Water-Soluble Polymers. 77. Amphoteric Cyclocopolymers with Sulfobetaine Units: Phase Behavior in Aqueous Media and Solubilization of *p*-Cresol in Microdomains

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ABSTRACT: A novel series of cyclocopolymers containing the pH-responsive hydrophobic monomer, *N,N*-diallyl-*N*-methylamine (DAMA), and the sulfobetaine monomer, 3-(*N,N*-diallyl-*N*-methylammonio)-propanesulfonate (DAMAPS), have been prepared in 0.5 M NaCl aqueous solution (pH = 4.0) using 2-hydroxy-1-[4-(hydroxyethoxy)phenyl]-2-methyl-1-propanone (Irgacure 2959) as the free-radical photoinitiator. The feed ratio of DAMA:DAMAPS was varied from 100:0 to 0:100 mol % with the total monomer concentration held constant at 2.5 M. ^{13}C NMR data indicate that the resulting polymers maintain the five-membered-ring structure in the cis conformation common to cyclized diallylammonium salts. Reactivity ratio studies predict that the sulfobetaine monomer is incorporated randomly along the polymer backbone. Weight-average molecular weights and second virial coefficients vary from (4.00 to 8.42) $\times 10^4$ and (2.14 to 4.62) $\times 10^{-4}$ mL mol g^{-2}, respectively. Solution behavior is dependent upon pH as determined by turbidimetric titration, steady-shear viscometry, and equilibrium surface tensiometry. At high degrees of ionization, the copolymers assume an extended conformation due to the charge−charge repulsions along the copolymer backbone. As the molar incorporation of the sulfobetaine increases, the copolymer assumes a more globule-like conformation due to zwitterionic interactions. With decreasing degree of ionization of the DAMA units, hydrophobic associations increasingly dominate the solution behavior. For copolymers with a low incorporation of the sulfobetaine, chain collapse leading to phase separation occurs. However, at higher incorporations, the sulfobetaine acts as a hydrophilic segment to limit hydrophobic packing and minimizes the chain collapse. Equilibrium dialysis experiments demonstrate that these pH-reversible microdomains can be used to control the sequestration of organic foulants and thus have potential application as polymeric surfactants in micellar enhanced ultrafiltration processes for water purification.

Introduction

The need to separate water-soluble organic compounds from aqueous streams is a frequently encountered industrial problem. One proposed technique for water remediation is micellar-enhanced ultrafiltration (MEUF).[1−5] This method is characterized by the addition of a surfactant above its critical micelle concentration to the aqueous stream containing the organic foulant allowing phase transfer to the hydrophobic core of the micelle. The stream is then passed through a microporous membrane, such that most of the organic foulant and surfactant remain in the retentate. Although this method can result in efficient foulant removal, monomeric surfactant continuously crosses the membrane into the permeate. Therefore, added surfactant is required as time progresses in order to maintain a critical micelle concentration. One method that has been utilized to reduce the loss of surfactant is the addition of an oppositely charged polyelectrolyte to the retentate.[6−8] Whereas this methodology drastically reduces the loss of surfactant to the permeate by allowing the surfactant to associate with the polyelectrolyte, the ultimate problem of separating the foulant from the polymer/surfactant complex still remains. A more promising purification method utilizes stimuli-responsive polymeric micelles in an extension of the MEUF process.[9]

Hydrophobically modified polymers demonstrating surfactant-like or "polysoap" behavior have been the subject of considerable research,[10−13] beginning with the classical studies of Strauss.[14−17] The nature of hydrophobic associations is related to many factors including polymer microstructure,[18−23] the "bulkiness" of the hydrophobe,[24−27] and the chemical composition of the hydrophobe (hydrocarbon vs fluorocarbon).[28,29]

To obtain an understanding of how the rigidity of the polymer backbone affects the hydrophobic associations of a polysoap, we synthesized a series of hydrophobically modified, quaternary ammonium monomers and polyelectrolytes.[30] In that work, consistent with other reports,[31−33] we demonstrated that the introduction of long hydrophobic side chains along the backbone of cationic, quaternary ammonium cyclopolymers can result in the formation of polymeric micelles or polymeric aggregates under specified conditions. The polymeric structures that were formed did not exhibit responsiveness that would be required of an ideal remediative polymer. However, twin-tailed quaternary ammonium monomers formed vesicle-like aggregates capable of sequestration of organic model compounds.[34,35]

In this paper, we report the synthesis and solution properties of cyclocopolymers of *N,N*-diallyl-*N*-methylamine and 3-(*N,N*-diallyl-*N*-methylammonio)propanesulfonate. Utilizing turbidimetric titrations, steady-shear viscometry, and equilibrium surface tension, we examine the effects of the pH-responsive hydrophobic monomer (DAMA) and the zwitterionic comonomer (DAMPS) on associative interactions in aqueous media. Finally, we monitor the solubilization of *p*-cresol utilizing equilibrium dialysis experiments to demonstrate the potential of the cyclocopolymers as remediative agents.

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Experimental Section

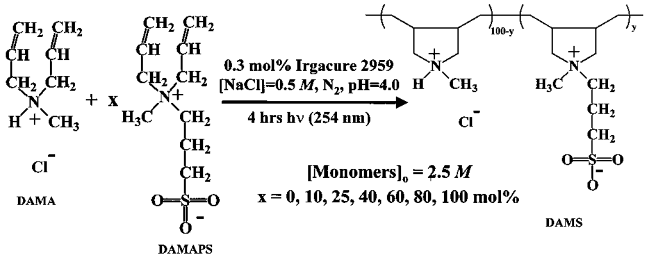
Materials. All reagents were purchased from Aldrich Chemical Co. and used as received unless otherwise noted. *N*,*N*-Diallyl-*N*-methylamine (DAMA)[30] and 3-(*N*,*N*-diallyl-*N*-methylammonio)propanesulfonate (DAMAPS)[36] were synthesized as previously described.

Synthesis of Copolymers of DAMA with DAMAPS. Homopolymers of DAMA, DAMAPS, and the copolymers of DAMA with DAMAPS (the DAMS series) were synthesized by free radical photopolymerization in a 0.5 M aqueous NaCl solution (pH = 4.0) under a nitrogen atmosphere at 35 ^{o}C using 0.3 mol % 2-hydroxy-1-[4-(hydroxyethoxy)phenyl]-2-methyl-1-propanone (Irgacure 2959) (Ciba) as the photoinitiator. The feed ratio of DAMA/DAMAPS was varied from 100/0 to 0/100 mol % with the total monomer concentration held constant at 2.5 M. NaCl (0.5 M) was added to the reaction medium to maintain solubility of polymers with high DAMAPS content. The pH of the reaction medium was adjusted to 4.0 to ensure protonation of the tertiary amine and to facilitate the intermolecular−intramolecular propagation mechanism common to diallylammonium salts. The polymerizations were conducted in a Rayonet photoreactor (Southern New England Ultraviolet Co.) operating at 300 nm for 4 h. Low conversion samples were obtained for reactivity ratio studies. The reaction was usually terminated at <50% conversion as a precaution against copolymer drift. The copolymers were purified by dialyzing against deionized water with 6000−8000 MWCO tubing (Spectrapor). The dialysis was conducted for 2 weeks with frequent changing of the permeate. The copolymers were recovered by lyophilization. Conversions were determined gravimetrically.

Instrumentation. ^{1}H and ^{13}C NMR spectra were recorded with a Bruker AC-300. ^{13}C NMR spectra of the cyclocopolymers were obtained at 50.3 MHz using 10−15 wt % 1.0 M NaCl (pH 4.0) aqueous (D_2O) polymer solutions with 3-(trimethylsilyl)-1-propanesulfonic acid, sodium salt (DSS), as a reference. DEPT135 experiments confirmed peaks assignments for both monomer and polymer samples. A recycle delay of 8 s, 90^o pulse length, and inverse gated decoupling to remove all NOE were used for quantitative spectral analysis. Experimental error for the inverse gated decoupled ^{13}C NMR was <5%. Elemental analyses were performed by MHW Laboratories, Phoenix, AZ. Molecular weight studies were performed with a Brookhaven Instruments 128-channel BI-2030 AT digital correlator using a Spectra Physics He−Ne Laser operating at 632.8 nm. Weight-average molecular weights (M_w) were determined through analysis of the Berry plots. Hydrodynamic radii were determined using the cumulants analysis of the autocorrelation function obtained at 90°. Refractive index measurements were carried out with a Chromatix KMX-16 differential refractometer. Potentiometric titrations were conducted with an Orion 950 Ross *FASTQC* Titrator and an Orion Ross Sure-Flow semi−micro combination pH electrode (model 8175BN) under a nitrogen atmosphere. Experimental error for all pH values was ±0.05. Turbidity was monitored during the titration with a Brinkmann PC800 colorimeter. Dilute solution viscometric studies were conducted with a Contraves LS-30 low-shear rheometer at a constant shear rate of 5.96 s^{-1} at 25 ^{o}C. Equilibrium surface tension measurements were performed utilizing a Kruss tensiometer (Wilhelmy plate) at 25 °C as a function of polymer concentration.

Equilibrium Dialysis Experiments. Equilibrium dialysis experiments were performed utilizing equilibrium dialysis cells (5 mL) from Bel-Art Products and regenerated cellulose membranes having a nominal molecular weight cutoff of 6000. Solutions containing the polymeric surfactant and *p*-cresol of known concentrations ([polymer] = 0.2 g/dL; $[\text{cresol}]_{\text{feed}}$ = 7−70 mM) at selected pH (pH = 4.5, 7.5, 8.5, or 9.5) were placed in one side of each dialysis cell (retentate), and deionized water (pH adjusted to 4.5, 7.5, 8.5, or 9.5) was placed in the other side (permeate). The cells were thermostated at 25 °C in a Napco incubator. The concentrations of *p*-cresol in the retentate, $[\text{cresol}]_{\text{ret}}$, and permeate, $[\text{cresol}]_{\text{per}}$, were determined by UV spectroscopy after a 24 h period. (Dialysis experiments in the absence of polymer indicated that equilibrium concentrations of *p*-cresol were obtained in 24 h.) Dynamic light scattering data indicated that the polymeric surfactant was quantitatively retained within the retentate compartment.

Scheme 1. Synthetic Pathway for Preparation of DAMS Cyclocopolymers



Analysis of Equilibrium Dialysis Experiments. From $[\text{cresol}]_{\text{ret}}$ and $[\text{cresol}]_{\text{per}}$, the concentration of *p*-cresol bound within the hydrophobic microdomains of the polymeric surfactant, $[\text{cresol}]_{\text{bnd}}$, was calculated from eq 1.

$$[\text{cresol}]_{\text{bnd}} = [\text{cresol}]_{\text{rel}} - [\text{cresol}]_{\text{per}} \qquad (1)$$

Equation 1 remains valid if the concentration of cresol in the permeate is equivalent to the free concentration of cresol (unbound cresol) in the retentate. From the concentration of bound cresol, the ratio of moles of cresol bound per mole of polymer, *r*, is then calculated from eq 2:

$$r = \frac{[\text{cresol}]_{\text{bnd}}}{[\text{polymer}]} \qquad (2)$$

where [polymer] is the concentration of polymer in the retentate. Binding isotherms were constructed by plotting *r* as a function of free cresol in the retentate, $[\text{cresol}]_{\text{free}}$.[37,38] Efficiency of foulant sequestration is analyzed by monitoring rejection ratios,[39] a term commonly used in membrane applications and defined in eq 3:

$$\text{rejection ratio} = \left(1 - \frac{[\text{cresol}]_{\text{per}}}{[\text{cresol}]_{\text{ret}}}\right) \times 100 \qquad (3)$$

Results and Discussion

Synthesis and Compositional Analysis of Cyclocopolymers. The photoinitiated cyclocopolymerization of DAMA and DAMAPs to produce the DAMS series is illustrated in Scheme 1. The facile manner in which this polymerization proceeds as compared to slower thermal polymerization can be attributed to the early formation of initiator radicals from Norrish type I cleavage of 2-hydroxy-1-[4-(hydroxyethoxy)phenyl]-2-methyl-1-propanone. DAMA and DAMPS units were maintained in their most hydrated form by adjusting the pH to 4.0 and maintaining high ionic strength during polymerization as described in the Experimental Section. Homogeneous conditions were thus maintained throughout the reactions. In the discussion to follow, numbers following the DAMS acronym represent the mole percent of the sulfobetaine monomer in the cyclocopolymer.

Representative inverse gated decoupled ^{13}C NMR spectra are shown in Figure 1 for the purified samples. Peak assignments were confirmed through DEPT135 analysis (data not shown). The five-membered-ring structures reported for cyclocopolymers of *N*,*N*-diallyl-*N*,*N*-dimethylammonium chloride (DADMAC)[40] were found in each cyclocopolymer regardless of the incorporation of the sulfobetaine mer unit. Also, the cis product, which is the primary isomer found in the DADMAC homopolymer,[40] was also confirmed to be predominant

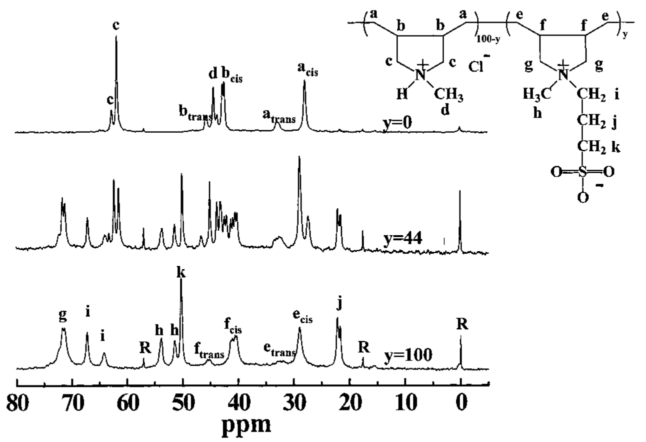


Figure 1. Representative inverse gated decoupled ^{13}C NMR spectra of the DAMS cyclocopolymers in D_2O (1 M NaCl, pH = 4.0). R = 3-(trimethylsily)-1-propanesulfonic acid, sodium salt, as a reference.

Table 1. Reaction Parameters and Polymer Composition for the Copolymerization of DAMA (M_1) and DAMAPS (M_2)

sample	rxn time (h)	% conv	M_2 feed (mol %)	M_2 in copolymer (mol %)[a]	cis isomer (mol %)[a]
DAMA	4.0	42.6	0	0[b]	80
DAMS12	4.0	47.2	10	12	82
DAMS34	4.0	41.5	25	34	82
DAMS44	4.0	41.5	40	44	84
DAMS66	4.0	43.1	60	66	85
DAMS82	4.0	51.1	80	82	88
DAMAPS	4.0	69.0	100	100[b]	89

[a] From inverse gated decoupled ^{13}C NMR (1 M NaCl, pH = 4.0, D_2O). [b] Theoretical value.

for this copolymer series by analysis of the backbone carbon resonances shown in Figure 1.

Copolymer compositions were determined by inverse gated decoupled ^{13}C NMR according to eq 4, where I_i, I_a, I_e, I_c, and I_g represent the integrated intensities of carbons i, a, e, c, and g, respectively (Figure 1). (Data are summarized in Table 1.)

$$\text{mol \% DAMAPS(M2)} = I_i\left(\frac{1}{I_a + I_e} + \frac{1}{I_c + I_g}\right) \times 100 \tag{4}$$

From the experimental compositions, reactivity ratios of $r_1 = 0.67 \pm 0.05$ and $r_2 = 1.13 \pm 0.05$ for DAMA(M_1)/DAMAPS(M_2) were determined by a nonlinear least-squares method.[41] The experimentally measured values of cyclocopolymer composition as a function of feed compositions are shown in Figure 2; the dashed line represents ideal incorporation. Random incorporation (with a slight tendency toward DAMAPS incorporation) is predicted for the resulting microstructure utilizing the methods of Igarashi[42] and these experimental reactivity ratios (Table 2).

Multiangle Laser Light Scattering. Table 3 shows the weight-average molecular weights varying from 4.13 to 8.42×10^4 g mol^{-1} as determined by Berry plots (25 °C in 1 M NaCl, at pH 4.0). While these values might seem low for free radical polymerizations, these are typical for cyclocopolymers from diallylammonium salts, probably due to chain transfer to monomer involving the labile allylic hydrogen atoms and relatively low k_p/k_t values. The second virial coefficients (A_2) for this copolymer series in 1 M NaCl at pH = 4.0 lie between 2.14×10^{-4} and 4.62×10^{-4} mL mol g^{-2}.

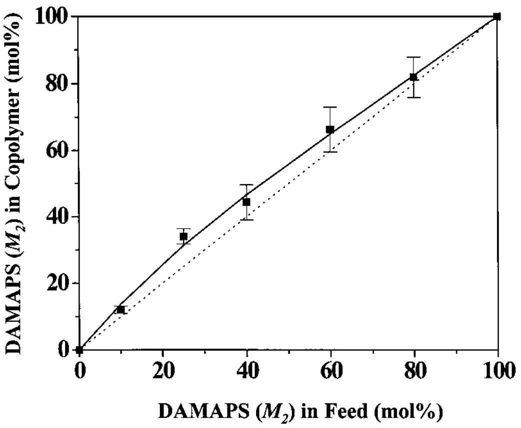


Figure 2. Mole percent sulfobetaine incorporation in DAMS copolymers as a function of mole percent sulfobetaine in the feed as determined by inverse gated decoupled ^{13}C NMR.

Table 2. Microarchitectural Analysis: Distribution of Monads, Dyads, and Triads per 100 Repeats as a Function of the Monomer Feed Ratio (M_1:M_2)

sequence	90:10	75:25	60:40	40:60	20:80
M_1	86.2	68.6	53.4	35.0	17.5
M_2	13.8	31.4	46.6	65.0	82.5
M_1-M_1	73.9	45.8	26.8	10.8	2.51
M_1-M_2	12.3	22.8	26.6	4.18	15.0
M_2-M_1	12.3	22.8	26.6	4.18	15.0
M_2-M_2	1.53	8.56	20.0	40.8	67.5
$M_1-M_1-M_1$	63.4	30.6	13.4	3.33	0.36
$M_1-M_1-M_2$	10.5	15.2	13.4	7.47	2.15
$M_1-M_2-M_1$	10.9	16.6	15.2	8.99	0.72
$M_1-M_2-M_2$	1.36	6.22	11.7	15.2	12.3
$M_2-M_1-M_1$	10.5	15.2	13.4	7.47	2.15
$M_2-M_1-M_2$	1.74	7.58	13.3	16.7	12.8
$M_2-M_2-M_1$	1.36	6.22	11.4	15.2	12.3
$M_2-M_2-M_2$	0.17	2.34	8.57	25.7	55.3

Table 3. Classical Light Scattering Data for the Copolymers of DAMA (M_1) with DAMAPS (M_2)

sample	M_2 in copolymer (mol %)[a]	$M_w \times 10^{-4}$ (g mol^{-1})	$A_2 \times 10^4$ (mL mol g^{-2})	DP × 10^{-2}
DAMA	0[b]	4.13	2.19	2.80
DAMS12	12	4.00	4.62	2.28
DAMS34	34	5.36	3.75	2.36
DAMS44	44	4.32	2.85	1.72
DAMS66	66	5.81	2.42	1.93
DAMS82	82	6.83	2.29	2.02
DAMAPS	100[b]	8.42	2.14	3.61

[a] From inverse gated decoupled ^{13}C NMR (1 M NaCl, pH = 4.0, D_2O). [b] Theoretical value.

Solution Behavior. Potentometric and Turbidimetric Measurements. The aqueous solution behavior of the DAMS copolymer series was initially studied by performing potentiometric and turbidimetric titrations to determine the phase behavior as a function of the degree of ionization of the DAMA mer unit (α). Figure 3 illustrates the percent transmittance and apparent pK_a as a function of the degree of ionization of the DAMA mer unit (α) for the homopolymer (DAMA) and three copolymers DAMS12, DAMS44, and DAMS66. The apparent pK_a was calculated utilizing the Henderson−Hasselbalch equation:[43]

$$\text{p}K_a = \text{pH} - \log\frac{\alpha}{1-\alpha} \tag{5}$$

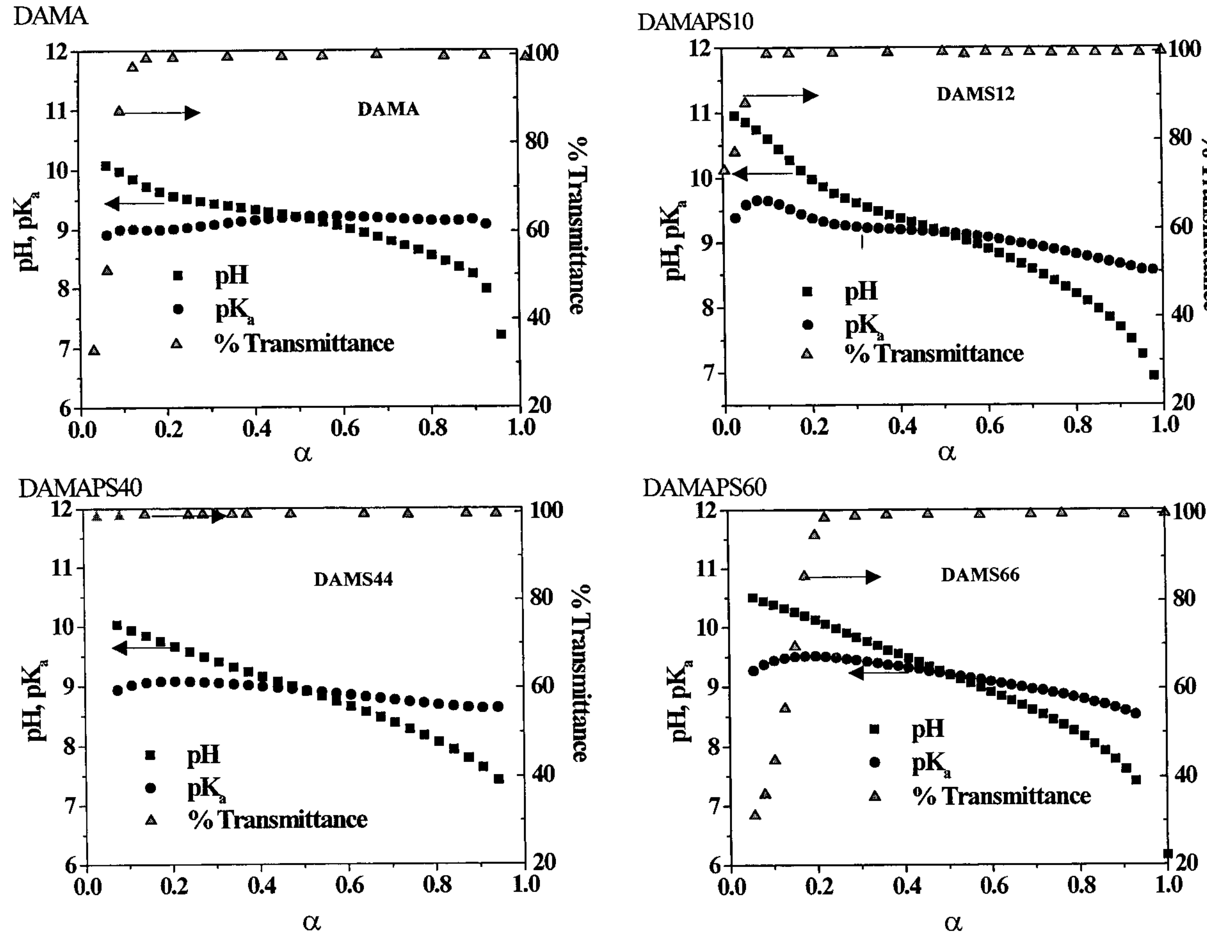


Figure 3. Potentiometric and turbidimentric titrations of DAMA and three DAMS cyclocopolymers (α represents the degree of ionization of the DAMA mer unit).

As shown in Figure 3, each of the polymers is soluble at high degrees of DAMA mer unit ionization. In this case, the polymers resemble copolymers of *N*,*N*-diallyl-*N*,*N*-dimethylammonium chloride (DADMAC) and DAMAPS which have been previously studied in our laboratories.[36] In those studies, it was discovered that DADMAC-*co*-DAMAPS copolymers containing less than 55 mol % of the sulfobetaine mer unit exhibit complete solubility (no phase separation) in deionized water due to a charge imbalance along the polymer backbone. The DAMS copolymers also exhibit this behavior when the DAMA mer unit is protonated. However, as the degree of ionization decreases, the turbidity of the solutions increase for DAMA, DAMS12, and DAMS66. In the case of the homopolymer, DAMA, the polymer precipitates from solution for $\alpha < 0.1$. Apparently, at low degrees of ionization, the hydrophobic tertiary amine functionality dominates the phase behavior and precipitation of the polymer results. DAMS12 does not precipitate from solution; however, macroscopic phase separation is observed for $\alpha < 0.1$. In this case, the incorporation of the hydrophilic sulfobetaine mer units help to stabilize the hydrophobic segments of the copolymer, but the molar content of the hydrophilic segment is not large enough to maintain solubility. DAMS34 (data not shown) and DAMS44, on the other hand, remain soluble throughout the entire range of α, due to sufficient hydrophilic content. However, as the sulfobetaine content increases to 66 mol % (DAMS66), macroscopic phase separation (but no precipitation) is again observed for low degrees of ionization of the DAMA mer unit ($\alpha < 0.2$). Instead of hydrophobic interactions dictating the phase separation, as in the case for DAMA and DAMS12, the likely molecular interactions causing the phase behavior are the dipole–dipole associations among the sulfobetaine mer units.

Viscometric Studies. To further study the solution behavior of the DAMS polymer series, low-shear viscosity experiments were performed. Figure 4 illustrates the apparent viscosity of the homopolymer, DAMA, and three cyclocopolymers (DAMS34, DAMS44, and DAMS66) as functions of the degree of ionization of the DAMA mer unit (α) and polymer concentration. Note that for each system the apparent viscosity of the polymer solution diminishes as α decreases. This behavior has been well documented as a polyelectrolyte-to-polysoap transition common to many responsive systems. At high α, the polymer assumes a more extended conformation due to the charge–charge repulsive forces along the polymer backbone. However, as the degree of ionization is lowered, the cyclic, cationic mer units are transformed into hydrophobic, nonprotonated amines, causing the polymer to assume a collapsed conformation.

Upon further analysis of Figure 4, one may discern the effects of the incorporation of sulfobetaine mer units on the conformation of the polymer chain in solution. Note that at high degrees of ionization of the DAMA mer units the apparent viscosities of the polymer systems decrease as sulfobetaine incorporation increases, a characteristic similar to that exhibited by DADMAC-*co*-DAMAPS copolymers.[36] The decrease in

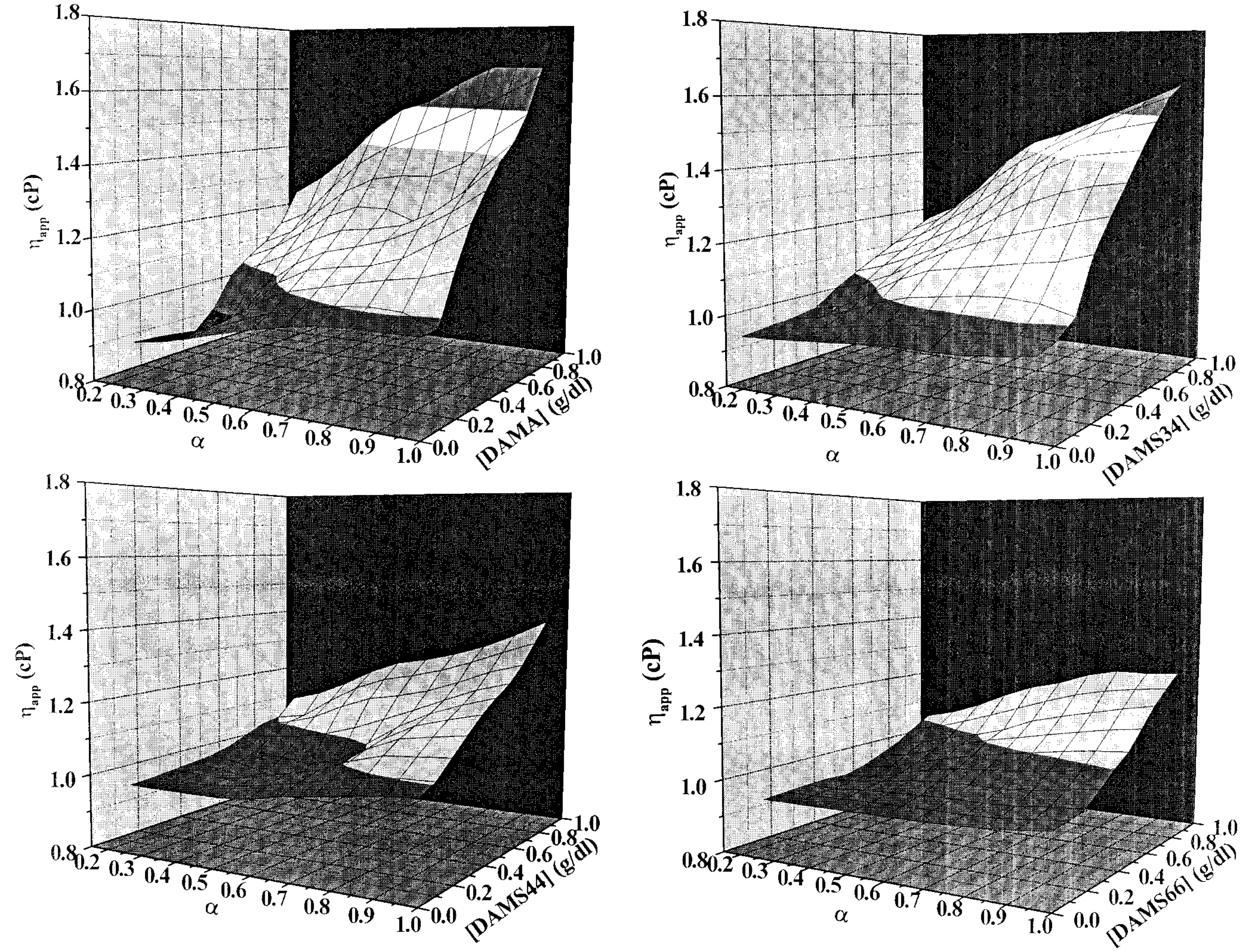


Figure 4. Apparent viscosity for the homopolymer of DAMA and three DAMS cyclocopolymer as functions of polymer concentration and the degree of ionization of the DAMA mer unit (α) (T = 25 °C, γ = 5.96 s^{-1}).

apparent viscosity is attributed to an increase of intramolecular dipole–dipole interactions among the zwitterionic moieties. These interactions lead to a decrease in coil dimensions and thus a decrease in the viscosity of the system.

For low degrees of ionization of the DAMA mer units, the copolymers assume a collapsed conformation as discussed above. However, for dilute solutions, as the molar incorporation of the sulfobetaine mer units is increased from 0 to 44 mol %, the apparent viscosity increases. This is followed by a decrease in the apparent viscosity as the molar incorporation reaches 66 mol %. The sulfobetaine mer units act as hydrophilic segments and thus stabilize the polymer in solution and hinder the total collapse of the polymer chain. However, if the molar incorporation of the sulfobetaine unit is increased above 44 mol %, it appears that the dipole–dipole interactions dominate the solution behavior as demonstrated by a decrease in viscosity and ultimate phase separation for α < 0.1.

Surface Tensiometry. Since the viscosity experiments indicate that a polyelectrolyte-to-polysoap transition is occurring as a function of the degree of ionization of the DAMA mer units (by changes in pH), equilibrium surface tension measurements were performed to monitor the packing of the polymer chains at an air–water interface. Figure 5 illustrates the equilibrium surface tension for DAMA and DAMS44 as a function of polymer concentration at specific pH values. As can be clearly seen from the figure, DAMA exhibits pH-responsive surface activity. At high degrees of ionization, the charge–charge repulsions along the polymer backbone hinder hydrophobic association and thus packing at the air–water interface. However, as the degree of ionization is decreased, the hydrophobic content of the homopolymer increases and packing at the surface is favored, thus causing the surface tension

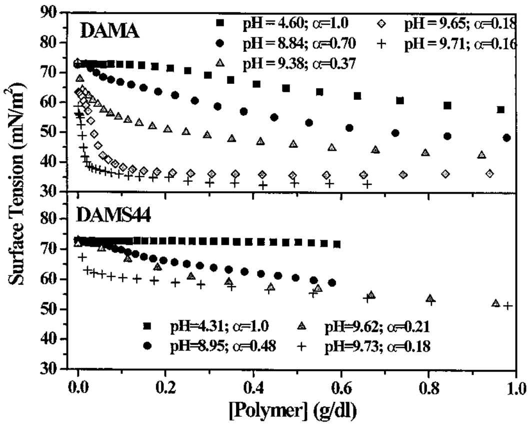


Figure 5. Equilibrium surface tension for DAMA and DAMS44 polymers as a function of polymer concentration at selected degrees of ionization of the DAMA mer units (α) (T = 25 °C).

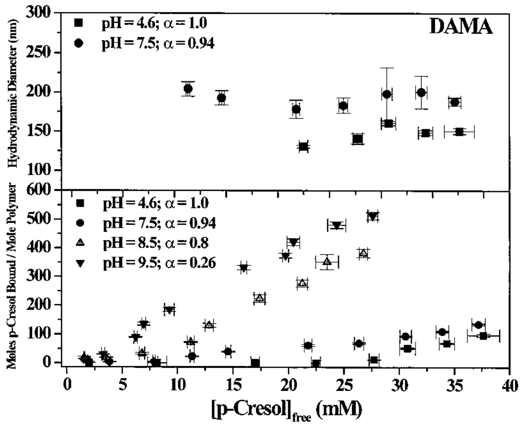


Figure 6. Binding isotherms for DAMA and *p*-cresol (A) and the corresponding hydrodynamic diameter of the polymer–foulant complex (B) as a function of *p*-cresol concentration and the degree of ionization of the DAMA mer unit (α) ([DAMA] = 0.2 g/dL, T = 25 °C).

to decrease dramatically to an equilibrium value of ~32 mN/m^2. For DAMS44, surface activity is observed only at very low degrees of ionization of the DAMA mer units. Even so, at pH 9.73 an equilibrium surface tension of ~55 mN/m^2 is measured. Once again the sulfobetaine mer unit is sufficiently hydrophilic to hinder the hydrophobic collapse of the polymer chain and packing at the air–water interface.

Equilibrium Dialysis/Sequestration Studies. The pH-responsive surface activity of the DAMS cyclocopolymers suggests application in micellar enhanced ultrafiltration for the removal of organic foulants from wastewater streams. To investigate the pH-controlled solubilization of a model organic solute (*p*-cresol), equilibrium dialysis experiments were performed utilizing DAMA and DAMS44 at specified pH conditions. Equilibrium dialysis experiments are often utilized to mimic micellar enhanced ultrafiltration processes[39] discussed in the Introduction. For these investigations, the polymer concentration was held constant at 0.2 g/dL, since at this concentration, the polymers exhibit no surface activity at high α and a maximum surface activity at low α.

The binding isotherms and the corresponding hydrodynamic diameters of the polymer–foulant complexes for DAMA and DAMS44 are illustrated in Figures 6 and 7, respectively. On the basis of the surface tension and viscometric data, which indicate that the DAMA homopolymer assumes an expanded conformation at high degrees of ionization, minimal sequestration of *p*-cresol by the polymer would be expected. Figure 6 confirms this expectation. However, at high concentrations of *p*-cresol, the model foulant induces intermolecular aggregation of the homopolymer, and binding is observed. Transition to the aggregated form is readily detected through dynamic light scattering experiments which indicate the formation of large aggregates of ~150 and ~200 nm for α = 1.0 and 0.94, respectively. It must be pointed out that the molecular dimensions of the DAMA homopolymer (α ~ 1.0 in dilute solution at low ionic strength and with no binding of *p*-cresol) could not be determined due to the appearance of the slow mode of relaxation common to polyelectrolytes.[44–46] As the degree of ionization of the DAMA homopolymer decreases, the polymer becomes more hydrophobic, and binding of *p*-cresol increases dramatically as indicated by the binding isotherm. The polymer binds such a large quantity of *p*-cresol that large macromolecular aggregate structures are formed, resulting in solution turbidity which precludes the determination of the molecular dimensions of the multichain/*p*-cresol complexes by dynamic light scattering.

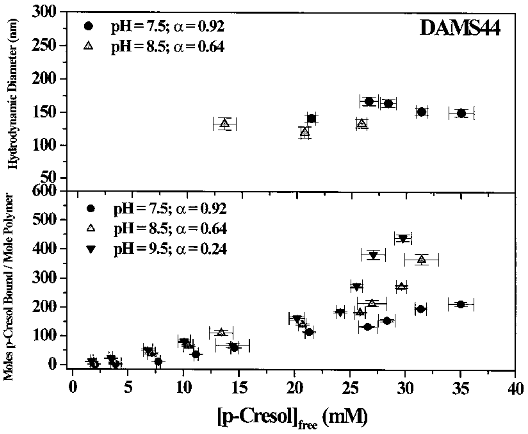


Figure 7. Binding isotherms for DAMA and *p*-cresol (A) and the corresponding hydrodynamic diameter of the polymer–foulant complex (B) as a function of *p*-cresol concentration and the degree of ionization of the DAMA mer unit (α) ([DAMS44] = 0.2 g/dL, T = 25 °C).

In closely analyzing the binding of *p*-cresol to DAMS44, several differences from that obtained for the DAMA homopolymer can be noted. At high degrees of ionization, the DAMS44 copolymer solubilizes slightly more *p*-cresol than the DAMA homopolymer. From the viscometric data at α ~ 1, it was determined dipole–dipole interactions among sulfobetaine mer units cause the polymer chain to assume a more collapsed conformation than the DAMA homopolymer. This globule-like conformation appears to facilitate the sequestration of the organic solute. As the degree of ionization decreases, solubilization of *p*-cresol by DAMS44 is increasingly favored due to the formation of larger hydrophobic segments along the polymer backbone. However, the amount of the organic solute sequestered within the hydrophobic domains is much less than that of the DAMA homopolymer. This is not unexpected on the basis of the surface tension and viscosity data, which indicate that the incorporation of the sulfobetaine hinders packing of the hydrophobic moieties and therefore hinders sequestration of the organic solute.

Once again, determination of the dimensions of the polymer/foulant complex was unsuccessful due to experimental complications of the appearance of the slow mode of relaxation for samples at high degrees of ionization and the turbidity developed at high concentrations of *p*-cresol and lower degrees of ionization. However, despite these complications, it is quite apparent that the complexes formed are comprised of multiple polymer chains.

To evaluate utility in a micellar enhanced ultrafiltration application, rejection ratios were calculated for each copolymer under various environmental conditions (Table 4). Rejection ratios indicate the percentage of the small molecular solute retained within hydrophobic domains. As can be seen in Table 4, the maximum rejection ratio obtained is ~60%. Although this value might seem low for ultimate utility in an ultrafiltration application (rejection ratios for 1-hexadecylpyridinium chloride/*p*-cresol complexes are often >97%),[3] the efficiency of DAMS-based copolymer systems may be

Table 4. Rejection Ratios as a Function of $[\text{Cresol}]_{\text{feed}}$ (%) and pH for DAMA and DAMS44

$[\text{cresol}]_{\text{feed}}$ (mM)	DAMA pH = 4.6	DAMA pH = 7.5	DAMA pH = 8.5	DAMA pH = 9.4	DAMS44 pH = 7.5	DAMS44 pH = 8.5	DAMS44 pH = 9.5
4	<1	<1	36 ± 8	12 ± 1	<1	4.5 ± 0.2	23 ± 2
8	<1	<1%	21 ± 1	31 ± 3	2.7 ± 0.3	6.9 ± 0.1	22 ± 1
16	<1	<1%	26 ± 2	36 ± 2	5.8 ± 0.1	20 ± 1	25 ± 2
24	<1	2 ± 1	24 ± 1	59 ± 3	13 ± 1	23 ± 1	27 ± 2
32	<1	4 ± 1	33 ± 2	59 ± 5	16 ± 1	28 ± 2	26 ± 2
48	<1	5 ± 1	43 ± 2	50 ± 2	20 ± 2	24 ± 1	27 ± 1
56	2 ± 1	6 ± 1	39 ± 2	45 ± 6	19 ± 1	22 ± 1	28 ± 1
64	8 ± 1	8 ± 1	42 ± 3	53 ± 3	20 ± 2	27 ± 1	33 ± 1
72	9 ± 1	11 ± 1	41 ± 2	49 ± 2	22 ± 2	30 ± 1	39 ± 2
80	11 ± 1	13 ± 1	41 ± 2	47 ± 2	22 ± 2	35 ± 2	40 ± 1

increased with a multiple-pass configuration (for example, hollow fiber ultrafiltration cartridges). In addition, the DAMA-based copolymers offer other advantages over conventional surfactants in MEUF applications. These polymeric micelles are quantitatively retained by the filtration membrane since their dimensions are larger than the pores. Therefore, there is no need to remove surfactant from the permeate stream (a common problem in conventional MEUF applications). Also, as evidenced by the dynamic light scattering data, the molecular dimensions of the polymer/foulant complex are much larger than the surfactant/foulant complexes found in typical micellar enhanced ultrafiltration. Because of the larger size of the aggregates, membranes with larger pore sizes may be selected, therefore increasing the permeate flux. Finally, due to the pH-responsive behavior of the DAMA-based copolymers, the polymer/foulant complex should dissociate with changes in pH, thus providing a facile mechanism of foulant removal from sequestering domains.

Conclusions

The sulfobetaine monomer, 3-(*N*,*N*-diallyl-*N*-methylammonio)propanesulfonate, has been cyclocopolymerized with *N*,*N*-diallyl-*N*-methylamine. ^{13}C NMR analysis indicates that the resulting polymers maintain the five-membered-ring structure common to cyclopolymerized diallylammonium salts. Reactivity ratio studies indicate random incorporation of the two mer units. Turbidimetric titration, low-shear viscosity, and equilibrium surface tension experiments were utilized to study the complicated solution behavior of the resulting copolymers. A proposed model of association is depicted in Figure 8. At high degrees of ionization, the copolymers assume an extended conformation due to the charge–charge repulsions of the cationic mer units along the copolymer backbone. As the molar incorporation of the sulfobetaine increases (at high degrees of ionization), the copolymer assumes a more relaxed, globule-like conformation due to dipole–dipole interactions of the zwitterionic units. As the degree of ionization of the tertiary amine decreases, hydrophobic associations dominate the solution behavior. For copolymers with low incorporation of sulfobetaine, chain collapse leading to precipitation occurs. However, at higher incorporations, the sulfobetaine acts as a hydrophilic segment to limit hydrophobic packing and minimize the chain collapse.

Equilibrium dialysis experiments have demonstrated that the DAMS-based copolymers may be utilized in micellar-enhanced ultrafiltration applications. A facile mechanism of foulant capture and release is potentially provided by the pH-reversible domains. Further studies of these micelle-like, polysoap domains utilizing dynamic photophysical and light scattering techniques with appropriate models and fluorescence labels are underway and will be the subject of a future submission.

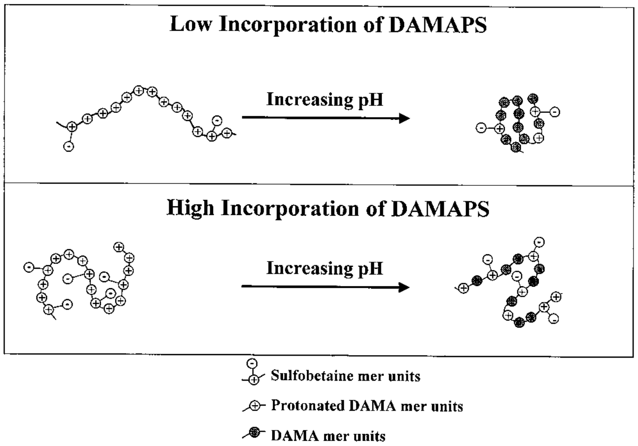


Figure 8. Proposed polymer conformational changes for DAMS cyclocopolymers as a function of pH in dilute solution.

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