Water-Soluble Copolymers. 65. Environmentally Responsive Associations Probed by Nonradiative Energy Transfer Studies of Naphthalene and Pyrene-Labeled Poly(acrylamide-*co*-sodium 11-(acrylamido)undecanoate)

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ABSTRACT: The synthesis and photophysical characterization of terpolymers of acrylamide (AM) with the surface-active monomer sodium 11-(acrylamido)undecanoate (SA) and either [(1-naphthyl)methyl]-acrylamide or [2-(1-pyrenesulfonamido)ethyl]acrylamide are reported. The pronounced spectral overlap between the excited state of the naphthylmethyl group and the ground state of the pyrenesulfonamido group allows analysis by nonradiative energy transfer (NRET) studies. Pyrene-labeled AM/SA copolymers exhibit strong associative behavior in aqueous solution, as evidenced by the viscosity profile as a function of polymer concentration. The concurrent increase in excimer emission with polymer concentration is reflective of interpolymer association between pyrene groups to form the dimeric excited state. NRET analysis of mixed solutions of naphthalene (NRET donor)- and pyrene (NRET acceptor)-labeled copolymers indicates sensitization of pyrene emission by naphthalene labels. The enhancement in acceptor emission at low polymer concentrations implies that intermolecular associations occur at polymer concentrations where association-driven viscosification is not observed. Open, intermolecular associations and inter-polymer NRET are controllable by pH and electrolyte concentration. As ionic strength increases or pH decreases, open associations are broken up. This response had previously been reported as a macroscopic phenomenon by viscosity changes at higher polymer concentrations, but NRET studies confirm that the pH and salt responsiveness inherent to AMSA-based materials is also a molecular-level event.

Introduction

Our research group continues to investigate the photophysical properties of fluorescently labeled, hydrophobically modified, water-soluble polymers.[1−4] Amphiphilic polymers functionalized with hydrophobic groups are of considerable technological interest since micelle-like microdomains can be formed that dissolve small molecule hydrophobes in aqueous media.[5−8] These materials are also known to exhibit strong interactions with a variety of surfactants[9−14] and phospholipids.[15,16]

More recently, studies have focused on fluorescently labeled water-soluble polymers in order to correlate the microscopic, photophysical response with a macroscopic event such as phase separation,[17] aggregation,[18,19] or latex film formation.[20] Nonradiative energy transfer (NRET) is a useful technique for probing associations and structural changes in polymer solutions. The photophysical phenomenon of NRET between a donor and an acceptor covalently attached to a polymer has been termed “photon harvesting” by Webber[21] and the “antenna effect” by Guillet.[22]

In this study, naphthalene and pyrene labels are incorporated into acrylamide/sodium 11-(acrylamido)-undecanoate (AMSA) copolymers.[23,24] Comparison of results from dilute solution NRET studies with data from viscosity and other fluorescence emission studies[25,26] provides a more detailed description of the nature of the associations exhibited by these materials in aqueous media. Photophysical analysis of these fluorescently labeled polyelectrolytes has shown that pH- and salt-dependent intermolecular (open) and intramolecular (closed) associations are both macroscopic and microscopic in nature. NRET between naphthalene and pyrene labels on separate AMSA polymer chains in dilute solution confirms significant variations in the degree of polymer−polymer aggregation as a function of polymer concentration, ionic strength, and pH. Environmental responsiveness measurable by macroscopic techniques is driven by angstrom-level interactions in the dilute state.

The naphthalene/pyrene energy transfer pair has been employed by Winnik to investigate the effects of thermoreversible phase transitions on NRET in aqueous solutions of naphthalene- and pyrene-labeled poly(*N*-isopropylacrylamide).[17,18,27] NRET between terpolymers of acrylamide (AM), sodium 11-(acrylamido)undecanoate (SA), and a fluorescent comonomer is investigated as a function of polymer concentration and donor/acceptor ratio. The fluorescent monomer [(1-naphthyl)methyl]-acrylamide (**1**) (Figure 1) is employed as the energy transfer donor, and [2-(1-pyrenesulfonamido)ethyl]acrylamide (**3**) (Figure 1) acts as the energy transfer acceptor.

Experimental Section

Materials. All reagents and solvents were purchased from Aldrich Chemical Co. (Milwaukee, WI). Acrylamide was recrystallized twice from acetone. Other materials were used as received. Water for synthesis and solution preparation was deionized and possessed a conductance $<10^{-7}$ Ω^{-1} cm.

Sodium 11-(acrylamido)undecanoate. The methods of Gan[23] were employed in the synthesis of SA monomer. Purity was confirmed via NMR and melting point determination.

[(1-Naphthyl)methyl]acrylamide (1). The structures of all fluorescent monomers and model compounds used in this study are shown in Figure 1. The procedure employed by Morishima[28] was followed. Acryloyl chloride was used instead of methacryloyl chloride for the acylation of [(1-naphthyl)-

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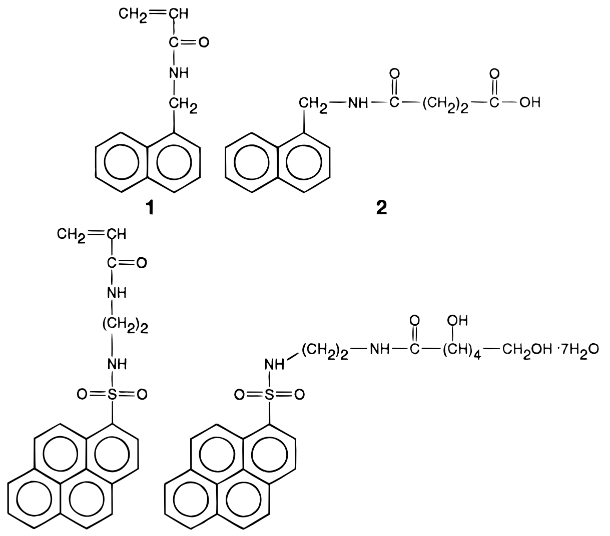

Figure 1. Nonradiative energy transfer donors: [(1-naphthyl)methyl]acrylamide monomer (**1**) and 3-[(((1-naphthyl)-methyl)amino)carbonyl]propionic acid model compound (**2**). Nonradiative energy transfer acceptors: [2-(1-pyrenesulfonamido)ethyl]acrylamide monomer (**3**) and [2-(1-pyrenesulfonamido)ethyl]gluconamide heptahydrate model compound (**4**).

methyl]amine. A yield of 70% was obtained. Purity (>99%) was confirmed by HPLC and ^{1}H NMR.

Succinic Acid *N*-[(1-Naphthyl)methyl]monoamide (2). Into a 25 mL round-bottomed flask fitted with a magnetic stirring bar, N$_2$ inlet, and bubbler was added succinic anhydride (1.0 g, 10 mmol) dissolved in 10 mL DMF. A solution of [(1-naphthyl)methyl]amine (1.3 g, 8.3 mmol) in 3 mL of DMF was added after the succinic anhydride had dissolved. The reaction mixture was allowed to stir for 1 h at room temperature. The off-white slurry was then precipitated in water, and the solids were recovered by vacuum filtration. The solid product was then recrystallized from boiling water after treatment with activated charcoal. HPLC indicated 99+% purity: mp 172−174 °C; ^{13}C NMR (DMSO-d_6) δ 29.2, 30.0, 40.2, 123.4, 125.3, 125.7, 126.1, 127.4, 128.4, 130.8, 133.2, 134.6, 171.0, 173.9.

[2-(1-Pyrenesulfonamido)ethyl]acrylamide (3). The procedure employed by Ezzell and McCormick was followed to give **3** in good yield and purity.

***N*-[2-(1-Pyrenesulfonamido)ethyl]gluconamide Heptahydrate (4).** Model compound **4** was synthesized according to the literature.[1]

Naphthalene- (5) and Pyrene-Labeled (6) Poly(acrylamide-*co*-sodium 11-(acrylamido)undecanoate). A solution of sodium 11-(acrylamido)undecanoate (1.8 g, 6.5 mmol) and acrylamide (9.0 g, 127 mmol) in 340 mL of H$_2$O was added to the reaction flask immersed in a 50 °C water bath. After [2-(1-pyrenesulfonamido)ethyl]acrylamide (0.51 g, 1.3 mmol) or [(1-naphthyl)methyl]acrylamide (0.27 g, 1.3 mmol) finely ground with a mortar and pestle was added to the flask, the solution was degassed with nitrogen. After 1 h, sodium dodecyl sulfate (21.7 g, 75.2 mmol) was added. At this point direct bubbling of nitrogen through the solution was stopped to prevent excessive foaming. After the solution was stirred under nitrogen for 3 h, most of the fluorescent comonomer had dissolved into SDS micelles. A degassed solution of potassium persulfate (50 mg, 0.19 mmol) in 5 mL of H$_2$O was then injected into the monomer/surfactant solution. After stirring under nitrogen for 3 h, the viscous polymer solution was added to 1400 mL of acetone to yield an off-white rubbery precipitate. The polymer was washed with refluxing methanol for 16 h in a Soxhlet extractor to remove residual monomer and surfactant. Yields of >70% were obtained in both syntheses.

Instrumentation. A Bruker AC-200 NMR spectrometer was used to obtain ^{1}H and ^{13}C NMR spectra. Molecular weights were determined with a Chromatix KMX-6 low-angle laser light scattering photometer equipped with a 633 nm He/Ne laser. Refractive index increments (dn/dc) were measured with a Chromatix KMX-16 laser differential refractometer. UV−vis spectra were recorded with a Hewlett Packard 8452A diode array spectrophotometer. HPLC was carried out on a Hewlett Packard 1050 Series chromatograph equipped with a photodiode array UV detector, an Alltech Versapak C$_{18}$ reversed-phase column, and methanol as the mobile phase. Steady-state fluorescence spectra were measured on a Spex Fluorolog-2 fluorescence spectrometer and a DM3000F data system. Excitation and emission slit widths of 1 mm and right angle geometry were employed.

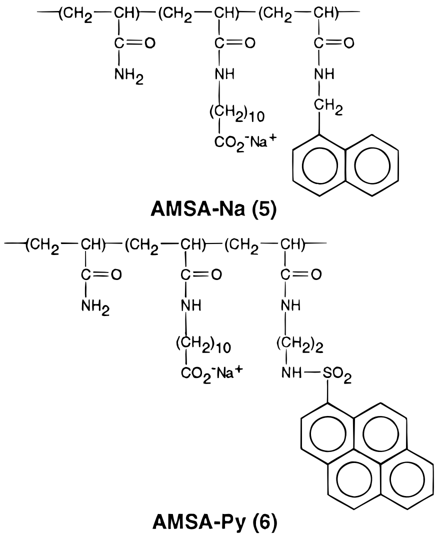

Figure 2. Naphthalene-labeled polymer **5** and pyrene-labeled polymer **6**.

Sample Preparation. Polymer solutions were prepared by mixing stock solutions of naphthalene- and pyrene-labeled polymer in deionized water. For the salt studies, aqueous 5 M NaCl solution and deionized water were added to give the desired polymer and electrolyte concentrations. Solution pH was adjusted by dilution with its respective citric acid/disodium phosphate (Na$_2$HPO$_4$) buffer.[29]

For the three-dimensional surface plots, mixed solutions of naphthalene- and pyrene-labeled polymer were diluted with deionized water, NaCl solution, and buffer to give total polymer concentrations of 0.016−0.08 g/dL in 0.016 g/dL increments. A solution at each concentration was prepared with NaCl concentrations of 0−0.5 M in 0.1 M increments or pH 4−8 in increments of 1 pH unit.

Results and Discussion

Polymer Syntheses. The copolymerization of acrylamide (AM) with sodium 11-(acrylamido)undecanoate (SA) proceeds rapidly under micellar conditions. When a growing radical encounters a micelle that contains vinyl monomers, the localized monomer concentration is very high. High local monomer concentration and orientation lead to rapid propagation. Recruitment of additional monomer to polymerizing hemimicelles has also been proposed.[30,31] Thus, a rapid overall polymerization rate that yields high molecular weight polymer results. The molecular weights of terpolymers **5** and **6** (Figure 2) are reported in Table 1. Molecular weights are somewhat higher than that reported for SA homopolymer and AM/SA copolymer;[23,24] this may result from the high purity of the monomers employed.

The label incorporation for both terpolymers is also shown in Table 1. Molar SA incorporation is assumed to equal SA mole fraction in monomer feed for this study. Gan has shown stoichiometric incorporation of SA repeat units into AM/SA copolymers,[24] and NMR analysis of a copolymer containing 10 mol % SA has

Table 1. Terpolymer Molecular Weight and Composition

polymer	$10^{-6}M_w$	AM content (mol %)[a]	SA content (mol %)[a]	label content (mol %)[b]
5 (AMSA/Na)	2.7	≈94	5	0.6
6 (AMSA/Py)	1.8	≈94	5	0.6

[a] SA mole fraction in monomer feed. [b] Determined from UV−vis studies.

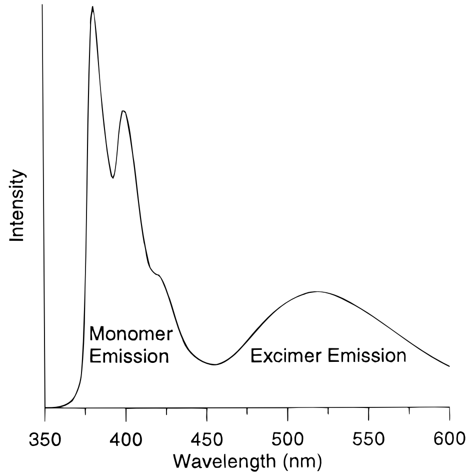

Figure 3. Fluorescence emission spectrum of pyrene-labeled polymer **6**. Polymer concentration: 0.052 g/dL in H_2O. Chromophore concentration: 3.3×10^{-5} M. Excitation wavelength: 340 nm. pH: 7.

supported this assumption.[26] When 5 mol % SA content was inferred, UV analysis indicated 0.6 mol % labeling of both naphthalene and pyrene onto their respective copolymers. This is calculated from the molar absorptivity, ϵ, of model compounds **2** (6800 M^{-1} cm^{-1} at 282 nm) and **4** (24 000 M^{-1} cm^{-1} at 350 nm). Both polymerizations utilized 1 mol % fluorescent monomer in the monomer feed, but only 60% of the monomer is incorporated. This is not an unusual result. Ezzell and McCormick also reported low pyrene comonomer **3** content in acrylamide/**3** copolymers synthesized by homogeneous and microheterogeneous techniques.[1] Pyrene and naphthalene labels may not be sufficiently soluble in SDS micelles, and incomplete dissolution in aqueous SDS would result.

Viscosity and Excimer Emission Studies. Our research group has utilized excimer emission studies of polyaromatic chromophores to probe the solution behavior of other amphiphilic polymers.[1−4] Naphthalene or pyrene groups bound to polymer interact in aqueous media to form a sandwich-like dimeric conformation (excimer). Hydrophobic association can drive these interactions; thus, changes in excimer relative to "monomer" emission parallel changes in macroscopic solution properties such as viscosity. A fluorescence emission spectrum of pyrene-labeled polymer **6** is shown in Figure 3. The peaks at 380, 400, and 420 nm correspond to the fluorescence emission of isolated pyrenes (monomer emission). The broad, structureless band centered at 520 nm results from excimer emission. Although we have previously noted naphthalene excimer emission in naphthyl-labeled acrylic acid and methacrylic acid copolymers,[3,4] naphthalene excimer does not form to any significant degree in these polymers. Other water-soluble polymers labeled with the naphthylmethyl moiety have also failed to form excimer in measurable amounts.[32] The proximity of the label to the polymer backbone may hinder the motion necessary for excimer formation.

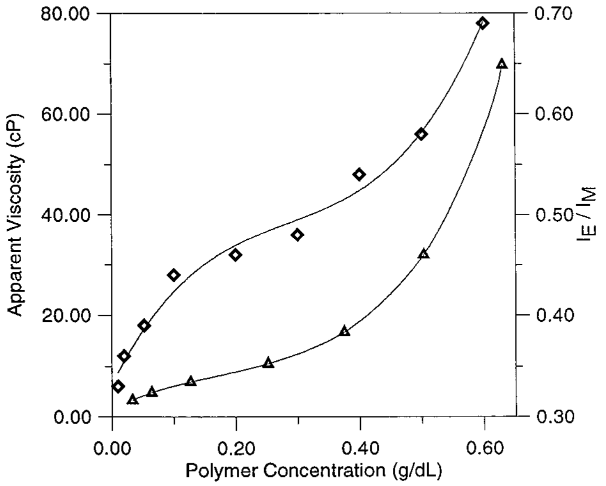

Figure 4. Apparent viscosity (△) and excimer emission/monomer emission (I_E/I_M) (◇) as a function of polymer **6** concentration in H_2O. (I_E/I_M = intensity at 519 nm/intensity at 400 nm.) pH: 7.

If the intensity of pyrene excimer emission relative to that of the monomer emission (I_E/I_M; I_E = intensity at 519 nm, I_M = intensity at 400 nm) is measured as a function of polymer concentration, an intermolecularly associating system may exhibit an increase in I_E/I_M. Both pyrene-labeled polyacrylamide and AMSA−Py obey this trend.[2,25,26] I_E/I_M and apparent viscosity of AMSA−Py are plotted as a function of polymer concentration in Figure 4. The apparent viscosity response displays an upward curvature with an onset at about 0.3−0.4 g/dL; acrylamide homopolymer does not exhibit this response below 0.6 g/dL. I_E/I_M steadily increases as well, and interpolymer association appears to predominate in deionized H_2O.

Intramolecular associations are also reflected by changes in I_E/I_M. As NaCl is added to solutions of SA copolymers or pH is lowered, the shielding or elimination of electrostatic repulsions between carboxylate groups of the SA unit leads to coil shrinkage; viscosity decreases and I_E/I_M increases in these systems.[25,26,33] As coil dimensions shrink, intrapolymer associations between chromophores that drive excimer formation are augmented.

Nonradiative Energy Transfer Studies. According to Förster,[34] the probability of a nonradiative transfer of excitation energy from one chromophore to another (NRET) has a sixth power dependence expressed as eq 1, where E is the energy transfer ef-

$$E = \frac{{R_0}^6}{{R_0}^6 + R^6} \tag{1}$$

ficiency, R_0 is the energy transfer donor/acceptor separation distance for which E = 0.5, and R is the donor/acceptor separation distance. The sixth power dependence arises from dipole−dipole interactions between chromophores participating in NRET. A simplified NRET mechanism is described in eq 2, where D is the

$$D^* + A \rightarrow D + A^* \tag{2}$$

NRET donor, A is the NRET acceptor, and an asterisk denotes the excited state. For NRET to occur to any significant degree, the excited state energy of an NRET donor must approximate that of the ground state energy of the NRET acceptor; this is illustrated experimentally

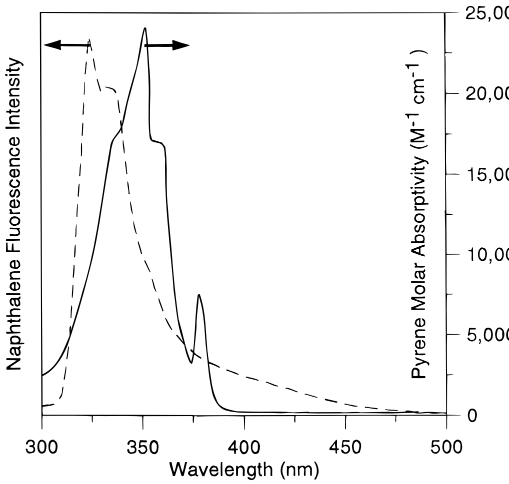

Figure 5. Spectral overlap of naphthalene model **2** fluorescence (- - -) with pyrene model **4** UV absorbance (—). Excitation wavelength: 290 nm. [Naphthalene model **2**] = 7 × 10^{-6} M. pH: 7.

as the spectral overlap of donor fluorescence emission and acceptor UV–vis absorbance, as shown in Figure 5. Overlap occurs between 300 and 400 nm and is readily quantitated as J, the overlap integral

$$J = \int_0^\infty \lambda^4\, I(\lambda)\, \epsilon(\lambda)\, d\lambda \qquad (3)$$

where λ is the wavelength, I is the fluorescence intensity of NRET donor, and ϵ is the molar absorptivity of NRET acceptor. I is normalized such that

$$\int_0^\infty I(\lambda)\, d\lambda = 1 \qquad (4)$$

If J is known, R_0 is readily calculated from eq 5, where

$$R_0^{\,6} = \frac{9000(\ln 10)\kappa^2 \Phi_D J}{128\pi n^4 N} \qquad (5)$$

κ^2 is a function of the mutual orientation of donor and acceptor and is usually assumed to equal $^2/_3$ for random orientation in fluid media, Φ_D is the emission quantum yield of the donor in the absence of NRET acceptor, n is the solvent refractive index, and N is Avogadro's number.

For the naphthylmethyl/pyrenesulfonamido donor/acceptor pair, $J = 1.90 \times 10^{-14}$ cm^6 mol^{-1}, $\Phi_D = 0.11$, and $R_0 = 26.6$ Å.[32] These values are in agreement with other naphthalene/pyrene combinations.[17,18]

If a constant naphthalene/pyrene ratio is employed, as in the salt and pH studies, changes in NRET are proportional to the ratio of pyrene emission to naphthalene emission.

$$\Delta\mathrm{NRET} \propto \Delta\frac{I_{\mathrm{Py}}}{I_{\mathrm{Na}}} \qquad (6)$$

where I_{Py} represents pyrene emission intensity and I_{Na} represents naphthalene emission intensity. In this study, fluorescence emission intensities at 340 and 400 nm were assigned to naphthalene and pyrene fluorescence, respectively. The ratio of the fluorescence intensity of the acceptor to the donor has been used in previous literature to observe molecular interactions. Morishima[35] followed interpolymer NRET of fluorescently labeled amphiphilic polyelectrolytes by measuring the ratio of the fluorescence intensity of pyrenylmethyl emission relative to that of naphthylmethyl emission. $I_{\mathrm{Py}}/I_{\mathrm{Na}}$ was then referenced to an $I_{\mathrm{Py}}/I_{\mathrm{Na}}$ value where no measurable associations take place. A similar ratio was used by Morawetz[36] to follow the compatibility of polymers labeled with naphthalene and anthracene.

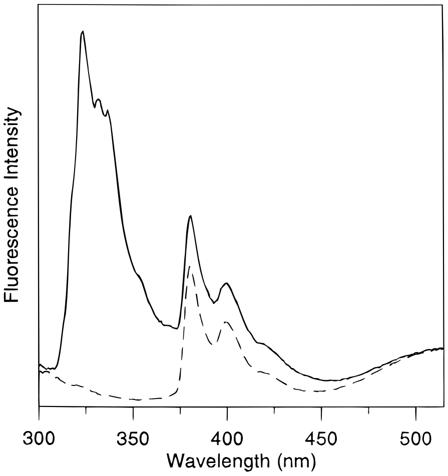

Figure 6. Fluorescence intensity of 0.01 g/dL pyrene-labeled polymer **6** (- - -) and mixed solution of 0.01 g/dL pyrene-labeled polymer **6** with 0.07 g/dL added naphthalene-labeled polymer **5** (—). Excitation wavelength: 290 nm. pH: 7.

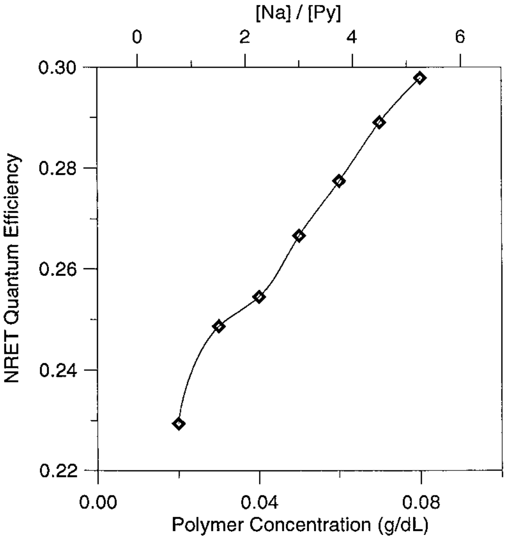

Figure 7. Nonradiative energy transfer quantum efficiency of mixed AMSA–Na/AMSA–Py solutions as a function of polymer concentration and naphthalene/pyrene ratio. Excitation wavelength: 290 nm. pH: 7.

Nonradiative Energy Transfer in Deionized Water. Qualitatively, NRET occurs as an increase in pyrene fluorescence in the presence of the naphthalene label, as shown in Figure 6. The spectrum represented by the dashed line depicts the fluorescence emission of a 0.01 g/dL solution of AMSA–Py, and the solid line spectrum is that of a 7/1 (w/w) mixed solution of AMSA–Na/AMSA–Py. The pyrene label concentration is the same in both solutions, yet the intensity of the characteristic pyrene emission bands increases considerably in the mixed solution. This result indicates a sensitization of pyrene emission by naphthalene labels in solution. This photophysical response may be attributable to interpolymer NRET between naphthalene and pyrene.

In Figure 7, NRET quantum efficiency is plotted vs increasing polymer concentration and naphthalene/pyrene ratio ([Na]/[Py]). As polymer concentration increases, so does [Na]/[Py]. This is accomplished by preparing samples of mixed polymer solutions of AMSA−Na and AMSA−Py. AMSA−Py concentration remains constant at 0.01 g/dL, and AMSA−Na concentration varies from 0.01 to 0.07 g/dL. In this manner, the total polymer concentration increases from 0.02 to 0.08 g/dL. It is quite apparent that an increase in polymer concentration (and in [Na]/[Py]) increases NRET. This results from a decrease in the average naphthalene/pyrene separation distance. The photophysical response may be explained by interpolymer aggregation via hydrophobic association between naphthalene and pyrene labels. This result is similar to that reported by Ringsdorf and Winnik in a study of naphthalene- and pyrene-labeled, hydrophobically-modified poly(*N*-isopropylacrylamide) (PNIPAM).[18] As the naphthalene/pyrene ratio is increased with polymer concentration, pyrene emission increases and I_E/I_M decreases. This has been attributed to pre-C* interpolymer aggregation of naphthalene- and pyrene-labeled polymer. Hydrophobic association of naphthalene-labeled polymer with pyrene-labeled polymer would result in the breakup of intermolecularly aggregated pyrene-labeled PNIPAM. Labeling in our systems may be sufficiently low such that association between hydrophobic groups on the same chain becomes less favorable than interpolymer chromophore aggregation. The local concentration of surfactant groups along the polymer chain is also probably not sufficiently high for extensive intramolecular or closed association in deionized water. The polymer would then behave as an extended polyelectrolyte rather than as a compact, globular "polysoap" with water as a poor solvent,[37] and interpolymer association through naphthalene and pyrene labels becomes feasible.

Electrolyte and pH Effects on Nonradiative Energy Transfer. It has been shown that the shielding or elimination or electrostatic repulsive forces in AMSA copolymers induces a pronounced coil contraction. In the labeled systems that we have investigated, this is observed as an increase in I_E/I_M.[25,26] The decrease in viscosity accompanied by an increase in intramolecular associations alludes to a mechanism whereby intramolecular interactions occur at the expense of intermolecular events. This proposed open-closed association transition is supported by data from fluorescence quenching studies of aqueous AMSA−Py solutions. Salt-induced reductions in quencher-label migration imply that mixed micelles formed by pyrene and SA repeat units become more organized as ionic strength increases.

As NaCl concentration increases, viscosity decreases, and excimer yield is enhanced in aqueous AMSA−Py solutions. If changes in the degree of interpolymer association are occurring on the molecular level, NRET should change as a function of electrolyte concentration. A three-dimensional polymer concentration−[NaCl]−I_{Py}/I_{Na} plot at a constant Na/Py ratio of 2.25 is shown in Figure 8. NRET increases slightly with polymer concentration for a given NaCl concentration. The weak response may be attributable to the low Na/Py ratio employed. The quantum yield of the naphthylmethyl group is low (0.11) even in the absence of pyrenesulfonamido chromophores, and any detectable sensitization of pyrene emission by naphthalene would result from interaction between chromophores on different polymer chains. For a given polymer concentration, NRET drops considerably with increasing [NaCl]. The observed changes in NRET efficiency indicate that polymer chains aggegate in a concentration regime that is not detectable by macroscopic methods such as viscometry and that these associations are broken up by salt-triggered coil shrinkage.

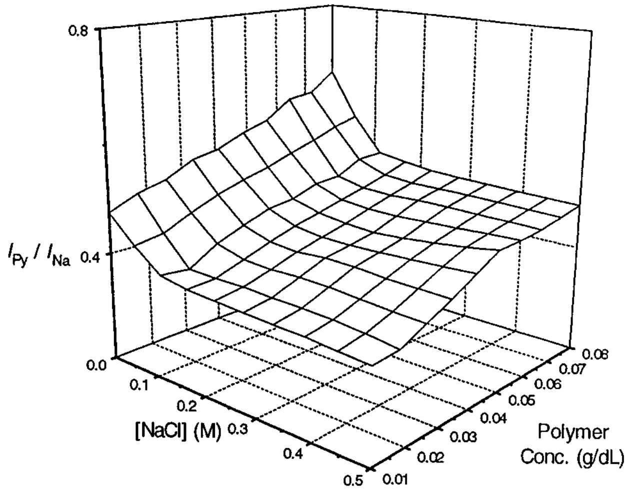

Figure 8. Pyrene emission/naphthalene emission ratio (I_{Py} = pyrene emission at 400 nm, I_{Na} = naphthalene emission at 340 nm) of 3/1 (w/w) AMSA−Na/AMSA−Py as a function of polymer concentration and NaCl concentration. Excitation wavelength: 290 nm. pH: 7.

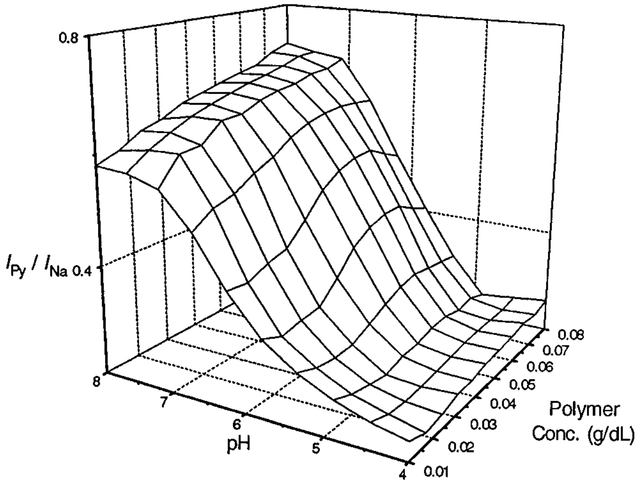

Figure 9. Pyrene emission/naphthalene emission ratio (I_{Py} = pyrene emission at 400 nm, I_{Na} = naphthalene emission at 340 nm) of 3/1 (w/w) AMSA−Na/AMSA−Py as a function of polymer concentration and pH. Excitation wavelength: 290 nm.

The effect of conformation-driven breakup of interpolymer association is even more pronounced with changes in pH. Previous studies of pyrene-labeled AMSA copolymer have shown that I_E/I_M increases dramatically as pH is lowered.[25,26] Viscosity also decreases through this pH range. The photophysical response suggests a compactness that brings pyrenes within a polymer chain in closer proximity to one another. However, the excimer yield studies do not specifically address the effects of acid on intermolecular aggregation.

A three-dimensional polymer concentration−pH−I_{Py}/I_{Na} plot is shown in Figure 9. NRET does not significantly increase for a given pH, but an appreciable transition in NRET efficiency occurs from pH 4 to 8 for a given polymer concentration. The change reflects a transition from intra- to interpolymer association as the polymer conformation changes from that of a compact

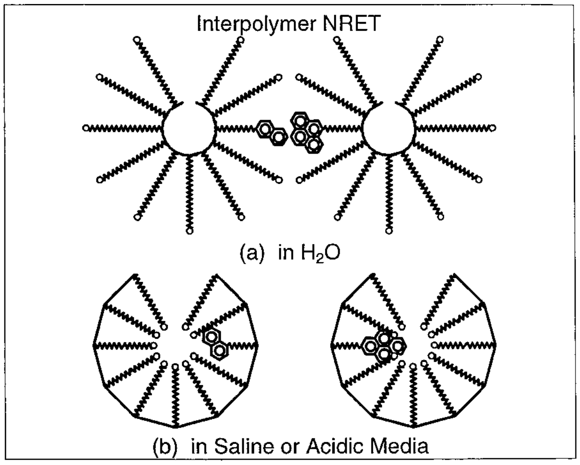

Figure 10. Proposed mechanism of inter/intramolecular association and effects on NRET response. (a) Intermolecular association in deionized water. (b) Intramolecular compartmentalization of surfactant groups and chromophores with added electrolyte or at low pH.

structure stabilized by intramolecular micellization to a more open, random coil conformation.

The photophysical response as a function of salt concentration and pH verifies that the degree and nature of intra- and interpolymer associations are controllable by environmental changes. The effects of acidic and saline media are conceptually illustrated in Figure 10. When a more open conformation is adopted, interpolymer hydrophobic associations between labels occur, and NRET increases in mixed solutions of singly labeled polymers. As the polymer chain contracts and labels sequester themselves within more organized micellar microdomains, donor–acceptor interactions diminish. The pronounced pH and salt responsiveness has important ramifications with respect to the potential applicability of such materials as associative thickeners, and as vehicles for controlled release and sequestration.

Conclusions

This study confirms the profound pH and salt responsiveness of acrylamide polymers with a low substitution (5 mol %) of the surface-active monomer sodium 11-(acrylamido)undecanoate (SA). Viscosity studies had indicated that aqueous solutions of AM/SA copolymers labeled with pyrene exhibit extensive considerable viscosification relative to unmodified polymer. Concurrent increases in I_E/I_M with polymer concentration support an association mechanism involving chromophore groups on different polymer chains. Excimer yield is enhanced by the addition of electrolyte or acid.

Nonradiative energy transfer (NRET) studies of mixed solutions of naphthalene- and pyrene-labeled AMSA copolymer as a function of polymer concentration, electrolyte concentration, and pH support the mechanism of a salt- and pH-triggered transition from open to closed association. In deionized water and at high pH, interpolymer NRET between naphthalene and pyrene groups is much higher than at low pH and high electrolyte concentration. The conformational changes that occur on the angstrom level are not observable by macroscopic techniques. However, the salt- and pH-induced microdomain structuring reported by photophysical analysis is highly significant in the development of structure/property relationships for applications in aqueous media. NRET studies have effectively shown that changes in the medium which affect the macroscopic solution properties of AMSA copolymers also trigger changes in molecular-level microdomain organization.

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