volmer plot in Figure 6a for pyrene in water and in the aqueous graft copolymers. All of the graft copolymers exhibited a substantial decrease in the accessibility of the solubilized probe. In contrast to the block copolymers, the degree of screening shows a definite correlation to the amount of styrene per micelle in the reaction mixtures, which is presumably related to the styrene side-chain length as discussed later. Comparison with Figure 6b reveals that even the "largest" grafts are not as effective in screening the pyrene from the bulk-phase quenchers as the smallest polystyrene blocks. These observations suggest that the graft sites do not have an additional protective mantle of the backbone poly(acrylamide), making their effective size both smaller and more dependent upon the size of the polystyrene units. Thus, the graft styrene chains do not provide centers for coiling of the acrylamide backbone as readily as styrene blocks incorporated within the backbone.

Rigidity of the Host Sites. Site rigidity may also play a role in the accessibility of solubilized hydrophobic probes by aqueous-phase quenchers. The degree of polarization, P (as defined by eq 5 below), provides a qualitative estimate of probe mobility from fluorescence depolarization experiments and, consequently, a comparison of site rigidity.[16]

$$P = \frac{I_{ee} - (I_{eb}/I_{bb})I_{be}}{I_{ee} + (I_{eb}/I_{bb})I_{be}} \tag{5}$$

A high degree of polarization is indicative of a rigid medium, as the probe is unable to reorient on the time scale of fluorescence. The steady-state degree of polarization, P, for 9-methylanthracene varies from 0.14 in a rigid methylcyclohexane glass to 0.00 in liquid methylcyclohexane. The block copolymers were shown to have very rigid sites; $P = 0.13$. An intermediate value, $P = 0.09$, was measured in each of the graft copolymers. The increased depolarization indicates a less rigid site in the graft polymer, i.e., an increased mobility of the probe within these polymers compared to block copolymers and/or a greater rotational freedom of the sites themselves. The greater accessibility of quenchers could conceivably be attributed to the former situation. However, the degree of polarization in the graft copolymers does not vary appreciably from polymer to polymer. Smaller sites would be expected to exhibit greater depolarization if the mobility depended on the physical structure of the sites. The depolarization experiments suggest that the sites themselves are able to reorient independently of bulk polymer motions in the graft copolymers.

Size of Host Sites. A strict comparison between the properties of the graft and the block amphiphilic copolymers requires at least a qualitative knowledge of the sizes of the polystyrene units. The kinetic model derived assuming a Poissonian distribution of hydrophobic quenchers among the available sites has been used to count hydrophobic sites in several micellar systems.[17,18] It was shown to be applicable in the block copolymers of acrylamide and styrene as well.[7] The similarities between the graft and block copolymers suggest this model might prove useful in the determination of the site sizes in the G(AM/Sty) copolymers.

The hydrophobic quencher, 1-nitrodecane (NC_{12}), was added to aqueous solutions of the styrene-grafted poly(acrylamide) copolymers. The negligible solubility of NC_{12} in water, coupled with its ease of solubilization by the graft copolymers, indicated it was distributed solely among the hydrophobic sites. These systems contained a low enough loading of the probe, pyrene, to ensure the probability of two probes occupying the same site was negligible. Thus, ideal conditions for the application of the Poisson kinetic model were achieved. The equations derived for steady-state and transient fluorescence intensity response to added quencher have been developed elsewhere.[18] The important equations are presented below:

transient

$$I(t)/I(0) = \exp\{-n_{av}\}\sum n_{av}{}^{i}/[1 + i(k_q/k_0)]i! \tag{6}$$

where n_{av} = [quenchers]/[sites] and k_0 and k_q are the decay rate constants for the probe in vacant sites and in sites occupied by a quencher, respectively

steady state

$$\ln(I_0/I) = n_{av} \tag{7}$$

where I_0 and I are the steady-state fluorescence intensities in the absence of quencher and with quencher concentration [Q], respectively. Thus, a plot of $\ln(I_0/I)$ vs [Q] yields a straight line with slope = 1/[sites].

Curve fitting of the pyrene fluorescence transient decays to eq 6 in the graft copolymer solutions allowed calculation of the Poisson model parameters, k_0, k_q, and n_{av}. Fits obtained holding k_0 and k_q constant while NC_{12} concentrations were increased are shown in Figure 7. There was no observable static component to the quenching. The application of the Poisson scheme is justified for these systems by the linear increase in n_{av} with quencher concentration, exemplified in Figure 8. The slope of this plot is the reciprocal of the concentration of hydrophobic sites by the Poisson model. From the measured polystyrene content of the copolymers, the average number of styrenes per site, N, was calculated.

Independent experimental confirmation of the site size calculated by the Poisson model was obtained through steady-state illumination measurements. From eq 7 for steady-state fluorescence intensities, the quantity, $\ln(I_0/I)$, should increase linearly with NC_{12} concentrations, where I_0 and I are the steady-state fluorescence intensities without and with quencher, respectively. These graphs are provided in Figure 9. The slopes of these plots allow the independent calculation of the concentration of microdomains, from which N is calculated.

Table III presents a summary of the Poisson parameters calculated from both the steady-state and transient measurements. There is good agreement between the N values calculated by the two methods. However, the calculated number of styrene units per site is considerably lower than the number expected from the styrene monomer occupancy of the CPC micelles in the reaction mixtures.

The lower side-chain length can be understood with regard to the grafting reaction mechanism. The γ radiation directly initiates some polymerization of styrene in the micelles, as do the aqueous radical species. The growing polystyrene chain within a micelle can be terminated by encounters with other radical species including other growing polystyrene chains and hydroxyl radicals. PAM radical sites may also terminate the growing polystyrene chains prematurely, resulting in shorter grafts. Also, these processes effectively decrease the amount of monomer remaining in the micelle that can be initiated by PAM radical sites, decreasing the average size of the grafts. Thermally and photolytically produced hydroxyl radical mechanisms encounter the same difficulties. Since initiation of the styrene polymerization is energetically more favorable than abstraction of an H atom from PAM, and the PAM concentrations cannot be increased without introducing high degrees of cross-linking, experimental conditions were not found to avoid these interferences.

The correlation between larger styrene loadings in the micelles and larger average site size indicates this synthetic route to grafted copolymers provides some measure of control over side-chain lengths. A wide distribution of side-chain lengths may be expected based on the above arguments. Unfortunately, no information on the variations in site sizes evolves from the Poisson counting method. Other models, including the Gaussian Distribution approximation,[19,20] define parameters based upon the distribution of site characteristics. However, first-order decays are obtained in the Stern–Volmer quench-

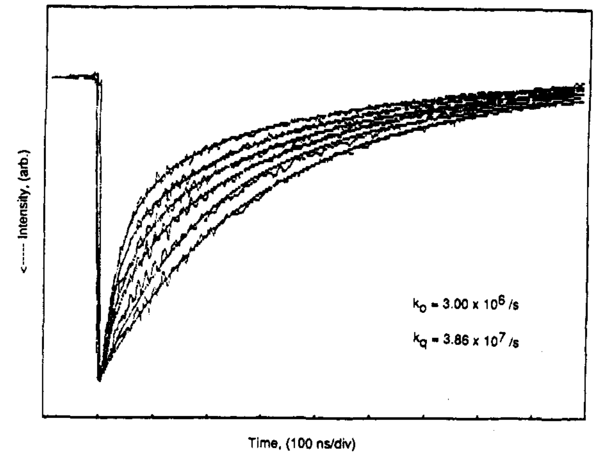

Figure 7. 1-Nitrododecane quenching of pyrene emission: decays and curves fitted to the Poisson kinetic model. Solutions are 5 g/L G(AM/Sty)-57; $k_0 = 3.00 \times 10^6$/s; $k_q = 3.86 \times 10^7$/s; n_{av} values are fitted, and vary with NC_{12} concentration.

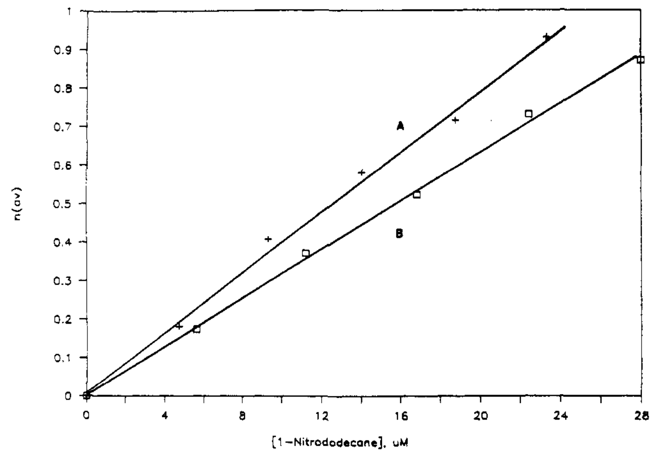

Figure 8. Poisson parameter (n_{av}) from curve fitting versus quencher concentration. (A) G(AM/Sty)-57, 5 g/L; (B) G(AM/Sty)-35, 5 g/L.

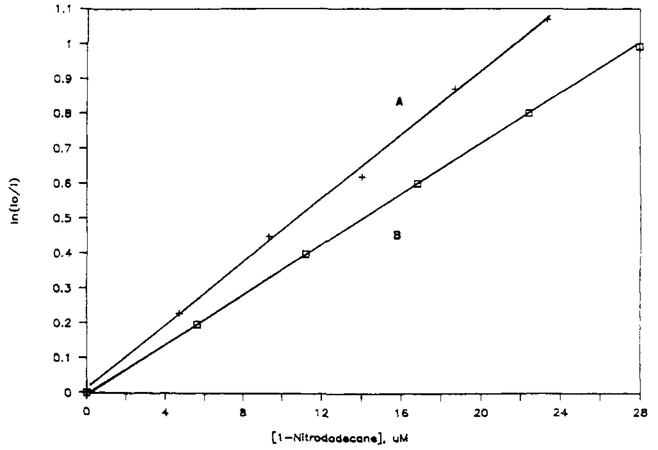

Figure 9. Log plot of steady-state quenching of pyrene in aqueous graft copolymer solutions by NC_{12}. (A) G(AM/Sty)-57, 5 g/L; (B) G(AM/Sty)-35, 5 g/L.

ing. The k_0 values are relatively constant in the different size sites, and little deviation from first-order behavior in k_{obs} as quencher concentrations are increased indicates nearly uniform accessibilities in a given polymer. Therefore, the distributions were concluded to be narrow.

Hydrolyzed Copolymers. Hydrolysis of the graft copolymers was carried out to elucidate the effects of the poly(acrylamide) conformations on the nature of the hydrophobic domains. The hydrolysis reaction converts the poly(acrylamide) backbone to its poly(acrylic acid) derivative, but does not chemically alter the polystyrene side chains. In addition to the changes due to chemical composition, poly(acrylic acid) is known to undergo a conformational change as a function of solution pH.[21] At pH > 7, an open configuration results from the electrostatic repulsion of neighboring charges. A coiled, slightly hydrophobic structure exists at pH < 4 due to the predominance of the acid form and the resulting hydrophobic interactions. The differences in these configurations affect the accessibility of the sites in the block copolymers of acrylamide and styrene.[7]

Table III
Average Site Sizes by the Poisson Model

	steady state		transient		
copolymer (5 g/L)	[sites], μmol/g	N, Sty/site	N, Sty/site	$10^{-6}k_0$, s^{-1}	$10^{-7}k_q$, s^{-1}
G(AM/Sty)-35	5.50	25	23	3.11	3.39
G(AM/Sty)-57	4.67	35	31	3.00	3.86
G(AM/Sty)-85	2.60	42	43	3.15	3.15
G(AM/Sty)-112	2.54	49	55	2.86	4.20

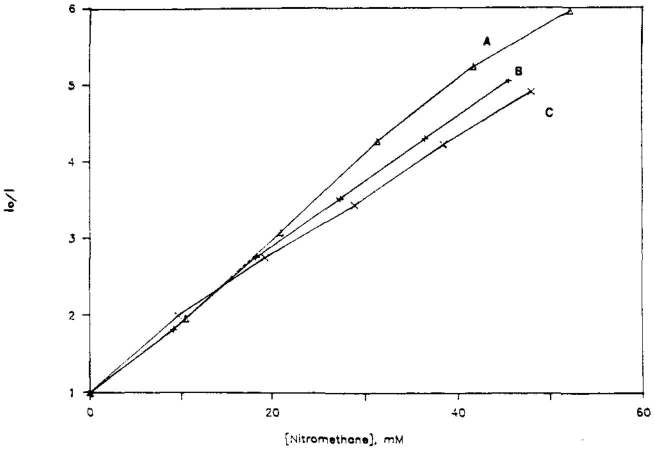

Figure 10. Effects of hydrolysis on the accessibility of sites by nitromethane. (A) 3 g/L hydrolyzed G(AA/Sty)-35; pH = 3; (B) 3 g/L hydrolyzed G(AA/Sty)-35; pH = 8; (C) 3 g/L G(AM/Sty)-35, pH = 7.

Figure 10 reports the steady-state quenching of pyrene by nitromethane in G(AM/Sty)-57 and its hydrolyzed derivative at low and high pH. In contrast to the block copolymers, there is little change in the accessibility for the hydrolyzed derivatives. Also, there is only a slight increase in the quenching as pH is increased. Thus, the hydrophilic polymer backbone, while playing an important role in the screening effect in block copolymers, does not appreciably affect the characteristics of the microdomains in the graft copolymers. The grafted polystyrene, being pendant from rather than incorporated in the polymer backbone, does not provide similar centers for coiling of the main chain. Consequently, the accessibility of the hydrophobic regimes (Figure 5) depends primarily upon the size of the grafted units.

Conclusions

A micellar medium was used to graft polystyrene side chains to a poly(acrylamide) backbone, with some control over the average side-chain lengths. The radiation grafting procedure was inefficient; less than 20% of the styrene monomer was incorporated in the final copolymer products. The average site size, a quantity related to the side-chain lengths, was determined by evaluating the kinetics of fluorescence quenching in terms of the Poisson model. The average lengths were shorter than expected due to side reactions in the radiation grafting.

The grafted polystyrene side chains provided hydrophobic domains for the solubilization of hydrophobic molecules in aqueous solutions. These domains are less rigid and provide less screening from the aqueous phase than those in block copolymers of the same monomers. In contrast to block copolymer sites, the accessibility of the grafted sites depends strongly on the average polystyrene unit size. Hydrolysis and subsequent pH variations do little to change that accessibility, indicating the polymer backbone does not contribute to the hydrophobic regimes. It is concluded that a length of polystyrene grafted as a side chain on a poly(acrylamide) main chain does not provide a center for coiling of the PAM. Pendant side chains provide sites without the assistance of the backbone, but these sites are less able to solvate hydrophobic molecules based on the observed equilibrium between aqueous- and site-solvated pyrene. The equilibrium constant defined from eq 2 was determined for G(AM/Sty)-57 at 0.2 g/L from the calculated distribution of pyrene between the two environments ($[\mathrm{Py}]_{\mathrm{aq}}/[\mathrm{Py{-}sites}] = 0.3/0.7$) and the calculated number of sites from values measured in Table III ($0.2\ \mathrm{g/L} \times 4.67 \times 10^{-6}$ mol sites/g = [sites]). $K_{\mathrm{eq}} = [\mathrm{Py}]_{\mathrm{aq}}[\mathrm{sites}]/[\mathrm{Py{-}sites}] = 4 \times 10^{-7}$ M.

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