Water-Soluble Polymers. 78. Viscosity and NRET Fluorescence Studies of pH-Responsive Twin-Tailed Associative Terpolymers Based on Acrylic Acid and Methacrylamide

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Received September 7, 2000; Revised Manuscript Received December 7, 2000

ABSTRACT: A series of terpolymers containing acrylic acid (AA), methacrylamide (MAM), and a twin-tailed hydrophobic monomer (DiC_6AM, DiC_8AM, or $DiC_{10}AM$) were synthesized using micellar polymerization methods. These polymer systems were characterized using light scattering, viscometry, and fluorescence methods. Viscosity studies indicate that increasing the nonpolar character of the hydrophobic monomer (longer chain length or twin tailed vs single tailed) results in enhanced viscosity in aqueous solutions. The terpolymer with the highest hydrophobicity (MAM/AA/$DiC_{10}AM$ terpolymer) exhibited the most pronounced viscosity increase with polymer concentration and thus the best associative thickening. Fluorescence nonradiative energy transfer measurements performed on this terpolymer indicate the onset of association (c^*) at a concentration of ∼0.1 g/dL. Also, changes in the energy transfer efficiency and viscosity behavior as a function of pH are consistent with a concentration-dependent transition from closed to open associations.

Introduction

The incorporation of hydrophobic groups within a hydrophilic polymer can dramatically alter its solution properties in an aqueous environment. Water forms an organized, icelike structure around hydrophobic molecules that is entropically unfavorable. As a result, water forces hydrophobic molecules together so that the amount of water structuring is minimized. If hydrophobes are covalently bound to a hydrophilic polymer, associations of hydrophobic moieties either within or between polymer chains occur in aqueous solution. The nature of the associations depends on a variety of factors including the degree of hydrophobic modification, microstructure, and polymer concentration. At the extremes, two distinct types of polymer behavior are observed based on intrapolymer (closed) or interpolymer (open) association.

Intrapolymer hydrophobic associations become more prominent at low polymer concentrations and high hydrophobe density along the polymer backbone. A compact, globular conformation is often adopted in these systems, and the organized, hydrophobic microdomains that form have micelle-like properties. Polymers with this characteristic have been termed “polysoaps”[1,2] and “polymeric micelles”.[3,4] These systems were classically studied by Strauss et al.[1,2] utilizing a series of poly(4-vinylpyridine)s quaternized with ethyl and dodecyl (C_{12}) groups. More recently, McCormick[5,6] and Morishima[7,8] have examined a number of polymer systems exhibiting predominantly intrapolymer association behavior.

Interpolymer associations, on the other hand, usually occur at lower hydrophobe/hydrophile ratios and at polymer concentrations sufficient for chain overlap. Hydrophobic clustering at network junctions is responsible for the dramatic increase in aqueous solution viscosity. These systems, termed “associative thickeners” (ATs), have desirable rheological properties including shear-induced network dissociation that have been exploited in formulation of “smart” fluids in oil field, coatings, and pharmaceutical applications.

Among the first ATs reported in industrial[9,10] and academic[11,12] laboratories were “microblocky” amphiphilic copolymers prepared by micellar polymerization. Later other AT polymers, including the hydrophobically modified, ethoxylated urethane polymers (HEURs) and the hydrophobically modified alkali-swellable emulsion polymers (HASEs), were also synthesized and examined in great detail.[13,14] The behavior of microblocky ATs, however, is less well understood.

The synthesis of microblocky ATs using micellar polymerization is attractive from a commercial standpoint since a wide range of amphiphilic copolymers are possible utilizing free radical polymerization directly in water. In this technique an external surfactant (above its cmc) is added to solubilize the hydrophobic monomer. Typically, water-soluble free radical initiators are used, with polymerization of the hydrophilic monomer occurring in the aqueous phase and polymerization of the hydrophobic monomers occurring in the micellar phase. The microblocky hydrophobe incorporation which results in these systems was first suggested by Peer[15] and later demonstrated by McCormick and Ezzel using pyrenesulfonamide-labeled (APS) monomers.[16,17] This phenomenon has primarily been ascribed to the microheterogeneous nature of the system.

The surfactant in micellar polymerization serves to solubilize of the hydrophobic monomer and control the hydrophobic sequence length. By varying the surfactant/hydrophobe ratio, hydrophobic sequence length can be adjusted. Photophysical studies conducted on copolymers of acrylamide and pyrene labeled comonomers have shown that sequence length of the hydrophobic blocks decreases with increasing surfactant/hydrophobe ratio.[18] Similarly, lower surfactant/hydrophobe ratios result in larger hydrophobic blocks. However, block lengths do not always correspond to the numbers of hydrophobic monomers per micelle. Using NMR techniques, Candau and Selb[19] have reported compositional drift behavior for micellar polymerizations incorporating *N*-monoalkyl hydrophobic monomers. However, when

10.1021/ma001549l CCC: $20.00

N,N-disubstituted acrylamides were utilized, no compositional drift was observed. This differential behavior was attributed to the nonpolar environment of the micelles, which, through hydrogen bonding, enhances the reactivity of the polar N-monosubstituted species but leaves N,N-disubstituted hydrophobic comonomers unaffected.[19]

Another benefit realized by incorporating *N*,*N*-dialkylacrylamide hydrophobes into a polymer chain using micellar polymerization is that the resulting polymers are often much better associative thickeners than their monoalkylacrylamide counterparts.[20-22] *N*,*N*-Dihexylacrylamido hydrophobes increase the associative behavior of hydrophobically modified polyacrylamides over that of *N*-monohexylacrylamido hydrophobes.[20] The stronger intermolecular association behavior can be attributed to the greater hydrophobicity and increased microblocky character of the polymers. Thus, micellar polymerization of N,N-disubstituted hydrophobic comonomers not only allows for the synthesis of homogeneous polymer samples but also provides a new technique for increasing associative thickening efficiency of microblocky polymers.

On the basis of the above work, our group recently has been investigating hydrophobic twin-tailed monomers (from *N*,*N*-dihexylacrylamide up to *N*,*N*-didecylacrylamide) and ionizable comonomers for affording pH responsive associative thickeners.[21,22] One major objective is to optimize an associative thickening system by incorporating twin-tailed hydrophobic monomers of varied lengths into a hydrophilic backbone in a microblocky fashion. In this paper we demonstrate the existence of reversible, stimuli-responsive microdomains as measured by viscometric and photophysical (fluorescence) techniques. A further objective is the determination of c^* for these systems using nonradiative energy transfer (NRET). Our group has previously used NRET to study the transition from intrapolymer (closed) to interpolymer (open) association.[5,6] In this paper we use a similar technique to examine the behavior of twin-tailed associative polymers.

Experimental Section

Materials and Monomers. All chemicals were purchased from Fisher Chemical Co. or Aldrich Chemical Co. at the highest purity available. Purification of VA-044 and methacrylamide (MAM) was accomplished by recrystallization from methanol and acetone, respectively. Acrylic acid (AA) was purified by vacuum distillation. The twin-tailed hydrophobic monomers, dihexylacrylamide (DiC_6AM), dioctylacrylamide (DiC_8AM), and didecylacrylamide ($DiC_{10}AM$), were prepared using a similar procedure to that already previously reported.[11,12,23]

Dansyl-2-aminocaprylic acid and succinic acid *N*-(1-naphthylmethyl)monoamide were chosen as model compounds. The former was purchased from Sigma and was recrystallized from methanol. The nonradiative energy transfer (NRET) donor used for labeling the copolymer backbone was 7-(1-naphthylmethoxy)heptylamine synthesized using the methods of McCormick and Chang.[24] The NRET acceptor, 8-dansyloctylamine, was synthesized as described by Shea et al.[25] The structures of these chromophores are shown in Figure 1.

Polymer Synthesis. Co- and terpolymers were synthesized by micellar polymerization using SDS as the surfactant to solubilize the hydrophobic comonomer and VA-044 as the free-radical initiator. The total monomer concentration was held constant at 0.44 M and the [monomer]/[initiator] ratio at 2000. Also, the hydrophobic monomer content and the surfactant-to-hydrophobe ratio (SMR) were maintained at 1 mol % and 25, respectively. The reactions were performed for 3−6 h at 50 °C. A typical micellar polymerization is shown in Figure 2 for the synthesis of a terpolymer with $MAM/AA/DiC_{10}AM$ at a feed ratio of 49/50/1.

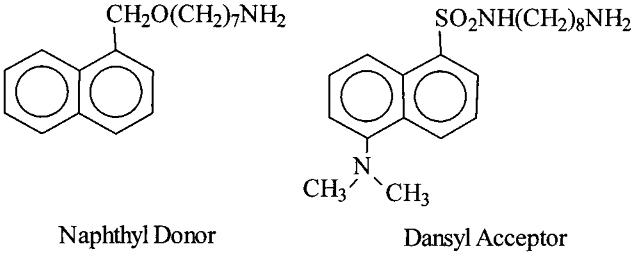

Figure 1. Fluorescence chromophores utilized for fluorescence energy transfer experiments.

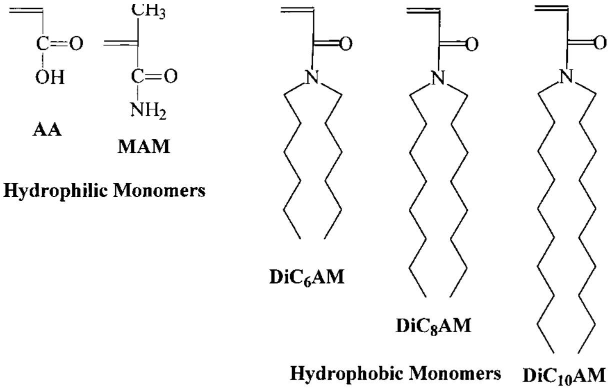

Figure 2. Hydrophilic monomers: acrylic acid (AA) and methacrylamide (MAM). Hydrophobic monomers: *N*,*N*-dihexylacrylamide (DiC_6AM), *N*,*N*-dioctylacrylamide (DiC_8AM), and *N*,*N*-didecylacrylamide ($DiC_{10}AM$).

Table 1. Synthetic Parameters Utilized for Twin-Tailed Micellar Polymerizations

sample	[SDS] (M)	SMR	MAM (mol %)	AA (mol %)	hydrophobe (1 mol %)
$MAM/AA/DiC_6AM$	0.10	25	49.0	50.0	DiHexAM
$MAM/AA/DiC_8AM$	0.10	25	49.0	50.0	DiOctAM
$MAM/AA/DiC_{10}AM$	0.10	25	49.0	50.0	DiDecAM

In a typical polymerization, deionized water (600 mL) was sparged with N_2 for 30 min, and SDS (18.0 g) was added with stirring under N_2 purge. DiC_6AM (0.592 g) was then added with continued stirring for approximately 1 h or until the solution cleared. MAM (10.51 g) and AA (8.90 g) were then dissolved in the reaction mixture. The pH of the reaction feed was measured and kept below 4.5. To initiate polymerization, VA-044 (0.039 g) was dissolved in 5 mL of deoxygenated, deionized water and injected into the polymerization vessel. The reaction was allowed to proceed under N_2 for 6 h after which the terpolymer was precipitated into 1000 mL of methanol. The terpolymer was then washed with fresh methanol and dried overnight in a vacuum oven. Further purification was achieved by redissolving the terpolymer in water and dialyzing for 5 days against deionized water using Spectra Por No. 4 dialysis tubing with a molecular weight cutoff of 12 000−14 000. The purified polymer samples were then freeze-dried to a constant weight. Synthetic parameters for the terpolymers made in this study appear in Table 1.

Fluorescence Labeling. The $MAM/AA/DiC_{10}AM$ terpolymer was dissolved in a 70/20 (v/v) dioxane/formamide mixed solvent. The appropriate fluorescence label was added to the solution along with the typical dicyclohexylcarbodiimide (DCC)/(dimethylamino)pyridine (DMAP) mixture, and the solution was heated to 60 °C and allowed to react overnight. The details of this reaction are given elsewhere.[26] The resulting solutions were then poured into Spectra Por No. 4 dialysis tubing and allowed to dialyze against deionized water for 15 days. The purified, labeled polymer samples were then freeze-dried to a constant weight.

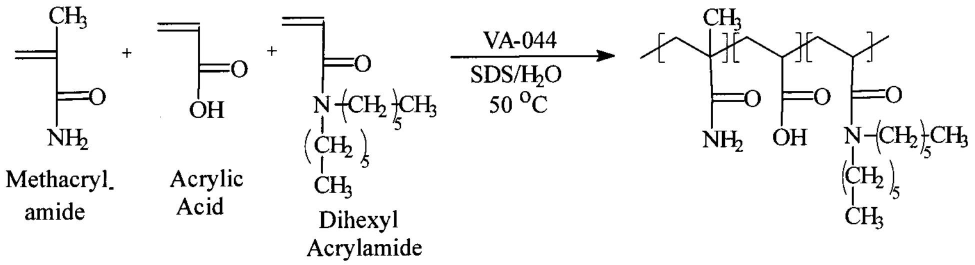

Figure 3. Micellar polymerization of methacrylamide, acrylic acid, and dihexyl acrylamide.

Analytical Methods. *Light Scattering Measurements.* Measurements of d*n*/d*c* were performed with a Chromatix KMX-16 laser differential refractometer ($\lambda = 632.8$). MAM/AA terpolymer d*n*/d*c* values and apparent molecular weights were determined in 0.5 M NaCl. Dust was removed from samples via centrifugation in a Brinkmann Instruments (5415C) Eppendorf microcentrifuge at 16 000*g* until no visible scattering due to dust was observed (30 min–5 h). Classical light scattering was performed using a Brookhaven Instruments BI-200SM automatic goniometer attached to a Spectra Physics He–Ne laser operating at 632.8 nm. Using standard Zimm analysis, the apparent molecular weights and radii of gyration were obtained. All dilution solvents were also cleaned by filtration though 0.45 μm filters to remove dust. Multiple analyses were performed to ensure reproducibility.

Viscosity Measurements. Viscosity measurements were performed with a Contraves LS-30 rheometer at 25 °C. All solutions were prepared at 1.0 g/dL in deionized water and diluted incrementally. Measurements at all concentrations were performed at a constant shear rate of 5.93 s^{-1} unless otherwise noted. Solution pH values were adjusted with aqueous HCl or NaOH.

Fluorescence Quantum Yield. Prior to quantum yield determination, the absorbance of the dansyl labels at 330 nm for a polymer concentration of 0.50 g/L was determined. This then allowed the calculation of the fluorescence quantum yield using eq 1:

$$\Phi_x = \Phi_{st}\frac{A_{st}}{A_x}\frac{I_x}{I_{st}}\frac{n_x^2}{n_{st}^2} \tag{1}$$

in which Φ is the quantum yield, *A* is the absorbance at the excitation wavelength, *I* is the integral area of the corrected emission spectrum, and *n* is the refractive index at the excitation wavelength. The subscript x refers to the utilized chromophore, and the subscript st refers to the standard compound.

Nonradiative Energy Transfer. For NRET measurements, an Acton cutoff WG-305 optical filter was used at the excitation wavelength (282 nm) to prevent scattering of the excitation beam from the samples. The dansyl chromophores were excited at 330 nm to observe the dansyl emission spectra. Quantum yields (Φ) of the fluorescent labels were calculated by integrating the areas of the corrected emission spectra in reference to 2-aminopyridine in 0.10 N H_2SO_4 as the standard ($\Phi = 0.60$ at 282 nm excitation).[27] Quantum yields (Φ) of the dansyl groups excited at 330 nm were calculated by integrating the areas of corrected emission spectra in reference to quinine bisulfate in 1.0 N H_2SO_4 as the standard ($\Phi = 0.55$ at 330 nm excitation).[28] Beer's law corrections were applied for optical density changes at the excitation wavelength. Corrections were also made for refractive index differences.

The Förster distance, r_0, has been determined previously to be ~23.45 Å for the naphthalene/dansyl donor/acceptor pair,[29] and the NRET quantum efficiency, χ, has been calculated using the method described by Guillet.[30] In this case, the modified Guillet method[19] is used for calculating NRET quantum efficiency, χ, due to the minor absorbance of the dansyl chromophore when 282 nm is used as the excitation wavelength. The modified Guillet equation is

$$\frac{\chi}{1-\chi} = \frac{\Phi_D^0(I_A - I_A^0)}{\Phi_A^0 I_D} \tag{2}$$

in which Φ_D^0 is the fluorescence emission quantum yield of the donor in the absence of acceptor-labeled polymer excited at 282 nm and Φ_A^0 is the fluorescence emission quantum yield of the acceptor on the acceptor-labeled polymer. I_A and I_D are the integrated emission intensities of donor and acceptor, respectively, in the presence of both donor- and acceptor-labeled polymer and I_A^0 is the integrated emission intensity of the acceptor in the absence of donor-labeled polymer.

Results and Discussion

Monomer Selection, Synthesis, and Characterization. The major objective of this research was the optimization of the associative thickening efficiency of twin-tailed, hydrophobically modified terpolymers; therefore, selection of the monomers was quite important. Acrylic acid (AA) and methacrylamide (MAM) provide water solubility and the potential for conformational restrictions (due to the ionizable site in the former and side chain methyl group in the latter) that would be expected to contribute to backbone stiffening. A stiff polymer backbone is an important characteristic for these systems in order to reduce the degree of intrapolymer (closed) association and to help promote interpolymer (open) association. The hydrophobic monomers are a series of twin-tailed acrylamido monomers: *N*,*N*-dihexylacrylamide, *N*,*N*-dioctylacrylamide, and *N*,*N*-didecylacrylamide (Figure 2). These were synthesized from their corresponding commercially available amines with acryloyl chloride using a Schotten–Baumann procedure.[24] Characterization of the hydrophobic monomers was accomplished using ^{1}H NMR, ^{13}C NMR, and FT-IR. Details are provided in the Experimental Section.

Polymer Synthesis and Characterization. *A. Synthesis of Twin-Tailed Associative Polymers.* Initial attempts were made to synthesize copolymers consisting of methacrylamide and 1 mol % of the DiC_6AM, DiC_8AM, or $DiC_{10}AM$ twin-tailed comonomer. Despite high concentrations of SDS, the polymers precipitated shortly after initiation, and the resulting polymers could not be resolubilized in aqueous media. Consequently, terpolymers were synthesized incorporating acrylic acid (AA) to impart pH responsiveness and to promote solubility in aqueous solution at high pH. A typical polymerization scheme is shown in Figure 3. All terpolymers synthesized (Table 1) consist of 49 mol % of MAM, 50 mol % of AA, and 1 mol % of the DiC_6AM, DiC_8AM, or $DiC_{10}AM$ twin-tailed hydrophobic monomer.

B. Apparent Molecular Weight Determination by Light Scattering. Apparent molecular weights and radii of

Table 2. Apparent Molecular Weights and Radii of Gyration for Synthesized Polymers

sample	hydrophobe	R_G (nm)	MW (g/mol) × 10^{-6}
MAM/AA/DiC$_6$AM	DiHexAM	72.3	1.02
MAM/AA/DiC$_8$AM	DiOctAM	46.2	0.747
MAM/AA/DiC$_{10}$AM	DiDecAM	63.1	1.12

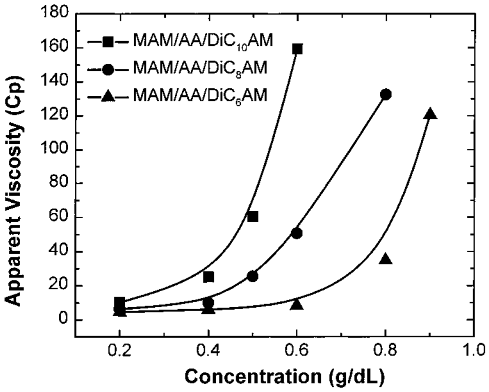

Figure 4. Apparent viscosity dependence on concentration for MAM twin-tailed terpolymers at pH 8.0 and 25 °C.

gyration were determined for each terpolymer. Initially, formamide was chosen due to excellent solubilizing power and the ease of dust removal. Formamide, however, proved not to be a suitable solvent since accurate refractive index increments (d*n*/d*c*) could not be measured for these systems. This problem is often encountered in low ionic strength media as documented in earlier reports by Branham and McCormick.[18] Thus, measurements were carried out at 25 °C in aqueous 0.5 M NaCl (pH 8).

Classical light scattering with the standard Zimm analysis was utilized to determine apparent weight-average molecular weight values (M_w) and the mean radii of gyration (R_g) for all three terpolymers at concentrations below 0.1 g/dL (Table 2). For the MAM/AA/DiC$_x$AM terpolymers, the apparent molecular weights ranged from 0.75 to 1.12 × 10^6 g/mol. Candau et al.[19,20] have determined with *N*-monoalkylacrylamide hydrophobic monomers that the polymer molecular weights increase with increasing monomer hydrophobicity due to hydrogen bonding. In our case, since the monomers are disubstituted, no polarity effect on molecular weight is observed. It must be noted that the determination of molecular weights and radii of gyration is not trivial for hydrophobically modified, ionic polymers in aqueous media, even with added small molecule electrolyte. Although precautions were taken to ensure accuracy and reproducibility, these measurements may be only qualitative at best.

C. Viscometric Studies. 1. Effect of Hydrophobe Length on Solution Viscosity for MAM/AA Terpolymers. Apparent viscosities as a function of concentration in deionized water at pH 8 were determined for the three MAM/AA/DiC$_x$AM ($x = 6, 8, 10$) terpolymers as shown in Figure 4. For all three polymers, as the concentration is increased, a sharp increase in the viscosity is observed. This viscosity enhancement results from the formation of hydrophobic interpolymer networks in which the alkyl hydrophobes are associated into micelle-like aggregates. The terpolymer incorporating the DiC$_{10}$ hydrophobe shows the most pronounced increase in viscosity with concentration. Above ~0.6 g/dL, the viscosity is beyond the measurable value of the Contraves LS-30 rheometer. Similar trends are observed for the DiC$_8$ terpolymer which reaches the measurable limit at ~0.8 g/dL and the DiC$_6$ terpolymer which reaches this limit at 0.9 g/dL. Thus, the viscosification efficiency of these three terpolymers closely follows the increasing hydrophobicity of the twin-tailed monomer. The smaller change in the viscosity profile observed in the DiC$_8$ and the DiC$_6$ terpolymers as compared to the DiC$_{10}$ terpolymer can be attributed to the lower apparent molecular weight of the DiC$_8$ terpolymer. This direct correlation of increasing hydrophobe chain length with aqueous solution viscosity is similar to behavior reported by McCormick and Johnson[11,12] for single-tailed, hydrophobically modified polyacrylamides, Jenkins[23-25] for hydrophobically modified alkali soluble/swellable emul-

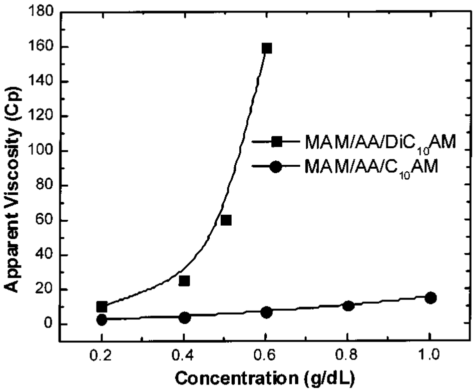

Figure 5. Apparent viscosity dependence on concentration for single and twin-tailed terpolymers at pH 8.0 and 25 °C normalized for the hydrophobe concentration.

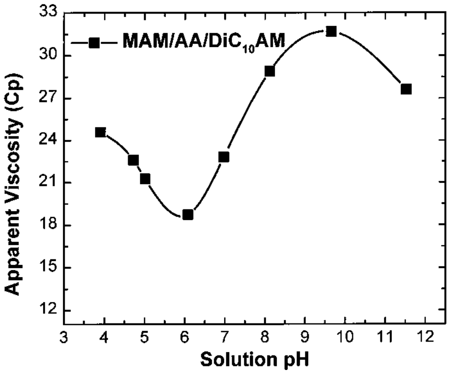

Figure 6. Apparent viscosity vs pH for the MAM/AA/DiC$_{10}$-AM terpolymer at a concentration of 0.3 g/dL.

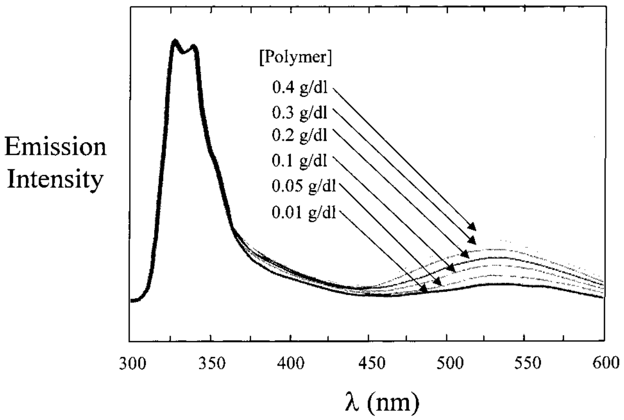

Figure 7. Normalized emission spectra for MAM/AA/DiC$_{10}$-AM polymers excited at 282 nm at pH 8.0.

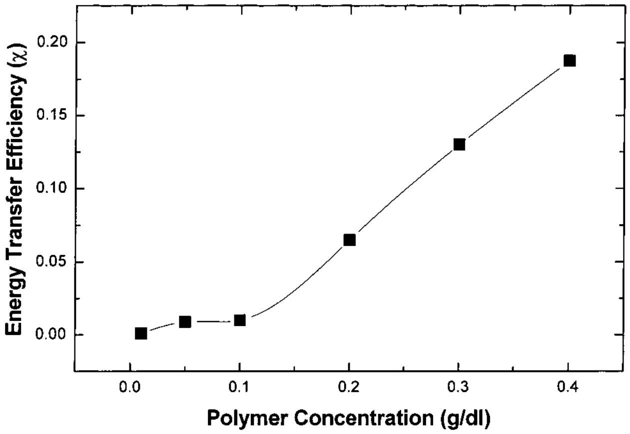

Figure 8. Energy transfer efficiency plot for two MAM/AA/$DiC_{10}AM$ terpolymers with naphthalene and dansyl labels mixed in equimolar amounts at pH 8.0 and 25 °C.

sion (HASE) associative thickeners, and Schulz et al.[34] for alkylated poly[acrylamide-*co*-sodium acrylates]. As the hydrophobicity of the alkyl substituent is increased, the propensity for interpolymer association and network formation also increases.

2. Single-Tailed vs Twin-Tailed Hydrophobes. The increased viscosification efficiency of the twin-tailed terpolymer as compared to the single-tailed terpolymer is illustrated in Figure 5 for C_{10} monosubstituted and C_{10} disubstituted terpolymers. Since the twin-tailed monomers have twice the amount of hydrophobe, synthesis of the monosubstituted terpolymer was performed with twice the number of moles[21] to allow for a more normalized comparison. From Figure 5 it can be seen that the twin-tailed terpolymer shows dramatically higher increases in viscosity than its single-tailed counterpart. This is likely due to a lower aggregation concentration required for twin-tailed amphiphiles as compared to analogous single-tailed amphiphiles. For mickroblocky *N*,*N*-dihexylacrylamide-substituted polyacrylamides, Candau et al.[20] also found the viscosity increase with concentration to be more pronounced in comparison with the corresponding *N*-hexylacrylamide analogue.

3. Effect of pH on Viscosity Behavior. Acrylic acid moieties, since they are responsive to pH and ionic strength, can greatly affect conformation of the polymer chain and the resulting hydrodynamic volume in aqueous solutions. To evaluate electrostatic interactions, apparent viscosities for the MAM/AA/$DiC_{10}AM$ terpolymer at a concentration of 0.3 g/dL were measured as a function of pH (Figure 6). At this concentration (refer to Figure 4) the polymer is in a dilute regime ($[\eta][c] < 1$), and largely unimeric micelles (closed associations) are expected. In Figure 6 the MAM/AA/$DiC_{10}AM$ terpolymer shows an initial decrease in viscosity over the pH range from 4 to 6. This behavior is typical for AA-based polymers and results from the partial ionization, leading to hydrogen bonding between ionized AA moieties and adjacent protonated ones and a subsequent decrease in the unimer hydrodynamic volume.[6] At pH 6, the MAM terpolymer reaches a critical degree of ionization beyond which AA moiety repulsion and chain expansion occur. Finally, around pH ~ 9.5−10, a slight decrease in viscosity is observed due to the high ionic strength of the solution and screening of the charge−charge repulsions. Unlike acrylic acid homopolymers, these systems exhibit a maximum at higher pH values. This is likely a result of the higher degrees of backbone ionization required to disrupt intrapolymer association and effect chain expansion for this highly hydrophobic system.

D. Fluorescence Energy Transfer Measurements. To obtain a better understanding of the solution behavior exhibited by twin-tailed, hydrophobically modified acrylic acid polymers on the molecular level, $DiC_{10}Am$ terpolymers (which showed the most pronounced associative thickening tendency) were individually labeled with naphthyl and dansyl chromophores. Mixed solutions containing naphthyl donor and the dansyl acceptor on these separate polymer chains were prepared, and nonradiative energy transfer (NRET) measurements were performed following a procedure previously reported by McCormick et al.[6] The Förster distance

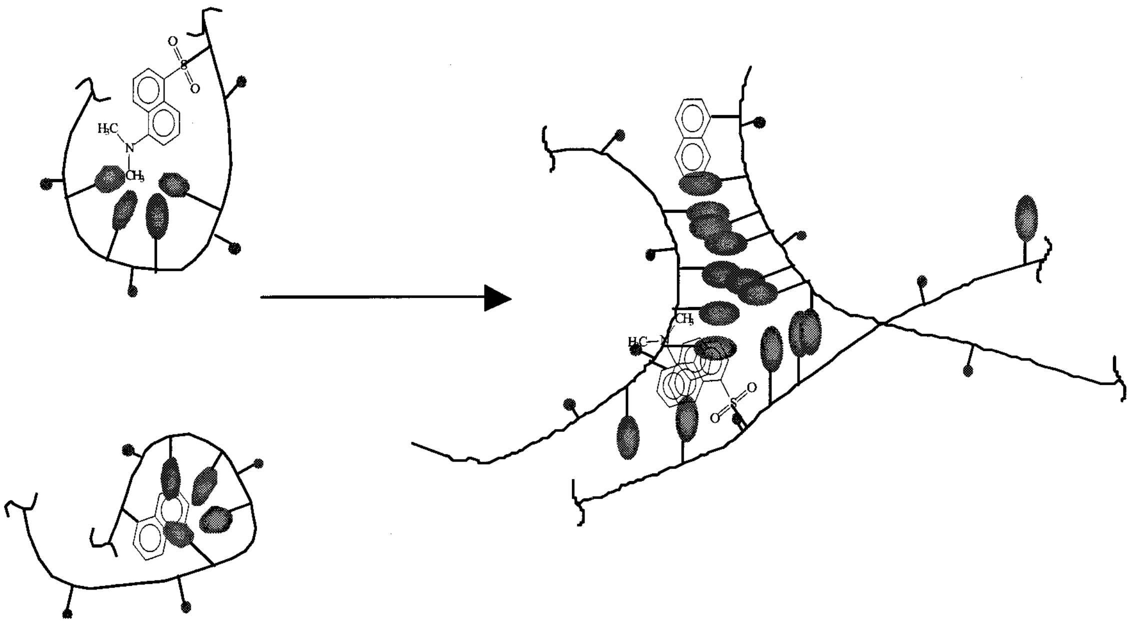

Figure 9. Model illustrating the effect of polymer concentration on nonradiative energy transfer efficiency below and above a critical concentration *C**.

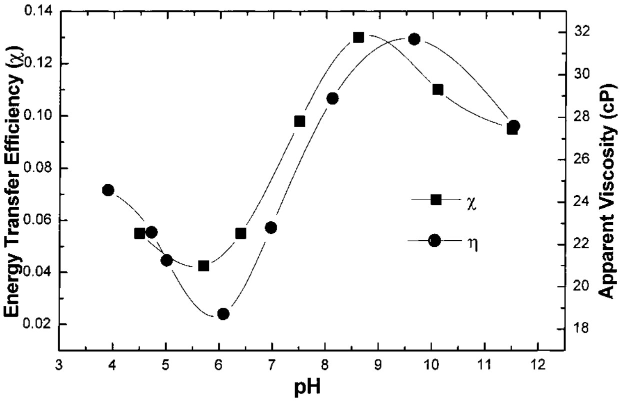

Figure 10. Energy transfer efficiency plot vs pH for two MAM/AA/DiC$_{10}$AM terpolymer with naphthalene and dansyl labels mixed in equimolar amounts at a fixed concentration of 0.3 g/dL.

(defined when energy transfer efficiency between chromophore pairs is 50%) for this energy transfer pair has previously been documented to be 23.45 Å. This method is very sensitive for indicating the onset of hydrophobic association and network formation.

1. Effect of Polymer Concentration on Energy Transfer. Figure 7 illustrates the emission intensity vs wavelength behavior for the mixed, individually labeled chains containing the dansyl and naphthyl chromophores (excitation wavelength = 282 nm). As the total polymer concentration is increased, an increase in the emission intensity is observed in the dansyl emission region between 450 and 580 nm. At 0.01 and 0.05 g/dL, little emission in this region is observed. Only above concentrations of ~0.1 g/dL does significant energy transfer occur. Although evident from direct examination of the emission spectra, a better picture regarding the extent of energy transfer may be obtained by plotting the NRET quantum efficiency as a function of polymer concentration (Figure 8) for the mixed MAM/AA/DiC$_{10}$AM terpolymers at pH 8.

A significant increase in NRET quantum efficiency occurs at ~0.1 g/dL. This concentration is indicative of initial chain overlap. Below this concentration, most polymer chains likely exist as unimers in solution. Above this concentration, intermolecular association is observed. Kramer and McCormick[5] have observed similar concentration-dependent behavior for labeled poly(acrylamide-*co*-sodium 11-(acrylamido)undecanoate) polymers. A simplistic model consistent with this behavior is illustrated in Figure 9. The overlap concentration determined by NRET is slightly lower than that determined by viscosity. This behavior is to be expected due to the enhanced sensitivity of fluorescence techniques for determining interchain associations.

2. Effect of Solution pH on Energy Transfer. NRET experiments were also performed on mixed, individually labeled MAM/AA/DiC$_{10}$AM terpolymers at a fixed concentration of 0.3 g/dL as a function of solution pH. At this concentration, viscosity measurements indicate that the polymer is in the dilute regime, although NRET measurements indicate some interpolymer association occurring at the molecular level. Following corrections for direct excitation, the Guillet equation was utilized to calculate the NRET quantum efficiency at seven pH values between 4 and 10. These data are presented in Figure 10.

Although changes in the solution pH are expected to affect the population of reporting dansyl chromophores, calculation of the NRET quantum efficiency based on quantum yields corrects these data for concentration differences. Between pH values of 4–5.5, an initial decrease in viscosity is observed. This behavior is characteristic of AA-based polymers and is caused by hydrogen bonding between partially ionized AA functionalities as discussed above. At pH 5.7, the terpolymer is sufficiently charged such that further ionization leads to chain expansion. Finally, at pH values between 8.5 and 11.5, a small decrease in viscosity is observed due to the high ionic strength of the medium, resulting in charge–charge shielding and a slight collapse in the hydrodynamic volume. Hu and McCormick[6] have observed similar pH responsive behavior for labeled hydrophobically modified poly(sodium maleate-*alt*-ethyl vinyl ether) polymers.

Also plotted in Figure 10 are the viscosity data from Figure 6. While both show the same trends, changes in chain expansion and label interaction indicated by

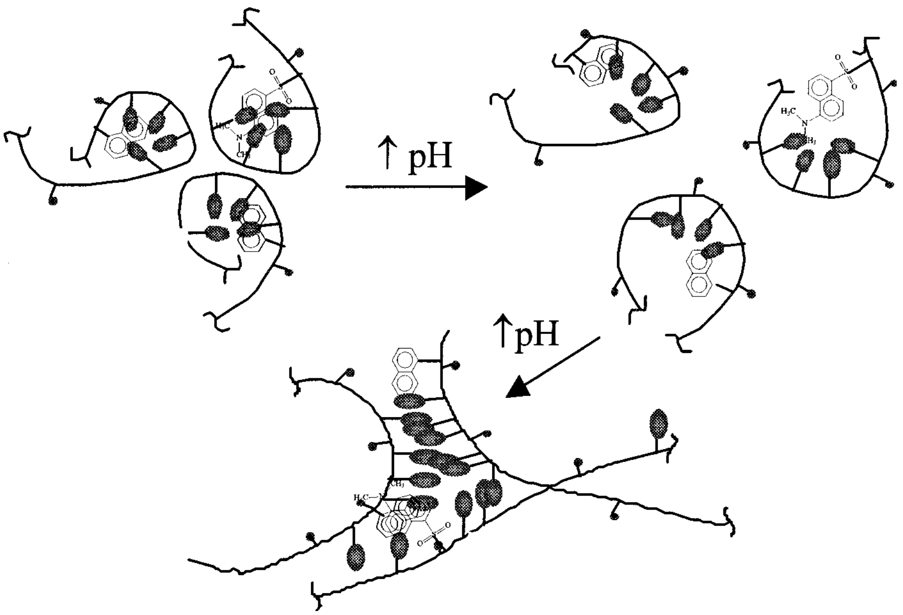

Figure 11. Model illustrating the effect of solution pH on nonradiative energy transfer efficiency.

NRET quantum efficiency occur at slightly lower pH values. This once again is believed due to the greater sensitivity of fluorescence methods as compared to rheological methods for indicating changes in labeled polymer chain interactions. The pH responsive behavior of the $DiC_{10}Am$ terpolymer is illustrated in Figure 11.

Conclusions

MAM/AA terpolymers with twin-tailed hydrophobes exhibit solution properties conducive to associative thickening. Their tendencies toward intermolecular association closely follow the increase in hydrocarbon chain length (hydrophobicity), the terpolymer containing the $DiC_{10}Am$ hydrophobe exhibiting the most pronounced associative thickening. Twin-tailed terpolymers show dramatically higher increases in viscosity than their single-tailed counterparts. This is likely due to the greater hydrophobe density of the twin-tailed monomers which allow enhanced associative junction formation. Energy transfer measurements performed using separately labeled polymers indicate the onset of association at ~0.1 g/dL for the MAM/AA/$DiC_{10}AM$ terpolymer. This concentration is slightly below that indicated by viscosity measurements. Changes in the energy transfer efficiency as a function of pH at specific concentrations closely follow analogous viscosity behavior. A maxiumum in viscosity and interpolymer interaction is observed between pH values of 8 and 10. At higher pH values, chain collapse occurs due to the high solution ionic strength. At lower pH values, chain collapse results from backbone protonation and an enhancement in intrapolymer hydrophobe association. Thus, it is apparent that the MAM/AA/$DiC_{10}Am$ terpolymer at a pH value between 8 and 10 provides for the most effective thickening of an aqueous solution. The present results suggest that systems incorporating higher number hydrophobic, twin-tailed monomers should be studied.

Acknowledgment. Financial support for this research from ICI, the Department of Energy, and the Office of Naval Research is gratefully acknowledged.

References and Notes

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MA001549L