Water-Soluble Copolymers. 58. Associative Interactions and Photophysical Behavior of Amphiphilic Terpolymers Prepared by Modification of Maleic Anhydride/Ethyl Vinyl Ether Copolymers

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ABSTRACT: A series of amphiphilic terpolymers were prepared by sequentially copolymerizing maleic anhydride and ethyl vinyl ether, adding octyl-, dodecyl-, or naphthylamine, and then hydrolyzing the remaining anhydride units. Viscosity studies indicate that these amphiphilic systems form intramolecular associations in dilute and semidilute solutions at various values of pH and ionic strength. The dodecyl terpolymers show more pronounced hydrophobic associations than do the octyl analogs. Change in solution pH or addition of NaCl lowers significantly the viscosity of the polymer solutions, indicating more collapsed conformations. Fluorescence lifetimes increase with increasing hydrophobe content. The lifetime of the monomer emission decreases with increasing pH, demonstrating a more hydrated environment experienced by the probe within the polymer coil. I_E/I_M values of the terpolymers with low hydrophobe content decrease with increasing pH from 3 to 10 while the terpolymers with moderate hydrophobe content exhibit a maximum I_E/I_M in the same pH range. Systems with high hydrophobe content show little pH dependence. These results are interpreted in terms of the relative concentration of the chromophore in the hydrophobic domains as well as the change in the mobility of the naphthyl labels.

Introduction

Intramolecular associative polymers, also called polymeric micelles or "polysoaps" due to their surfactant properties, were first studied as models to mimic the conformational behavior of proteins. Strauss and coworkers[1,2] demonstrated the formation of intramolecular micelles using the random copolymers of *N*-ethyl-4-vinylpyridinium bromide and *N*-dodecyl-4-vinylpyridinium bromide. The intrinsic viscosity decreased dramatically with increasing dodecyl group content and reached a minimum value of 0.04 dL/g at a hydrophobe content of 28.5 mol %. This value is of the same order of magnitude as that observed for globular proteins, indicating a highly collapsed conformation. The transition from extended to compact coils was reported to occur at a critical hydrophobe concentration of ~11 mol %. The Huggins constant exhibited an almost 25-fold increase as the dodecyl group content was changed from 0 to 37 mol %, verifying increased compaction of the polymer coils in aqueous media.

Loucheux et al.[3] studied the solution properties of poly(4-vinylpyridine) modified with alkyl bromides utilizing viscometry and NMR techniques. Their data showed that a conformational transition occured only when the alkyl groups contained more than eight carbon atoms. The critical hydrophobe concentration shifted to lower value with increasing alkyl group length.

Another widely studied associative polymer is based on hydrolyzed alternating copolymers of maleic anhydride and *n*-alkyl vinyl ethers. These copolymers with moderate concentration of alkyl side chains (alkyl = butyl, pentyl, hexyl, octyl) in aqueous solutions undergo conformational transitions from hypercoil to random coil as the degree of ionization is increased.[4-12] The transition, however, is shifted to a higher value of ionization with increasing alkyl group size.[7] The conformation of the copolymers with longer hydrophobic chains (alkyl = decyl, cetyl) is essentially independent of the degree of ionization since these copolymers remain in a collapsed conformation at all values of pH.[13-15]

A series of studies have been conducted in our laboratories to further investigate the nature of intramolecular associations of various amphiphilic water-soluble polymers. Clark et al.[16] demonstrated the pH dependence of the chain associations in a 20:80 mol % copolymer of 2-(1-naphthylacetyl)ethyl acrylate (NAEA) and methacrylic acid (MAA). The copolymer adopts a highly collapsed conformation at low pH due to the hydrophobic interactions of both methyl and naphthyl groups. At high pH, the copolymer remains in a micelle-like conformation with the naphthyl groups forming a hydrophobic core surrounded by a charged shell of methacrylic acid units. Such a conformation is attributed to the presence of a large quantity of the naphthyl groups in the copolymer and the relatively long spacer between the naphthyl groups and the polymer backbone.

In this paper, we report the synthesis and solution properties of copolymers of maleic anhydride and ethyl vinyl ether reacted with controlled amounts of octyl- and dodecylamine. A small concentration (~1 mol %) of naphthalene labels with long spacer groups is incorporated. Hydrolysis of the remaining anhydride groups yields water-soluble terpolymers with degrees of amidation ranging from 8 to 50 mol %. Key features of this study include variation in hydrophobe length and content, maintenance of a small quantity of naphthyl groups to avoid perturbation of the parent copolymers, and the presence of comparatively large hydrophobes relative to the naphthyl label. These terpolymers provide useful models for elucidating the nature of hydrophobic associations in systems having a random distribution of the hydrophobic groups. Changes in polymer conformation upon altering the concentration and length of the hydrophobic groups as well as the solution pH and ionic strength are examined by viscosity and fluorescence studies.

Experimental Section

Materials. Chemicals were obtained from Aldrich Chemical Co. and used as received. Benzene was dried over CaH_2 and

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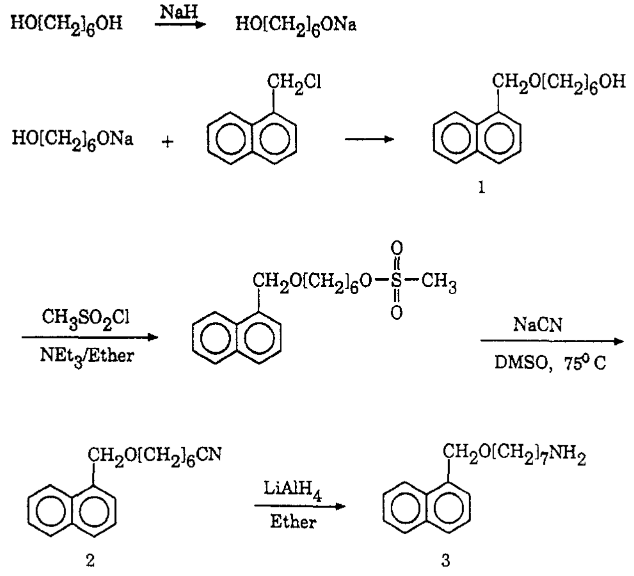
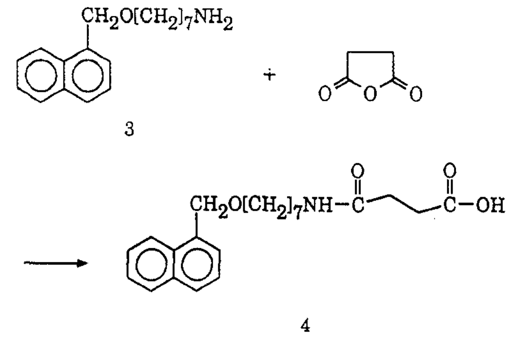
Scheme 1. Synthesis of 1-(((7-Aminoheptyl)oxy)methyl)naphthalene (3)



Scheme 2. Synthesis of Naphthalene-Containing Model Compound 4



distilled under nitrogen prior to use. Other solvents were reagent grade and used without further purification. Water was deionized to a conductance of 1 × 10^{-17} mho/cm.

Synthesis of Naphthalene-Containing Fluorescence Label 3 (Scheme 1). 1-(((6-Hydroxyhexyl)oxy)methyl)naphthalene (1). 1,6-Hexanediol (100.0 g, 0.846 mol) was placed in a 1000-mL round-bottomed flask equipped with a mechanical stirrer and heated to melt at 55 °C. Sodium hydride (4.06 g, 0.169 mol) was added, and the mixture was stirred at 70 °C for 4 h until all NaH reacted. A precipitate was formed immediately upon addition of (chloromethyl)naphthalene (30.0 g, 0.169 mol). The mixture was stirred vigorously at 80 °C for 3 h. Thin-layer chromatography (TLC) indicated that most of the (chloromethyl)-naphthalene had been reacted. The reaction was allowed to proceed for another 3 h. Excess hexanediol was then removed at 106 °C/0.5 mmHg. The residue was diluted with 150 mL of acetone, and the precipitate was filtered. The concentrated filtrate was distilled under reduced pressure to yield a colorless oil: bp 166.5 °C at 0.5 mmHg, yield 41 g (94%). GC purity was determined to be >99.9%. ^{1}H NMR (CDCl$_3$) δ 1.22–1.70 (m, 8 H), 2.01 (s, 1 H), 3.47–3.55 (2 t, 2 H), 4.91 (s, 2 H), 7.39–8.15 (m, 7 H); ^{13}C NMR (CDCl$_3$) δ 25.5, 25.9, 29.7, 32.6, 62.6, 70.3, 71.4, 124.0, 125.1, 125.7, 126.0, 126.3, 128.5(2), 131.7, 133.7, 133.9; FTIR 3383 (O–H), 1597, 1510, 1460 (aromatic C–C stretch), 1099 (C–O–C), 794, 775 (aromatic C–H bend) cm^{-1}.

1-(((6-Cyanohexyl)oxy)methyl)naphthalene (2). A modified literature procedure[17] was used in the preparation of 2. Methanesulfonyl chloride (28.6 g, 0.250 mol) was added dropwise at 8–15 °C to a solution of 1-(((6-hydroxyhexyl)oxy)methyl)-naphthalene (51.7 g, 0.200 mol) and trimethylamine (30.4 g, 0.300 mol) in 150 mL of ether. After addition was complete, the mixture was stirred at room temperature for 1 h. The precipitate was filtered and washed twice with 50 mL of anhydrous ether. A light yellow oil was obtained from the filtrate upon removal of the solvent. ^{1}H NMR (CDCl$_3$) δ 1.29–1.73 (m, 8 H), 2.90 (s, 3 H), 3.52 (t, 2 H), 4.13 (t, 2 H), 4.91 (s, 2 H), 7.36–8.12 (m, 7 H); ^{13}C NMR δ 25.1, 25.6, 29.0, 29.5, 37.0, 70.1(2), 71.3, 124.0, 125.2, 125.7, 126.0, 126.3, 128.3(2), 131.7, 133.7, 134.0.

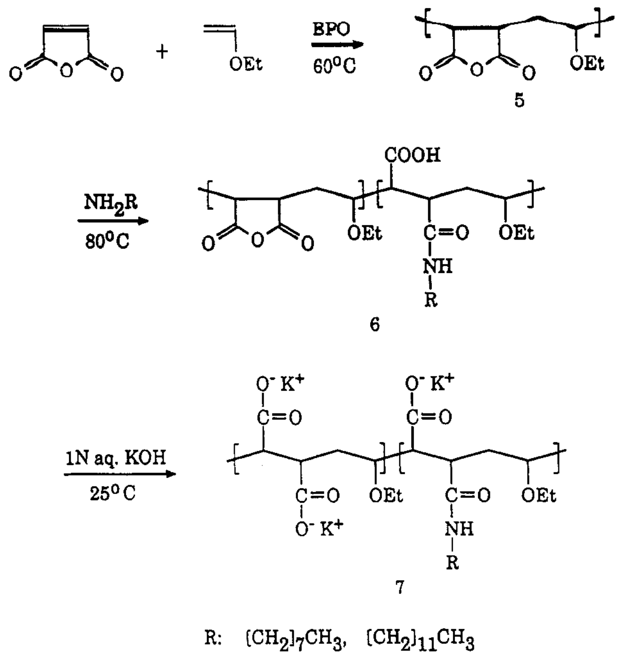
The oil was heated at 75 °C with sodium cyanide (15.5 g, 0.300 mol) in 200 mL of anhydrous DMSO for 3.5 h in a 500-mL round-bottomed flask. TLC confirmed the disappearance of the starting compound. The solution was cooled and poured into 800 mL of water. The product was extracted with 200 mL of methylene chloride three times. The organic extracts were combined and dried with MgSO$_4$. A dark red oil was obtained upon removal of the solvent. Vacuum distillation yielded a slightly yellow oil: bp 186–188 °C at 0.5 mmHg, yield 49.7 g (93%). ^{1}H NMR (CDCl$_3$) δ 1.20–1.66 (m, 8 H), 2.11 (t, 2 H), 3.46 (t, 2 H), 4.87 (s, 2 H), 7.32–8.11 (m, 7 H); ^{13}C NMR (CDCl$_3$) δ 16.8, 25.2, 25.3, 25.5, 28.2, 29.3, 69.9, 71.4, 124.0, 125.2, 125.7, 126.0, 126.3, 128.5(2), 131.7, 133.7, 133.9; FTIR 2245 (C$\equiv$N), 1597, 1510, 1462 (aromatic C–C stretch), 1099 (C–O–C), 801, 777 (aromatic C–H bend) cm^{-1}.

1(((7-Aminoheptyl)oxy)methyl)naphthalene (3). LiAlH$_4$ (0.789 g, 0.0196 mol) in 40 mL of anhydrous ether was placed in a 100-mL flask equipped with a thermometer, an addition funnel, and a magnetic stirring bar. When the mixture was cooled to 0 °C, 1-(((6-cyanohexyl)oxy)methyl)naphthalene (5.00 g, 0.0187 mol) in 5 mL of ether was added slowly at such a rate that the temperature did not exceed 5 °C. After addition was complete, 1 mL of water was added slowly (*Caution*: very vigorous reaction), followed by 1 mL of 20% NaOH solution and an additional 3 mL of water. The ether layer was decanted from the white, granular inorganic residue. This residue was washed once with 20 mL of ether. The organic solution was dried with Na$_2$SO$_4$. Removal of ether yielded a slightly yellow oil. GC indicated that the product contained ~6% of 1-(((6-hydroxyhexyl)oxy)methyl)-naphthalene (1). To remove unreacted alcohol, the oil was dissolved in 10 mL of ether, and 20 mL of 1 M HCl ether solution was added. The ammonium salt was precipitated as an off-white solid which was filtered, washed with ether, and dried under vacuum. Recrystallization in acetone gave pure white crystals. The solid was dissolved in water, and the solution pH was adjusted to ~12. The free amine was extracted with ether. The organic phase was dried with Na$_2$SO$_4$, and the solvent was removed to yield a slightly yellow oil: yield 3.68 g (73%). HPLC purity was determined to be >99.8%. ^{1}H NMR (CDCl$_3$) δ 1.03 (b, 2 H), 1.19–1.70 (m, 10 H), 2.62 (t, 2 H), 3.52 (t, 2 H), 4.92 (s, 2 H) 7.34–8.16 (m, 7 H); ^{13}C NMR (CDCl$_3$) δ 22.9, 26.2, 26.8, 29.3, 29.7, 33.8, 42.3, 70.5, 71.4, 124.1, 125.1, 125.7, 126.0, 126.2, 128.5(2), 131.8, 133.7, 134.1; FTIR 3374, 3300 (N–H), 1597, 1512, 1464 (aromatic C–C stretch), 1101 (C–O–C), 792, 777 (aromatic C–H bend) cm^{-1}.

Succinic Acid *N*-[7-(1-Naphthylmethoxy)heptyl] Monoamide (4). The synthesis of naphthalene-labeled model compound 4 is illustrated in Scheme 2. 1-(((7-Aminoheptyl)oxy)-methyl)naphthalene (3) (1.00 g, 3.69 mmol) in 10 mL of anhydrous DMF was placed in a 25-mL flask equipped with a condenser, an addition funnel, and a N$_2$ inlet and outlet. Succinic anhydride (0.380 g, 3.80 mmol) in 5 mL of DMF was added at 0 °C with stirring. The reaction was conducted at room temperature for 30 min and at 65 °C for an additional 30 min. TLC confirmed disappearance of the amine. The product was precipitated in water. The light yellow solid was filtered, washed with 10 mL of water, and dried under vacuum: yield 1.19 g (87%). The product was recrystallized in ethyl acetate to yield a pale yellow solid: mp 78–79.5 °C. ^{1}H NMR (CDCl$_3$) δ 1.10–1.84 (m, 10 H), 2.39 (t, 2 H), 2.59 (d, 2 H), 3.09 (d, 2 H), 3.51 (t, 2 H), 4.90 (s, 2 H), 6.43 (b, 1 H), 7.31–8.19 (m, 7 H), 10.07 (b, 1 H); ^{13}C NMR (CDCl$_3$) δ 26.0, 26.7, 28.9, 29.1, 29.5, 30.0, 30.7, 39.7, 70.4, 71.3, 124.0, 125.2, 125.7, 126.1, 126.4, 128.5(2), 131.7, 133.7, 133.9, 172.6, 176.1; FTIR (KBr) 3460–2370 (O–H), 3319 (N–H), 1696 (acid C=O), 1643 (amide C=O), 1596 (aromatic C–C stretch), 1537 (amide II band), 1120 (C–O–C), 797, 767, (aromatic C–H bend) cm^{-1}.

Synthesis of the Sodium Salt of Hydrophobically Modified Maleic Anhydride and Ethyl Vinyl Ether Copolymers 7 (Scheme 3). Copolymerization of Maleic Anhydride (MA) with Ethyl Vinyl Ether (EVE). Maleic anhydride (10.77 g, 0.110 mol) and benzoyl peroxide (0.0451 g, 1.86 × 10^{-4} mol) were dissolved in 100 mL of benzene in a 250-mL three-neck round-

Scheme 3. Synthesis of Hydrophobically Modified Maleic Anhydride and Ethyl Vinyl Ether Based Terpolymers 7



bottomed flask equipped with a magnetic stirring bar. The flask was sealed and fitted with a thermometer, a condenser, a long gas delivery needle, and a short needle on the top of the condenser to serve as a gas escape valve. Dry, oxygen-free nitrogen was purged through the flask for 45 min. The short needle was then removed and ethyl vinyl ether (9.11 g, 0.121 mol) was injected into the solution. The system was heated at 59–61 °C for 8 h, resulting in a white precipitate which was filtered and dried under vacuum. Copolymer **5** was purified by repeated precipitation in dry diethyl ether. The polymer was filtered and dried under vacuum.

Synthesis of Naphthalene-Labeled, Hydrophobically Modified Maleic Anhydride and Ethyl Vinyl Ether Terpolymers 6. Synthesis of naphthalene-labelled MA/EVE terpolymer containing 20 mol % of octyl groups is described below. Other terpolymers were prepared by the same procedure with differing amounts of alkylamines in the feed. 1-(((7-Aminoheptyl)oxy)methyl)naphthalene (0.162 g, 5.99×10^{-4} mol) (**3**) and octylamine (1.55 g, 1.20×10^{-2} mol) were added dropwise to a rapidly stirring solution of poly(maleic anhydride-*alt*-ethyl vinyl ether) (10.2 g, 5.99×10^{-2} mol) (**5**) in 100 mL of ethyl acetate at room temperature under nitrogen. The reaction was allowed to proceed at 60 °C for 10 h. The polymer was then precipitated into 300 mL of diethyl ether. The precipitate was stirred with 200 mL of diethyl ether overnight, filtered, and then dried under vacuum.

Hydrolysis of Hydrophobically Modified Maleic Anhydride and Ethyl Vinyl Ether Copolymers. The hydrolysis of the terpolymers **6** was performed in aqueous NaOH solution. A dilute NaOH solution containing an appropriate amount of dry polymer was placed on an orbital shaker at room temperature to facilitate the hydrolysis of the anhydride groups. After complete dissolution, the solution was dialyzed for 1 week against water at room temperature to remove low molecular weight oligomers and excess NaOH using dialysis tubing with a molecular weight cutoff of 12 000–14 000. The final products were obtained by freeze-drying.

Characterization. Naphthalene Derivatives. ^1H and ^{13}C NMR spectra were recorded using a Bruker AC-200. A Mattson 2020 Galaxy Series FTIR was used to obtain infrared spectra. GC analysis was performed on a Hewlett-Packard 5890 Series II gas chromatograph equipped with an Alltech AT-5 capillary column. A Hewlett-Packard Model 1050 HPLC was used to determine the purity of solid samples. A Waters Bondapak C18 column was employed with methanol as the mobile phase. The sample eluant was typically monitored at 280 nm.

Terpolymer Solution Preparation. The appropriate amount of dried terpolymer **7** was weighed and then dissolved in water in a volumetric flask from which further dilutions of this stock solution could be made. The solutions were allowed to stand for 2 weeks prior to viscosity measurement. The pH value of each solution was obtained with a Corning 130 pH meter at room temperature.

UV Analysis. Ultraviolet spectroscopy was used in determining the naphthalene content in the terpolymers. All spectra were recorded with a Hewlett-Packard 8452A diode array spectrophotometer. Beer–Lambert plots were obtained for the model compound, the sodium salt of succinic acid *N*-[7-(1-naphthylmethoxy)heptyl] monoamide (**4**) in water, and compared with polymer absorption.

Fluorescence Analysis. The concentrations of terpolymer solutions were 0.05 g/dL. The concentration of naphthyl moieties in these solutions varied from 2.5×10^{-6} to 3.0×10^{-6} M. Sample solutions were purged by bubbling with helium. All the samples were excited at 280 nm, and monomer intensities were measured at 330 nm. Emission spectra of the terpolymers were recorded with a Spex Fluorolog-2 fluorescence spectrometer. Fluorescence decays were measured with a Photochemical Research Associates (PRA) single-photon-counting instrument equipped with a H_2-filled 510-B flashlamp. A nonlinear iterative deconvolution technique was used to fit the decay curves.

Low-Angle Laser Light Scattering. Classical light scattering studies were performed with a Chromatix KMX-6 low-angle laser light scattering spectrophotometer with a 2-mW He–Ne laser operating at 633 nm. Refractive index increments (d*n*/d*c*) were obtained using a Chromatix KMX-16 differential refractometer. The molecular weight of hydrolyzed poly(maleic anhydride-*alt*-ethyl vinyl ether) was measured in 1 M NaCl solution.

Viscometry. Viscosity measurements were conducted with a Contraves LS-30 low-shear rheometer at a constant shear rate of 1.28 s^{-1} at 25 °C. A constant pH of 9–9.5 was used during the measurement, unless otherwise noted.

Results and Discussion

One synthetic objective of this work was to prepare amphiphilic water-soluble polymers with controlled placement of fluorescence labels. The random incorporation of the labels was achieved by first synthesizing the functionalized naphthalene derivative shown in Scheme 1. The synthesis of 1-(((7-aminoheptyl)oxy)methyl)naphthalene (**3**) proved to be facile with satisfactory yields. The spacer length (in this case heptyl) can be altered to decouple the naphthalene from the polymer backbone. A model compound, succinic acid *N*-[7-(1-naphthylmethoxy)heptyl]monoamide (**4**) (Scheme 2), was designed for fluorescence studies. The sodium salt form is soluble in aqueous media.

Terpolymer Synthesis and Characterization. Hydrophobically modified MA/EVE terpolymers **7** were prepared utilizing the synthetic procedures shown in Scheme 3. Terpolymers are designated by the number 7 followed by C8 or C12, designating octyl or dodecyl substitution. The final number represents the mole percent incorporation. Initially, MA/EVE copolymer **5** was prepared in benzene. Characteristic of this free-radical copolymerization is virtually complete alternation with little tendency of either monomer to homopolymerize.[18] The M_w of the copolymer obtained by light scattering in this study was 2.4×10^5 g/mol. The ^{13}C NMR spectrum of the MA/EVE copolymer is shown in Figure 1.

Initial attempts to induce the reaction of the MA/EVE copolymer **5** with alkylamines and naphthalene label **3** were performed in methyl ethyl ketone (MEK). The color of the products varied from pink to purple as the degree of incorporation of the hydrophobic groups increased from 8 to 50 mol %.

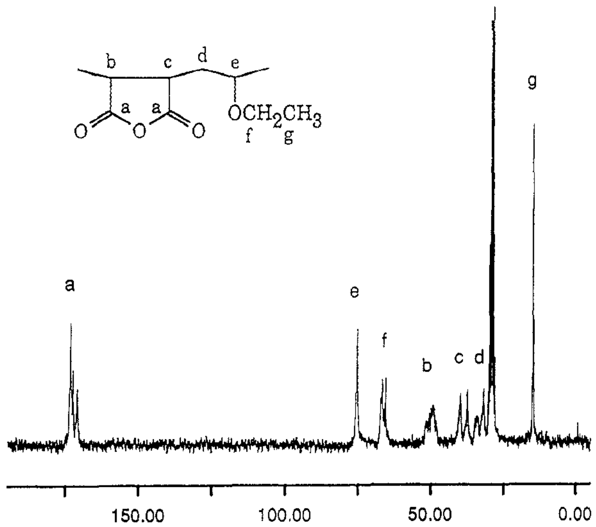
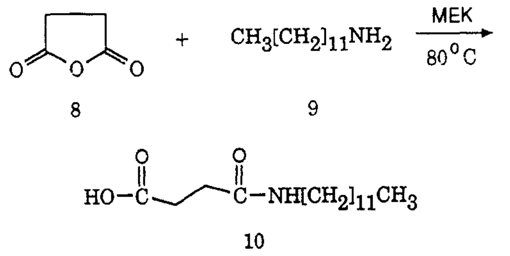


Figure 1. ^{13}C NMR spectrum of MA/EVE copolymer 5. Solvent: acetone-d_6.

Scheme 4. Model Reaction of Succinic Anhydride and Dodecylamine



To ascertain the possibility of charge-transfer complexation between the amine and anhydride functionality of the MA/EVE copolymer 5, we examined some model reactions. Reaction of succinic anhydride (SA) (8) with dodecylamine (9) yielded the corresponding amide 10 (Scheme 4) identified by NMR and FTIR. However, the solution of succinic anhydride and dimethyldodecylamine (DMDA) in MEK exhibited a color change from pink to brown at room temperature with increasing reagent concentration. It is known that pyridine can promote the hydrolysis of the anhydride group by forming a zwitterionic intermediate.[19,20] Kluger and Hunt[21] detected the formation of succinyl-4-(dimethylamino)pyridinium ion in the reaction of succinic anhydride with 4-(dimethylamino)-pyridine. It is likely that the color change in the succinic anhydride/dimethyldodecylamine solution is due to the formation of an analogous zwitterion. We also observed a similar color change for the reaction of the copolymer 5 with dimethyldodecylamine.

UV spectra of the solutions of SA/DMDA and the products from the reactions of the MA/EVE copolymer 5 with primary and tertiary amines exhibit the same absorption maximum at 556 nm (Figure 2), suggesting the presence of similar zwitterionic species in these three systems. The absorption intensity of the tertiary solution is stronger for the same feed ratio of amine to acid anhydride. This observation may be explained by partial dodecylamine conversion to the amide. This is consistent with the increase in intensities of the absorption at 562 nm for dodecylamine-modified terpolymers 7 as the degree of amidation varies from 8 to 50 mol % (Figure 3).

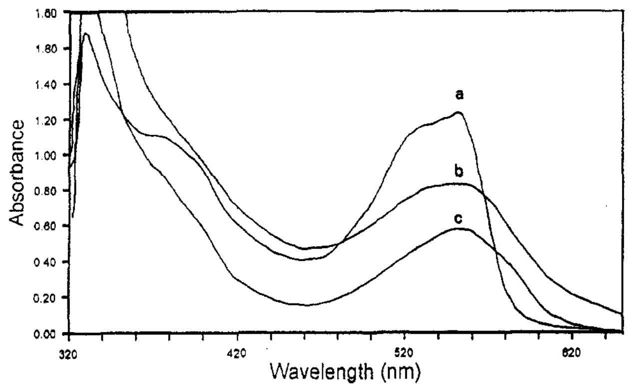


Figure 2. UV absorbance of 5/DMDA (a, 0.0036 g/mL), SA/DMDA (b, 0.036 g/mL), and 5/dodecylamine (c, 0.036 g/mL) obtained in MEK. Note that all three samples exhibit absorption maxima at 556 nm.

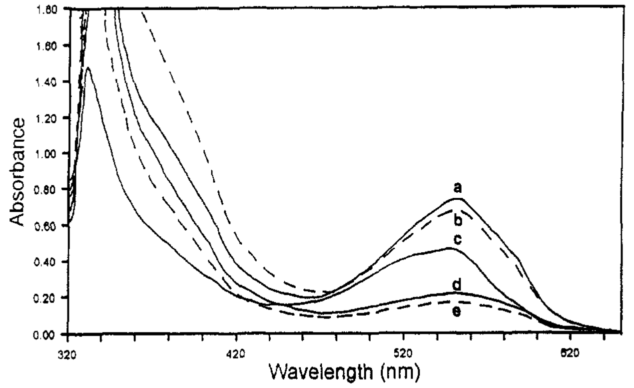


Figure 3. UV absorbance of 7–C12 terpolymers obtained in MEK. Sample concentration: 0.036 g/mL. (a) 7–C12–50; (b) 7–C12–40; (c) 7–C12–25; (d) 7–C12–16; (e) 7–C12–8.

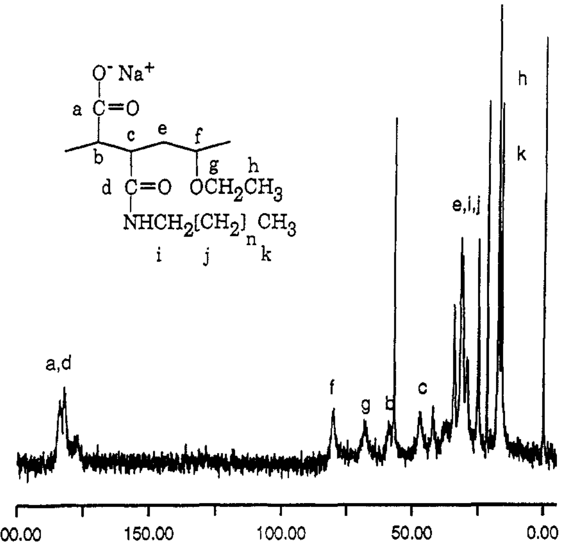


Figure 4. ^{13}C NMR spectrum of 7–C12–40 terpolymer. Solvent: D_2O.

Reactions of the MA/EVE copolymer 5 with octyl- and dodecylamine in ethyl acetate exhibit no color changes, and ^{13}C NMR studies demonstrate that the products are the expected amide and carboxylic acid derivatives (Figure 4). In this solvent, homogeneous conditions should allow uniform, random incorporation of the hydrophobic groups along the polymer chain. The hydrophobe concentration in the terpolymers can be easily controlled by the amount of the amine added to the reaction. To ensure complete conversion, the reactions were carried out at 80 °C for 10 h. It has been shown that 4-butylaniline reacts efficiently (100%) with the maleic anhydride and ethyl vinyl ether copolymer under the same reaction conditions.[22] Since the octyl- and dodecylamines used in this study are more reactive toward the anhydride group than aromatic amines, we feel confident that a complete reaction is also achieved. This is supported by the fact that the naphthalene content

Table 1. Terpolymer Compositions

terpolymer	hydrophobe content (mol %)	naphthalene content (mol %)
7-C8-10	10	1.05
7-C8-20	20	1.01
7-C8-30	30	0.995
7-C8-40	40	1.04
7-C8-50	50	1.04
7-C12-10	10	0.986
7-C12-20	20	1.00
7-C12-30	30	1.02
7-C12-40	40	1.06

in the terpolymers is the same as in the reaction mixture, about 1 mol %. The compositions of the terpolymers are summarized in Table 1.

The hydrolysis of the remaining anhydride groups of the modified terpolymers was performed in aqueous NaOH solutions at room temperature with the NaOH concentration varying from 0.1 to 0.5 M depending upon the degree of substitution. To completely dissolve the polymer with higher hydrophobe content, low NaOH concentration was necessary to avoid high ionic strength of the medium during neutralization. Complete hydrolysis was demonstrated through FTIR spectral analysis with disappearance of the C=O stretching vibration of the acid anhydride; it is assumed that no hydrolysis of the amide bond occurs since in previous work none was observed.[22] 7–C12–50 failed to dissolve completely in 0.01 M NaOH solution even over an extended period of time.

Solution Properties. The solution properties of amphiphilic water-soluble polymers are controlled by specific structural characteristics, molecular weight, and the solvent quality. The structural parameters including concentration and distribution of hydrophobic groups, hydrophilic segment length, and fixed ionic groups are among many which may be changed to yield the desired properties. For example, hydrophobic interactions of long-chain hydrocarbons incorporated along the polymer backbone can greatly affect the degree to which the polymer coil may expand or collapse. Changes in the degree of ionization and solvent characteristics such as ionic strength and pH alter the polymer conformations as well. In this study, influences of these parameters on the solution behavior of terpolymers 7 are examined by viscosity and fluorescence measurements.

Viscosity Studies. Aging Effects. Hydrophobically modified, water-soluble polymers often show time-dependent reorganization in solution.[23] To properly assess the effects of terpolymer composition, pH, and added electrolytes on solution behavior, aging studies were first conducted. Figure 5 shows the aging effects for the 7-C12–10 and 7–C12–40 polymers. Both terpolymers dissolve completely in deionized water within 24 h. The apparent viscosity of 7–C12–10 decreases only slightly before reaching a constant value within 3 days. A more pronounced aging effect was observed for 7–C12–40. Apparently, the stronger hydrophobic interactions require a longer period of time to reach equilibrium. Furthermore, freshly prepared 7–C12–40 solution exhibits intermolecular associating behavior (Figure 6). In contrast, intramolecular association is observed for the same solution at equilibrium. This indicates that the 7–C12–40 terpolymer undergoes a conformational transition from intermolecular to intramolecular during the aging process. No such conformational transition is observed for 7–C12 terpolymers at lower hydrophobe levels or for all 7–C8 terpolymers.

Effects of Hydrophobic Groups. To assess the effects of hydrophobic monomer content on viscosity behavior in deionized water, it was first necessary to determine intrinsic viscosity utilizing the Fuoss relationship.[24] For polymers with largely intramolecular association, the Fuoss plot should yield values which may be used to project molecular weights of single coils. Figure 7 shows the intrinsic viscosities of 7–C8 and 7–C12 terpolymers as a function of composition. The intrinsic viscosities decrease dramatically as the hydrophobe concentration in the terpolymers increases from 0 to 50 mol %. A larger quantity of hydrophobic groups effectively enhances the hydrophobic interactions, resulting in collapse of the polymer coil. A sharp drop in the intrinsic viscosity is

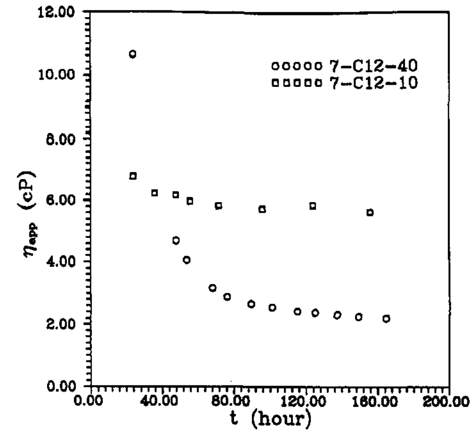


Figure 5. Aging effects of 7–C12–10 and 7–C12–40 terpolymers at 25 °C in deionized water. $C_P = 2.0$ g/dL. Shear rate: 1.28 s^{-1}.

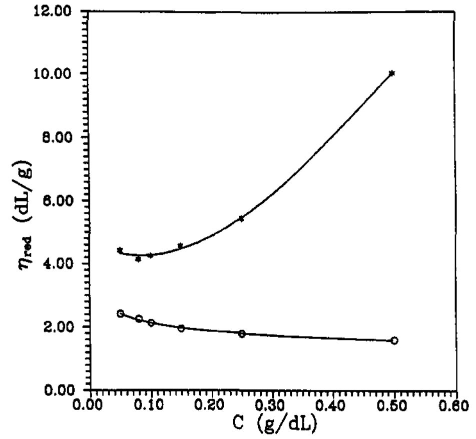


Figure 6. Comparisons of the viscosity behavior of 7–C12–40 terpolymer at 25 °C in deionized water at different times: (∗) 1 day after sample preparation; (○) 20 days after sample preparation. Shear rate: 1.28 s^{-1}.

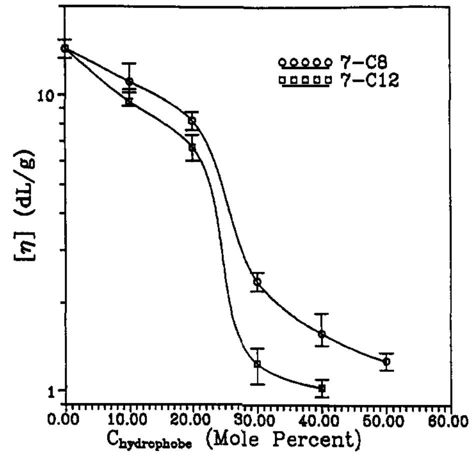


Figure 7. Effects of *n*-octyl and *n*-dodecyl group content on the intrinsic viscosity of 7–C8 and 7–C12 terpolymers in deionized water.

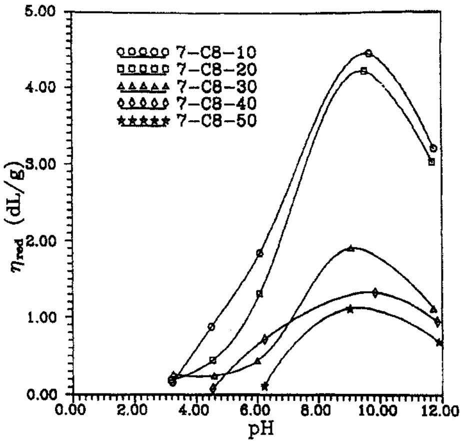


Figure 8. Effect of solution pH on η_{red} for 7–C8 terpolymers at 25 °C. C_P = 0.5 g/dL. Shear rate: 1.28 s^{-1}.

observed at hydrophobe concentrations between 20 and 30 mol % for both 7–C8 and 7–C12 terpolymers. Similar observations have been reported for other intramolecular associative copolymers[2–5] and have been attributed to a transition from random coil to tighter hypercoil. Dodecyl terpolymers possess a more compact structure than their octyl analogs at constant hydrophobe levels as indicated by the slightly lower intrinsic viscosities of the former (Figure 7).

Effect of pH. The amphiphilic terpolymers contain a large number of carboxyl functional groups as the major hydrophilic component. Variation in pH can impart significant change in solution properties. Figure 8 illustrates the viscosity behavior of the terpolymers containing varying *n*-octyl concentration at selected pH values. The reduced viscosities of all the polymer solutions initially increase with increasing pH and then decrease. The maximum value of reduced viscosity for all 7–C8 polymers is observed about pH 9.5. Changes in the reduced viscosity are qualitatively similar to those observed for maleic anhydride and alkyl vinyl ether copolymers.[7,9–11] The degree of ionization of the terpolymers increases with increasing pH, disrupting intramolecular associations. The terpolymers reach maximum charge density at the pH at which the highest reduced viscosity is achieved. Further increase in pH increases the concentration of sodium ions in the solution; therefore, the interaction between the charged groups along the polymer backbone is shielded, causing polymer coil collapse.

When the pH of the solution is below the pK_a of the carboxylic acid, most, if not all, of the charges carried by the terpolymers are neutralized. Therefore, there are not enough charged groups on the surface of the polymer coil to prevent macromolecular aggregation and macrophase separation occurs. For example, the terpolymers with 40 and 50 mol % octyl groups precipitate below pH 4 and 5, respectively.

Effect of Electrolyte Addition. The effect of NaCl on the viscosity of the terpolymer solutions was investigated using 7–C8 series (Figure 9). The reduced viscosity decreases for all terpolymers as the NaCl molarity increases due to the shielding of ionic interactions of the carboxylate groups. The terpolymers with high hydrophobe content such as 7–C8–50 precipitate at high salt concentration (~0.5 M).

Effect of Shear Rate. The effect of shear rate on the apparent viscosity of 7–C8–10, 7–C8–30, and 7–C8–50 terpolymers was investigated in pure water at both low and high polymer concentrations. Unlike some of the reported systems which showed shear-thickening behavior,[25] the terpolymers at 0.05 g/dL exhibit Newtonian behavior over the shear rate regime. Similar behavior is observed for the terpolymers at 0.5 g/dL.

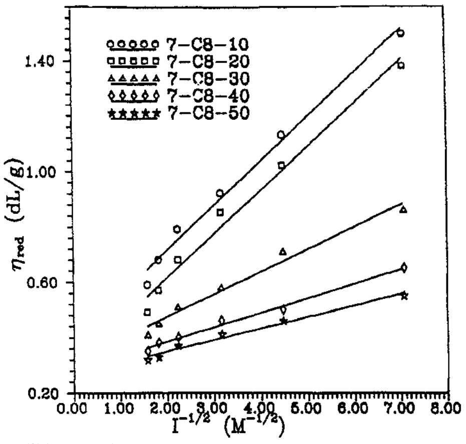


Figure 9. Effect of ionic strength on η_{red} of 7–C8 terpolymers at 25 °C. C = 0.15 g/dL. Shear rate: 1.28 s^{-1}.

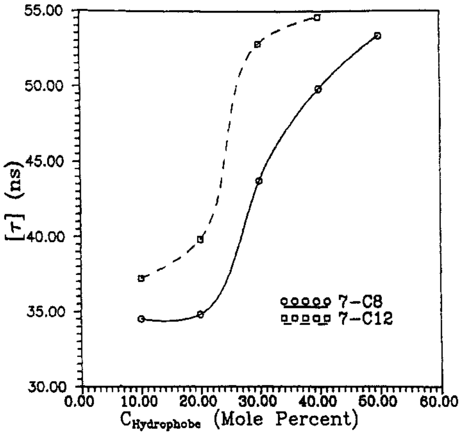


Figure 10. Dependence of average lifetime for monomer emission on hydrophobe content.

Table 2. Fluorescence Lifetime [τ] (ns) of Monomer Emission Decay for 7-C8 Terpolymers in Aqueous Solutions

pH	7-C8-10	7-C8-20	7-C8-30	7-C8-40	7-C8-50
3	44.3	52.5	57.1	58.8	60.8
5	41.2	44.3	49.1	54.1	58.1
7	34.5	34.8	43.7	49.8	54.3
8	28.9	31.4	40.1	48.5	52.6
10	24.1	28.3	36.6	44.3	51.6

Photophysical Studies. Fluorescence measurements were conducted in attempts to evaluate associative properties of the terpolymers in aqueous solutions. Naphthalene lifetimes and excimer to monomer ratios (I_E/I_M) were recorded to monitor the changes of terpolymer conformation.

Effects of Hydrophobic Groups. A significant change in the fluorescence decay of monomer fluorescence (330 nm) is observed upon altering the hydrophobe content (Figure 10). The decay profiles of the terpolymers are complex but can be approximately fit by a sum of two exponentials composed of a longer-lived component and a shorter-lived component. Table 2 summarizes the values of the average lifetime[26] defined by the following equation:

$$[\tau] = \sum a_i \tau_i^2 / \sum a_i \tau_i$$

where a_i is the preexponential factor of the ith component and τ_i is the corresponding lifetime.

Multiexponential fits have been reported for other associative polymers in aqueous media[16,27] and are probably

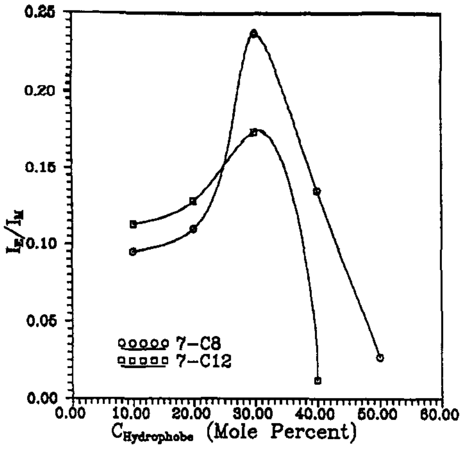


Figure 11. Dependence of I_E/I_M for both 7–C8 and 7–C12 terpolymers on the hydrophobe content at pH 7.

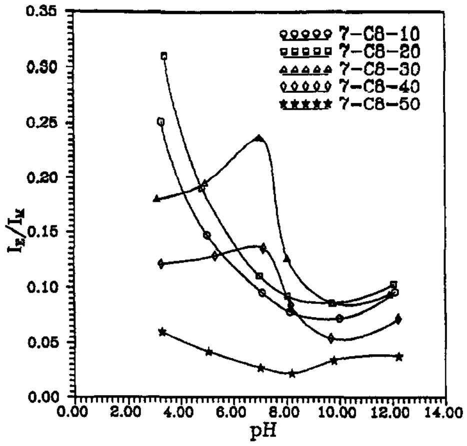


Figure 12. Dependence of I_E/I_M on solution pH for 7–C8 terpolymers. C_P = 0.05 g/dL.

due to labels in different environments contributing to the emission. It is noteworthy in our case that the values of [τ] increase with increasing hydrophobe concentration. The lifetimes of the naphthalene-labeled model compound 4 in solutions of THF, ethanol, methanol, and 50/50 methanol/water are 68.1, 47.2, 30.7, and 21.8 ns, respectively, demonstrating the effect of microenvironmental polarity on the decay of the excited state of the naphthalene label. Therefore, the increase in the average lifetime at higher hydrophobe content is consistent with coil collapse. Also, the 7–C12 series polymers have higher [τ] values than the 7–C8 analogs with the same hydrophobe mole percent. Longer side chains effectively enhance the hydrophobic effect, providing shielding of the naphthyl label from water. These results are similar to those previously reported for hydrophobically modified poly(allylamine)s.[28]

In addition to changes in the average lifetime, terpolymers also show a dramatic hydrophobe concentration dependence of I_E/I_M. As indicated in Figure 11, I_E/I_M values of the terpolymers increase as the hydrophobe concentration varies from 10 to 30 mol %. Further increases in the hydrophobe concentration result in decreases in I_E/I_M. It is unlikely that excimer formation is due to nearest-neighbor interactions since the number of naphthyl groups are small and they are separated over a large distance along the polymer backbone. The initial increase in I_E/I_M may be attributed to increased compaction of the polymer coil which facilitates the formation of the excimer due to the reduced separation of the chromophore within the hydrophobic microdomain. When the hydrophobe concentration is above 30 mol %, however, the large hydrophobe quantities within the polymer coil separate the naphthyl labels. Furthermore, the highly compact hydrophobic microdomains limit the mobility of the chromophores, preventing orientation in a manner favorable for excimer formation. The latter effect has been observed previously by our group[16] and elsewhere[29] for naphthalene-labeled methacrylic acid copolymers. The negligible formation of excimer in 7–C8–50 and 7–C12–40, which have high hydrophobe concentrations, lends credence to these arguments.

Effect of pH. The effect of solution pH on the conformation of the terpolymers was first examined by the lifetime measurement at 330 nm of the monomer decay of 7–C8 systems. Decrease in [τ] indicates the expansion of the hydrophobic domains with increasing pH (Table 2). The highly hydrophobic terpolymers such as 7–C8–40 and 7–C8–50 remain in the rather compact conformations at high pH as evidenced by the large [τ] values.

Figure 12 depicts the pH dependence of I_E/I_M for 7–C8 polymers in the aqueous solutions. For the 7–C8–10 and 7–C8–20 polymers, I_E/I_M decreases in the pH range 3–10 and then increases slightly at higher pH. This is consistent with the rheological response of the terpolymers. As the pH increases, the polymer coil expands and the naphthyl groups are separated, leading to decreased I_E/I_M. The lowest I_E/I_M occurs at the pH where maximum expansion of the polymer coil occurs. A slight rise in I_E/I_M at higher pH is attributed to an increase in ionic strength. 7–C8–20 exhibits a higher I_E/I_M value at a given pH than does 7–C8–10 due to a more compact structure of the former.

The 7–C8–30 polymer exhibits a different dependence of I_E/I_M on the pH. The curve first rises and then drops rapidly upon increasing the pH. The initial increase in the values of I_E/I_M may be explained by increased mobility of the naphthyl groups in the hydrophobic microdomains upon coil expansion. At pH 3, the terpolymer adopts a highly collapsed conformation, indicated by the very low reduced viscosity. The mobility of the chromophore is largely restricted. The probability of two chromophores approaching each other in a coplanar or sandwich manner, a necessity for the excimer formation, is small. As the pH is increased, chain expansion decreases polymer coil density. The relatively large separation of the naphthyl moities from the polymer backbone allows the chromophores to maintain proximity to one another upon moderate expansion; this, coupled with increased mobility of the chromophores, leads to increased I_E/I_M. Further increase in the coil size at higher pH, however, results in long-range separation of the chromophores and I_E/I_M decreases rapidly. This behavior is significantly different from that observed previously by our group[16] for naphthalene-labeled poly(methacrylic acid). In that case, I_E/I_M increased rapidly at a pH of 7.5 but exhibited no decrease thereafter. Relatively large quantities of naphthyl labels and long spacers in that copolymer were reported to allow association even in a highly expanded coil. For the 7–C8–30 terpolymer, however, each naphthyl group is surrounded by comparatively large neighboring octyl groups upon coil expansion,[6,7] resulting in a decrease in I_E/I_M. Interestingly, the I_E/I_M maximum is observed at lower pH than the reduced viscosity maximum (Figure 8), indicating that significant chromophore separation occurs before the polymer chain reaches its maximum expansion.

The terpolymer 7–C8–40 also shows an increase in I_E/I_M, but to a lesser extent. This can be attributed to the increased difficulty of two chromophores approaching each other in a large hydrophobe concentration within the

Table 3. Fluorescence Lifetime [τ] (ns) of Monomer Emission Decay for 7-C8 Terpolymers in NaCl Aqueous Solutions

C_{NaCl} (M)	7-C8-10	7-C8-20	7-C8-30	7-C8-40	7-C8-50
0.1	49.3	54.5	60.1	65.3	68.6
0.2	55.2	58.7	64.5	67.6	69.5
0.3	58.9	62.4	67.5	69.9	72.4
0.4	61.2	63.5	69.8	71.3	74.1

polymer coil. This is consistent with the observation that the 7–C8–40 polymer always exhibits a lower I_E/I_M value than 7–C8–30 at a constant pH.

Values of I_E/I_M for 7–C8–50 change little with pH. In this case, very high hydrophobe concentration within the polymer coil results in almost complete diminution of the naphthyl group interactions. Each naphthyl label is surrounded by a large number of octyl groups even in the expanded coil. Therefore, low I_E/I_M values are observed throughout the pH range.

Effect of Electrolyte Addition. Table 3 lists the average lifetimes of the monomer emission for 7–C8 polymers at different NaCl concentrations. Increased average lifetime is consistent with the compaction of the polymer coil with increasing salt concentration. The terpolymers with higher hydrophobe content are less sensitive to the ionic strength as indicated by the reduced curvature of the data. The reduced sensitivity may be explained by the already very compact conformation adopted by the terpolymers in the salt-free solution as well as the decreased quantity of charged groups along the terpolymer chain.

Conclusions

A series of naphthalene-labeled poly(maleic anhydride-*alt*-ethyl vinyl ether) copolymers containing pendent octyl and dodecyl groups have been synthesized. The fluorescence and viscosity behavior of the terpolymers have been studied as a function of the length and concentration of the hydrophobic groups, electrolyte concentration, and the solution pH. In all cases investigated, the terpolymers exhibit a tendency toward intramolecular association in dilute and semidilute aqueous solutions at specifically varied conditions of pH and ionic strength. The terpolymers with longer alkyl groups and/or higher alkyl group content tend to be more compact and exhibit lower viscosity in deionized water. Addition of either acid or base results in decreased solution viscosity. Addition of NaCl lowers significantly the viscosity of the polymer solutions, indicating a more collapsed conformation at higher ionic strength. Photophysical data parallel the rheological responses. I_E/I_M values of naphthyl moieties from steady-state fluorescence increase initially, reach a maximum, and then decrease upon increasing hydrophobe concentration from 10 to 50 mol %. Extended lifetime of the monomer fluorescence decay with increasing hydrophobe level indicates increased compaction of the polymer coil. As the pH values change from 3 to 10, significant decreases in the I_E/I_M values are observed for the terpolymers with low hydrophobe content due to coil expansion. I_E/I_M values of the terpolymers with moderate hydrophobe content rise initially and then decrease continuously over the same pH range. Systems with high hydrophobic content show little dependence on pH. These results are explained by considering the relative concentration of the chromophore in the hydrophobic microdomains as well as the change in the mobility of the naphthyl moieties with the compactness of the polymer coils. The lifetime of the monomer emission decreases with increasing pH, indicating a more hydrated environment experienced by the probe within the polymer coil.

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