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Water-soluble copolymers: 66. Phase transfer studies of structural and environmental effects on domain organization in aqueous solutions of hydrophobically modified poly(sodium maleate-*alt*-ethyl vinyl ether)s

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Hydrophobically modified, water-soluble terpolymers based on maleic anhydride and ethyl vinyl ether were evaluated for their ability to act as a host for hydrophobic molecules in water. Alternating copolymers of maleic anhydride and ethyl vinyl ether were reacted with primary amines in organic solvent, then hydrolysed in a dilute aqueous base. This modification technique allows precise, stoichiometric substitution with hydrophobic groups and accessibility to a wide range of association-driven conformations in aqueous media. The degree of naphthalene sequestration in solutions of hydrophobically modified poly(sodium maleate-*alt*-ethyl vinyl ether) was found to depend on hydrophobic modification, electrolyte concentration, and pH. As octyl substitution increased from 10 to 50 mol%, micellar domains formed by intrapolymer hydrophobic associations became more compact and mobility constraints within micelles hindered phase transfer. Increasing sodium chloride concentration and decreasing pH also enhanced micellar organization. The presence of hydrophobic groups on the micellar surface in some cases was postulated to account for the enhanced recruitment of naphthalene into hydrophobic domains. Data from these studies are discussed in relation to previous viscosity and fluorescence studies that confirm the conformational changes driving the transition from an extended polyelectrolyte to a compact, globular structure. Copyright © 1996 Elsevier Science Ltd.

(Keywords: hydrophobically modified polyelectrolytes; polysoaps; sequestration)

INTRODUCTION

Studies in our laboratories have focused on the associative properties of hydrophobically modified water-soluble polymers[1–3]. Most recently, elucidation of the domain-forming abilities of amphiphilic polyelectrolytes has been a subject of interest[4–9]. Viscosity studies of acrylamide/*N*-(*n*-decyl) acrylamide (AM/C_{10}AM) terpolymers with a charged monomer revealed that incorporation of small amounts of hydrophobe into the structure of a hydrophilic polymer dramatically alters the solution properties in aqueous media[2]. A pronounced enhancement in the viscosity response occurs well below concentrations corresponding to that of the onset of chain entanglement in unmodified poly(acrylamide). Interpolymer hydrophobic association between C_{10} groups drives this response. Incorporation of a charged monomer into a hydrophobically modified water-soluble polymer dramatically influences the nature and extent of associations. Factors including charged group placement[2], ionic strength and pH[1,2,4–9], and the presence of surfactants affect solution behaviour[5,7,10–13].

Many of the copolymer systems that have been investigated tend to exhibit associative thickening properties (open associations) similar to that AM/C_{10}AM systems[2,3]. When hydrophobe content in a polyelectrolyte increases, interactions within the polymer coil (closed associations) become more prominent. The compact, globular structures assumed by these intramolecularly associating systems have been termed 'unimolecular micelles'[14,15], 'polymeric micelles'[16,17], and 'polysoaps'[18,19]. Intrapolymer associations are confirmed by a considerable decrease in intrinsic viscosity ([η]) and an accompanying increase in the Huggins constant (k'). Strauss reported a drop in the intrinsic viscosity of dodecyl (C_{12})-quaternized poly(vinyl pyridine)s from 5 dl g^{-1} to less than 0.1 dl g^{-1} as quaternization was increased from 0 to 13.6 mol%. The concentration at which this transition occurs has been termed the 'critical micelle composition'[18]. If the local concentration of 'soap' molecules (amphiphilic groups) attached to a polymer chain is sufficiently high,

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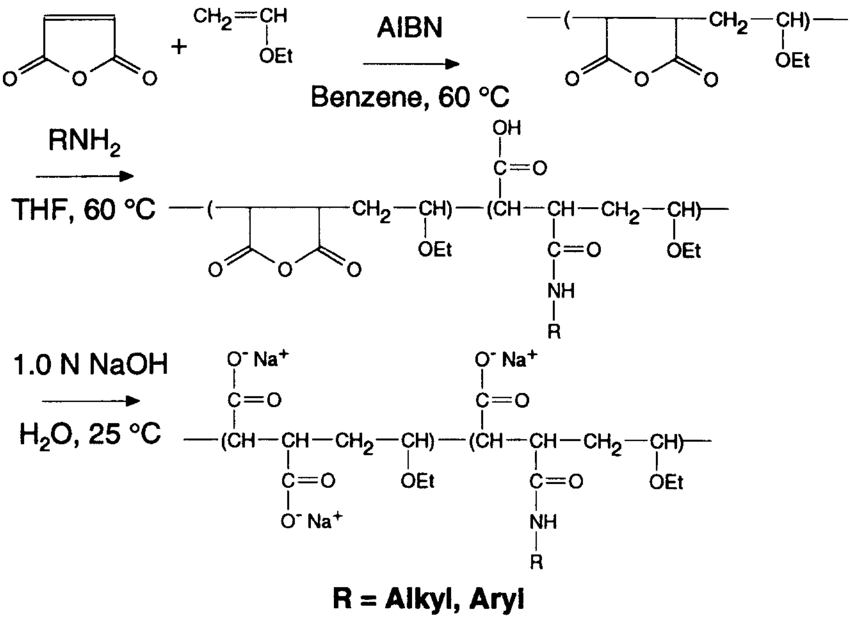


Scheme 1 Synthesis of hydrophobically modified poly(sodium maleate-*alt*-ethyl vinyl ether)

micellar structures will form along the polymer chain. The unusually high Huggins k' value and tendency for gel formation observed in highly substituted dodecylpyridinium-based polysoaps indicate strong interpolymer aggregation. Strauss proposed a mechanism whereby the compact structure of the polymer micelle lends to the exclusion of hydrophobic groups from the micellar core. Interaction between hydrophobic groups on the micellar surface may then facilitate interpolymer network formation[18].

Hydrolysed alternating copolymers of maleic anhydride and alkyl vinyl ethers also exhibit strong intramolecular associative properties[6,20–25]. As the pH is decreased through the pK_a of the carboxylate groups along the polymer coil, the polymer conformation varies from a relatively open, random coil conformation to a globular structure as electrostatic repulsive forces diminish. Fluorescence studies of dansyl-labelled maleate/alkyl vinyl ether copolymers confirm the presence of hydrophobic domains at low pH, and the globular–random coil transition occurs only when the alkyl group is a butyl group or of a longer alkyl chain[22].

Recently, we have begun the systematic investigation of the microdomain-forming properties of alkylamido-substituted maleic anhydride-ethyl vinyl ether (MAEVE)-based polysoaps (*Scheme 1*) as a function of hydrophobe content, electrolyte concentration, and pH. Free radical polymerization is carried out in an organic solvent to give a perfectly alternating MAEVE copolymer[26]. Random, stoichiometric hydrophobic modification is then achieved by reaction of an aliphatic or aromatic amine with anhydride polymer repeat units in the polymer structure. Hydrolysis in dilute aqueous base affords the water-soluble polymer[6,27].

Partitioning of the pyrene probe into hydrophobic microdomains has been confirmed by fluorescence emission studies of 4-butylphenyl modified poly(potassium maleate-*alt*-ethyl vinyl ether). The ratio of the first to the third vibronic band of pyrene emission (I_1/I_3) and the fluorescence lifetime (τ) were found to reflect the formation of a hydrophobic, micellar environment at low pH. Quasielastic light scattering studies also indicated that the effective diameter (d_{eff}) decreases with pH and increasing hydrophobe content[9], supporting the existence of a polyelectrolyte–polysoap transition (*Figure 1*).

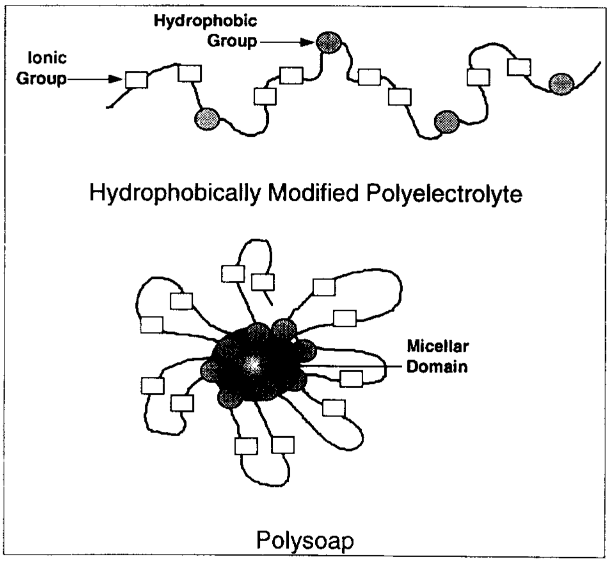


Figure 1 Proposed mechanism of polyelectrolyte–polysoap transition

Although environmental and conformational changes have been reported for this class of water-soluble polymers, sequestration of small molecule hydrophobes by aqueous micellar domains formed in these systems has only been directly quantitated in a few studies[28,29]. The major objective of this study is the correlation of the aqueous phase transfer properties of hydrophobically modified poly(sodium maleate-*alt*-ethyl vinyl ether) with polymer micelle structure. Dissolution of a hydrophobic, polyaromatic chromophore is readily assessed via ultra-violet–visible (u.v.–vis.) spectrophotometry[28–30]. Because hydrophobic modification[18,19], along with electrolyte concentration[6] and pH[6,9,22], affects the conformation adopted by this unique class of water-soluble polymers, sequestration shall be measured as a function of changes in these parameters. When sequestration data are compared with results from viscosity and fluorescence studies[6], a reasonable model of the associations that drive polymer micelle phase transfer may be derived. This may ultimately lead to the development of these novel materials in phase transfer and remediation applications.

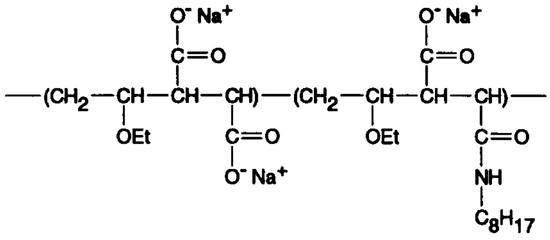
EXPERIMENTAL

Materials

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

*Hydrolysed, hydrophobically modified poly(maleic anhydride-*alt*-ethyl vinyl ether)*

The polymer utilized for subsequent hydrophobic modification and hydrolysis was previously synthesized[6]. Maleic anhydride was copolymerized with ethyl vinyl ether in benzene at 60°C using benzoyl peroxide as initiator. After 8 h the polymer precipitate that forms was purified by repeated dissolution in ethyl acetate and precipitation in diethyl ether. Copolymer molecular weight (M_w) determined by light scattering was $2.4 \times 10^5\,g\,mol^{-1}$.



C8-#, # = 10, 20, 30, 40, 50 Mole %

Figure 2 Octyl modified poly(sodium maleate-*alt*-ethyl vinyl ether)

n-*Octyl modified poly(sodium maleate-*alt*-ethyl vinyl ether)*

The modification and hydrolysis of poly(maleic anhydride-*alt*-ethyl vinyl ether) is shown in *Scheme 1*. Octyl (C_8) modified polymers were previously synthesized by Chang and McCormick[6], and substitution levels of 10, 20, 30, 40, and 50 mol% (with respect to maleic anhydride repeat units in the parent copolymer) were achieved. In the Results and Discussion section these polymers shall be designated C8-10, C8-20, C8-30, C8-40, and C8-50; the numbers following the hyphen describe octyl group content (*Figure 2*).

n-*Octyl modified, pyrene labelled poly(sodium maleate-*alt*-ethyl vinyl ether)*

Sodium maleate–ethyl vinyl ether copolymer modified with 30 mol% octyl groups and 1 mol% 2-(pyrenylsulfonamido)octyl groups was synthesized using the same procedure as that for the C8 series (*Figure 3*)[31].

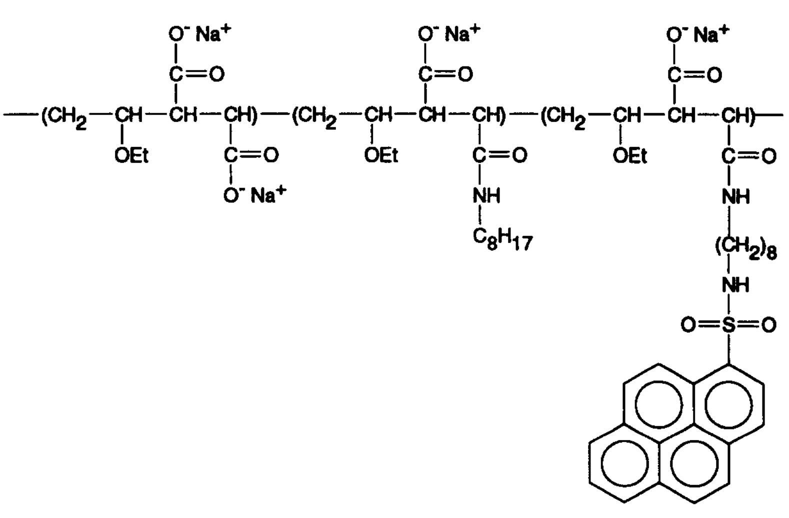
Instrumentation

U.v.–vis. spectra were recorded with a Hewlett Packard 8452A diode array spectrophotometer. Steady-state fluorescence spectra were measured with a Spex Fluorolog-2 fluorescence spectrometer and a DM3000F data system. Excitation and emission slit widths of 1 mm and right angle geometry were employed. For the fluorescence quenching studies, an excitation wavelength of 340 nm was used, and emission at 400 nm was monitored.

Sample preparation

Polymer solutions were prepared gravimetrically by dissolving the polymer samples either in deionized water or in citric acid/disodium phosphate (Na_2HPO_4) buffer. Buffered polymer solutions were prepared for the pH studies; aqueous sodium chloride (5.0 M) was added to give the desired NaCl concentration for the salt study.

Since naphthalene is only sparingly soluble in water ($2.5 \pm 0.2 \times 10^{-4}$ M), a modification of the technique employed by Lianos *et al.* was utilized[32]. To a glass scintillation vial, 100 μl of a 0.33 M solution of naphthalene was added. Solvent was then evaporated with a



C8-30-P8, 30 Mole % C8, 1 Mole % P8

Figure 3 Octyl modified, pyrene-labelled poly(sodium maleate-*alt*-etheyl vinyl ether) gentle nitrogen stream. Polymer solution was immediately added, and samples were shaken for 24 h. After periods of 1–2 days, phase separation occurred in many samples, especially in low pH and high ionic strength polymer solutions. Naphthalene concentration was quantitatively measured utilizing the u.v. absorbance at 312 nm ($\epsilon = 289\,\mathrm{M}^{-1}\,\mathrm{cm}^{-1}$)[33] after 24 h.

RESULTS AND DISCUSSION

The preparation of hydrophobically modified poly(sodium maleate-*alt*-ethyl vinyl ether)s proceeds by a simple two step modification of the parent copolymer. A primary amine reacts with maleic anhydride repeat units along the polymer chain. This reaction is carried out in ethyl acetate. Unreacted anhydride units are then hydrolysed to carboxylate groups by dissolution of the modified copolymer in 1 N aqueous NaOH at 25°C. Stoichiometric formation of amide linkages is achieved without any detectable hydrolysis. An advantage of this modification process is that a series of copolymers with varying substitution can be synthesized from the same MAEVE polymer, so the degree of polymerization remains the same for the entire copolymer series. Therefore, any significant changes in aqueous solution properties may be attributable to conformational and environmental changes brought about by hydrophobic interactions.

Poly(maleate-*alt*-alkyl vinyl ether)s are known to possess good water-solubility, and when the alkyl group is sufficiently hydrophobic, a compact structure results. The globular conformation is most prominent at low pH, where chain-expanding electrostatic interactions that compete with intrapolymer hydrophobic association are eliminated. When the alkyl group of the vinyl ether is longer than C_4, a transition from an intramolecularly associating system to an extended state occurs as carboxyl groups are ionized[34,35]. As alkyl group size is increased from C_5 to C_8 in dansylated copolymers, fluorescence studies indicate that environmental hydrophobicity in the fully ionized state increases with alkyl chain length. This behaviour is independent of polymer molecular weight, which suggests that short-range interactions are responsible for microdomain organization[22].

Naphthalene sequestration studies

The micellar environment formed by intrapolymer association of alkyl groups can act as an effective host for hydrophobic molecules[19,28–30]. Time-resolved fluorescence quenching studies by Binana-Limbelé and Zana indicate that micellar domains are present that can solubilize model hydrophobes, such as the pyrene probe. Polymer micelle aggregation number and probe-quencher diffusion are also found to be highly dependent upon the degree of ionization[20]. Hydrophobicity, ionic strength, and pH may also affect micellar domain size, as is the case for small molecule surfactant solutions[36–38]. When polymer micelle properties change, the phase transfer properties may also vary.

A simple, quantitative method to evaluate hydrocarbon uptake by polymer micelles involves the use of an aromatic or polyaromatic hydrocarbon. Ito *et al.* studied the effects of counterion type on azobenzene and naphthylazo dye uptake[28]. Hurter and Hatton evaluated micelle–water and octanol–water partition coefficients of poly(ethylene oxide–propylene oxide) block copolymers for naphthalene, phenanthrene, and pyrene[30]. Here we investigate the sequestering abilities of octyl modified maleate-*alt*-ethyl vinyl ether copolymers utilizing naphthalene. The high molar absorptivity of chromophores such as naphthalene allows accurate, rapid quantitation by u.v.–vis. spectrophotometry.

Initial efforts focused on the use of azobenzene as a solute for phase transfer studies, but *trans–cis* photoisomerization induced shifts in absorbance and $\lambda_{\max}$. Environmental fluidity has been shown to affect the rate of azobenzene *trans–cis* photoisomerization in hydrophobically modified, azobenzene-labelled poly(sodium 2-acrylamido-2-methylpropane sulfonate) (NaAMPS) unimolecular micelles [39,40]. A photostable chromophore such as naphthalene was found to be better suited for this study.

Naphthalene is sparingly soluble in water, and u.v. studies of saturated aqueous naphthalene solutions indicate a solubility of $2.5 \pm 0.2 \times 10^{-4}$ M at 25°C. In order to maximize naphthalene dissolution and phase transfer, a previously reported technique was utilized to prepare saturated aqueous naphthalene solutions[32]. Naphthalene solution was added to a vial and solvent then evaporated. Solubilization of naphthalene by polymer micelles was confirmed by increases in u.v. absorbance at 312 nm ($\epsilon = 289\,\mathrm{M}^{-1}\,\mathrm{cm}^{-1}$)[33] after 1 h. After several days, many polymer solutions began to precipitate. Accurate, reproducible results were obtained by measuring the absorbance after 24 h.

Because naphthalene is soluble in water, this must be taken into account when determining naphthalene partitioning into C8 polymer micelles. Normalized naphthalene sequestration is quantitated as follows:

$$\frac{[\mathrm{N}]}{[\mathrm{C8}]} = \frac{[\mathrm{Np}]_{\mathrm{Total}} - [\mathrm{Np}]_{\mathrm{H_2O}}}{[\mathrm{C8}]} \qquad (1)$$

where [Np]/[C8] describes the amount of naphthalene solubilized per hydrophobic group. [Np] is the concentration of micellized naphthalene and [C8] is the concentration of *n*-octylamide polymer repeat units in solution. $[\mathrm{Np}]_{\mathrm{Total}}$ is the total soluble naphthalene concentration determined from u.v. absorbance measurements, and $[\mathrm{Na}]_{\mathrm{H_2O}}$, the solubility of naphthalene in water, is subtracted from $[\mathrm{Np}]_{\mathrm{Total}}$ to obtain the concentration of micellized naphthalene, [Np].

Naphthalene uptake as a function of hydrophobic substitution. Naphthalene uptake by 0.6 g dl^{-1} solutions of the C8 series as a function of substitution are plotted in *Figure 4*. A maximum in naphthalene sequestration is noticeable at 20 mol% octyl substitution. We have previously shown that as C8 substitution is increased from 0 to 50 mol%, intrinsic viscosity ([η]) drops an order of magnitude from over 11 dl g^{-1} to less than 2 dl g^{-1} (ref. 6). The decrease in [η] is most pronounced as substitution is increased from 20 to 30 mol%. This transition parallels the polyelectrolyte–polysoap transition reported by Strauss[18].

The rise in [Np]/[C8] as substitution increases from 10 to 20 mol% is expected. The addition of octyl groups along the chain allows for a higher degree of intramolecular micelle formation. However, [η] drops only slightly in this range as hydrophobic modification is

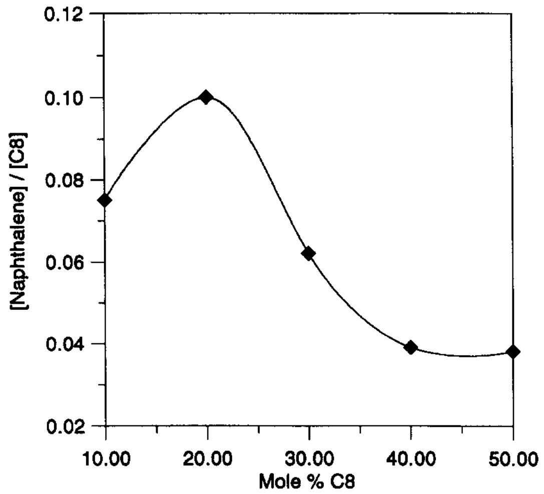


Figure 4 Normalized naphthalene uptake [Na]/[C8] as a function of octyl substitution for 0.6 g dl^{-1} aqueous polymer solutions in the C8 series

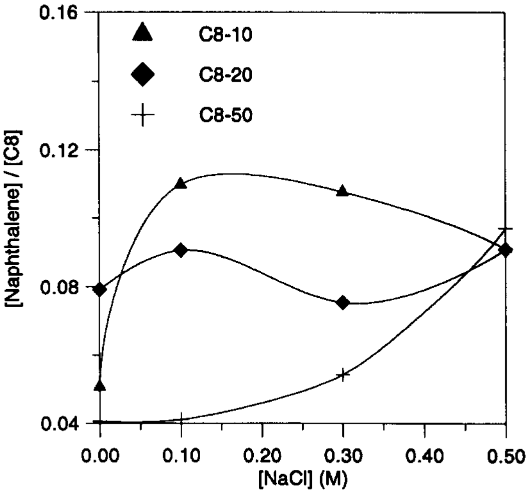


Figure 5 Normalized naphthalene uptake [Na]/[C8] as a function of sodium chloride concentration for 0.6 g dl^{-1} aqueous polymer solutions of C8-10, C8-20, and C8-50

doubled. Obviously, the localized concentration of octyl groups is not sufficiently high for significant coil concentration, but there is sufficient micellization of octyl groups to form organized microdomains. As substitution increases from 30 to 50 mol%, [Np]/[C8] drops to levels below that of 10 mol% modified C8 polymer. When micellar structure becomes more organized with increasing C8 content, naphthalene uptake is appreciably hindered. The compact conformation adopted likely is a rigid, vitrified phase.

Fluorescence emission studies of labelled polysoaps support this proposed mechanism. Excimer/monomer fluorescence emission studies of naphthalene–labelled C8 modified copolymers previously synthesized in our labs indicate a maximum in naphthalene dimer formation at 30 mol%[6]. As chain dimension decrease with increasing hydrophobicity, naphthalene labels are brought in closer contact. The probability of interaction between naphthyl groups in forming the sandwich-like dimeric excited state increases in this C8 incorporation range. With further hydrophobic substitution, naphthyl labels are 'diluted' within the micellar environment[41]. The compactness of the microdomains at high modification levels can also hinder the orientation that is requisite for excimer formation[42].

Changes in the rate of micelle formation–breakdown may also account for the reduction in solubilization efficiency. Lianes *et al.* reported changes in pyrene solubilization as micellar formation and breakdown rates changed. As the residence time of a surfactant within a micelle increases, pyrene solubilization decreases[32]. Solubilization studies by Carroll revealed that micelle formation–breakdown and adsorption–desorption of micelles at the oil–water interface dictate uptake kinetics, rather than oil diffusion into micelles[43]. Obviously, when surfactant groups are bound to a polymer chain, their motion is restricted considerably. This equates to the formation of a restricted environment that hinders the motion of amphiphilic repeat units and guest molecules. Chu and Thomas have reported this phenomenon in pyrene probe emission studies of poly(sodium 11-undecenoate) (SUe) and sodium undecanoate (SUa) micelles.[16] Probe–quencher mobility in SUe polymer micelles was found to be much less than the mobility in SUa small molecule micelles.

Salt effects. Normalized naphthalene sequestration ([Np]/[C8]) as a function of sodium chloride concentration for 0.6 g dl^{-1} solutions of C8-10, C8-20, and C8-50 is shown in *Figure 5*. These three samples are the most representative of the possible micellar structures within this series. C8-10 forms an inadequately organized polymer micelle in deionized water, C8-20 possesses optimum organization, and the environment in a C8-50 micelle is quite rigid. No noticeable trend is observed in C8-20; [Np]/[C8] values fluctuate around 0.08. However, in both C8-10 and C8-50, [Np]/[C8] is enhanced with salt-triggered coil contraction.

C8-10 possesses moderate sequestration properties in deionized water, even though a relatively open conformation is adopted. As added electrolyte shields electrostatic repulsions, the coil contracts, and hydrophobic microdomains become more organized when the localized octyl group concentration increases. Although C8-10 acts as a polyelectrolyte at low ionic strength, environmental changes that contract the chain impart a conformation more characteristic of a polysoap.

Micellar domains formed by C8-50 are highly organized, and it would seem that salt addition could further vitrify the microenvironment and inhibit phase transfer. As ionic strength increases, so does [Np]/[C8]. If an already compact structure is contracted further, an effective vehicle for water–micelle phase transfer may result. If the ionic surface of a polysoap contracts, a fraction of the micellar surface may then consist of hydrophobic groups. If a portion of the surface does indeed consist of hydrophobic groups, interpolymer hydrophobic aggregation is augmented. This has been shown to occur in poly(vinyl pyridine)s quaternized with dodecyl groups[18], and in poly(sodium maleate-*alt*-ethyl vinyl ether) modified with dodecyl groups[6]. In both cases, when a freshly prepared stock solution was diluted, the viscosity of the dilution slowly decreased over hours, and sometimes over a period of days. This effect is not observed rheologically in the C8 series, but nonradiative energy transfer studies of mixed solutions of naphthalene- and pyrene-labelled C8-30 indicate that

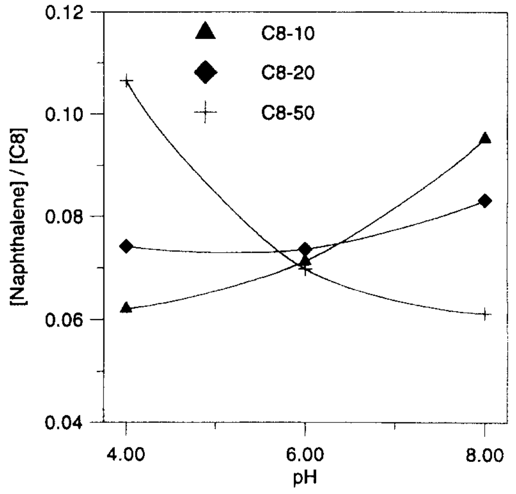


Figure 6 Normalized naphthalene uptake [Na]/[C8] as a function of pH for $0.6\,g\,dl^{-1}$ aqueous polymer solutions of C8-10, C8-20, and C8-50

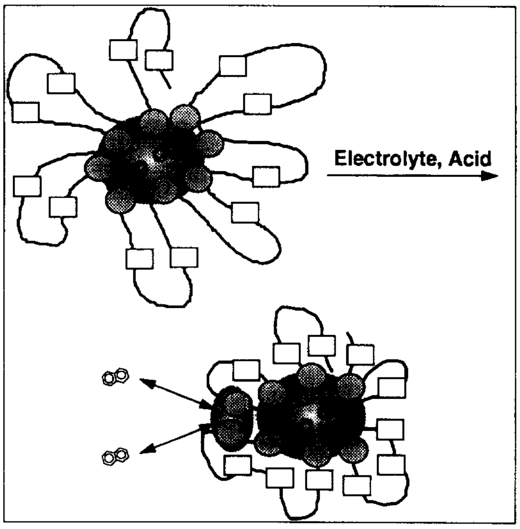


Figure 7 Conceptual model of naphthalene sequestration by unmicellized hydrophobic surface groups

interpolymer aggregation does occur at very low polymer concentrations ($<0.01\,g\,dl^{-1}$) in some cases[31].

pH effects. Naphthalene sequestration by $0.6\,g\,dl^{-1}$ solutions of C8-10, 20, and 50 at pH 4, 6, and 9 is plotted in *Figure 6*. As pH is increased from 4 to 8 in solutions of C8-10 and C8-20, slight increases in naphthalene sequestration are observed. C8-50 exhibits maximum sequestration at pH 4.

Ionic strength effects may be responsible for the increase in [Np]/[C8] with pH for C8-10 and C8-20. Buffered aqueous solutions were prepared for this study, and these buffers consisted of mixed solutions of 0.1 M citric acid and 0.2 M disodium phosphate (Na_2HPO_4). As pH is increased by increasing the disodium phosphate/sodium citric acid ratio, overall electrolyte concentration increases. The shielding of electrostatic repulsions may predominate over the elimination of charge–charge repulsions by acid addition as a mechanism for enhanced polymer micelle organization at these hydrophobe compositions.

As pH decreases, naphthalene sequestration by C8-50 is enhanced. The increase correlates well with the proposed formation of a hydrophobic micellar surface. As carboxylate groups are protonated, the elimination of Coulombic repulsive forces allows contraction of the micellar corona. As the number of charged groups on the surface decreases, and the fraction of uncharged carboxylic acid functionalities increases, a fraction of the micelle surface may become occupied by hydrophobic groups.

Recent photophysical studies of anionic polysoaps corroborate the existence of hydrophobe partitioning into unmicellized hydrophobic portions of the polymer coil. Zdanowicz and Strauss[29] and Binana-Limbelé and Zana[20,44] have carried out aggregation number studies on maleate–alkyl vinyl ether polymers to further elucidate the mechanism of polysoap micellization. Binana-Limbelé and Zana evaluated intramolecular micelle formation in poly(disodium maleate-*alt*-decyl vinyl ether) (PS10) and poly(disodium maleate-*alt*-hexadecyl vinyl ether) (PS16). Time-resolved fluorescence quenching studies of aqueous PS16 solutions showed that probe-quencher migration between microdomains through unmicellized repeat units is possible. Fluorescence quenching studies of aqueous poly(dilithium maleate-*alt*-hexyl vinyl ether) solutions by Zandowicz and Strauss support the existence of quencher partitioning between micellized and unmicellized portions of the polymer coil[29]. Benzophenone quencher solubility in hexyl copolymer micelles is independent of pH, and exit rate constants for benzophenone were higher than other quenchers.

A mechanism for pH- and salt-triggered sequestration by unmicellized hydrophobic groups is depicted in *Figure 7*. As a portion of the micelle surface becomes covered with hydrophobic groups, the nonpolar surface can effectively interact with a hydrophobe in solution or with an oil–water interface. Micelle formation–breakdown would then become less important than simple hydrophobic interactions between guest molecules and readily accessible hydrophobic groups on the micellar surface.

Fluorescence quenching studies

Results from naphthalene solubilization studies suggest that the environmental fluidity of micellar domains can affect the extent to which phase transfer occurs. Electrolyte concentration and pH also influence micelle organization. Fluorescence quenching studies of naphthalene- and pyrene-labelled anionic polyelectrolytes with nitromethane showed that coil shrinkage slows the diffusion of amphiphilic quencher molecules to fluorescent labels[45,46]. Dynamic diffusion-controlled quenching is described as follows:

$$\frac{I_0}{I} = 1 + K_{SV}[Q] \qquad (2)$$

$$K_{SV} = k_q \tau_0 \qquad (3)$$

where I_0 is the steady-state fluorescence intensity of a chromophore in solution prior to quencher addition, I is the fluorescence intensity at quencher concentration [Q], K_{SV} is the Stern–Volmer quenching constant (M^{-1}), k_q is the first order quenching constant ($M^{-1}\,s^{-1}$), and τ_0 is the fluorescence lifetime in the absence of quencher. If quenching were solely dynamic or static in nature, a plot

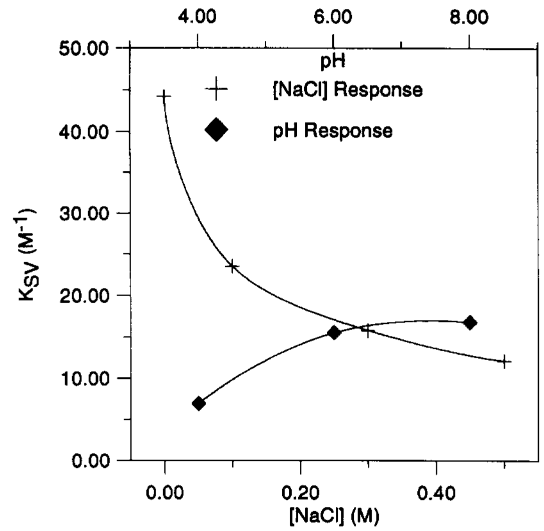


Figure 8 Stern–Volmer quenching constant of 0.1 g dl^{-1} aqueous polymer solutions of C8-30 polymer labelled with 1 mol% pyrenylsulfonamido octyl groups (C8-30-P8) as a function of sodium chloride concentration and pH

of I_0/I vs [Q] should give a straight line with a slope equal to K_{SV}. Steady-state quenching studies of 0.1 g dl^{-1} solutions of pyrenylsulfonamidooctyl-labelled C8-30 polymer (C8-30-P8) as a function of sodium chloride concentration and pH revealed linear I_0/I vs [Q] plots in all cases, with K_{SV} values in the range of dynamic, diffusion-controlled quenching.

The effects of sodium chloride concentration and pH on the quenching rate are depicted in *Figure 8*. Sodium chloride and buffer both have no effect on pyrene fluorescence, so changes in K_{SV} would reflect changes in the rate of label-quencher diffusion. As K_{SV} decreases, quencher mobility within the micellar environment becomes more restricted. As sodium chloride concentration increases, the Stern–Volmer quenching constant decreases. The enhancement in micellar organization induced by salt-triggered micelle contraction that increases sequestration also decreases mobility within the micelle. As pH is increased from 4 to 8, overall K_{SV} values are lower due to ionic strength effects of the citrate/phosphate buffer. A noticeable increase in K_{SV} is observed as pH is increased from 4 to 8. As a more open conformation is adopted via deprotonation of carboxyl groups, label-quencher diffusion becomes more facile. These results, in conjunction with data from naphthalene uptake studies, support the presence of soaplike structures capable of sequestering hydrophobic materials, and that the fluidity of the micelles present in solution is controllable by changes in sodium chloride concentration and pH.

CONCLUSIONS

In this study, u.v.–vis. analysis confirms the partitioning of naphthalene into hydrophobic microdomains formed by hydrophobically modified poly(sodium maleate-*alt*-ethyl vinyl ether)s in aqueous solution. The extent and also the mechanism of solute phase transfer is controllable by variation in polymer hydrophobicity, electrolyte concentration, and pH. As hydrophobic group substitution increases from 10 to 50 mol%, the polyelectrolyte–polysoap transition previously observed by fluorescence and viscosity studies occurs, resulting in the formation of a micellar environment that restricts the mobility of hydrophobic guest molecules. Optimum sequestration was observed at a composition of 20 mol% octyl substitution; this corresponds to a modification level just short of the polyelectrolyte–polysoap transition. With further increases in polymer hydrophobicity, sequestration is diminished by the formation of a highly compact, rigid microenvironment due to intrapolymer micellization of octyl groups. If electrolyte is added to C8 polymer solutions, micellar organization is enhanced, and similar effects are observed when pH is lowered. At the maximum level of octyl modification (50 mol%), salt- and pH-triggered micelle reorganization results in enhanced phase transfer properties.

A mechanism has been proposed whereby the shielding or elimination of electrostatic repulsive forces decreases micellar surface coverage by carboxyl and carboxylate groups, and a fraction of the surface becomes covered with hydrophobic groups. The interaction of micellar hydrophobic groups with a hydrophobic solute or an oil–water interface can increase as the formation of a hydrophobic surface creates an effective vehicle for phase transfer. Results from fluorescence quenching studies of pyrene-labelled, octyl modified copolymer support the vitrification of micellar domains with increasing salinity and acidity. Studies of this nature and the development of models for association and sequestration may ultimately aid in the design of water-soluble polysoaps as remediation and phase transfer agents by enabling the prediction and control of hydrocarbon uptake properties by structural and environmental changes.

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REFERENCES

1 McCormick, C. L., Middleton, J. C. and Grady, C. E. *Polymer* 1992, **33**, 4184
2 McCormick, C. L., Middleton, J. C. and Cummins, D. F. *Macromolecules* 1992, **25**, 1201
3 McCormick, C. L., Nonaka, T. and Johnson, C. B. *Polymer* 1988, **29**, 731
4 Branham, K. D., Davis, D. L. and McCormick, C. L. *Polymer* 1994, **35**, 4429
5 Chang, Y. and McCormick, C. L. *Polymer* 1994, **35**, 3503
6 McCormick, C. L. and Chang, Y. *Macromolecules* 1994, **27**, 2151
7 Chang, Y., Lochhead, R. Y. and McCormick, C. L. *Macromolecules* 1994, **27**, 2145
8 Chang, Y. and McCormick, C. L. *Macromolecules* 1993, **26**, 6121
9 McCormick, C. L., Hoyle, C. E. and Clark, M. D. *Polymer* 1992, **33**, 243
10 Magny, B., Iliopoulos, I., Zana, R. and Audebert, R. *Langmuir* 1994, **10**, 3180
11 Iliopoulos, I. and Olsson, U. *J. Phys. Chem.* 1994, **98**, 1500
12 Iliopoulos, I., Wang, T. K. and Audebert, R. *Langmuir* 1991, **7**, 617
13 Peiffer, D. G. *Polymer* 1990, **31**, 2353
14 Morishima, Y., Nomura, S., Ikeda, T., Seki, M. and Kamachi, M. *Macromolecules* 1995, **28**, 2894

15 Morishima, Y. and Kamachi, M. *Proc. Am. Chem. Soc. Div. Polym. Mater. Sci. Eng.* 1994, **71**, 271

16 Chu, D. Y. and Thomas, J. K. *Macromolecules* 1991, **24**, 2212

17 Chu, D. Y. and Thomas, J. K. *Macromolecules* 1987, **20**, 2133

18 Strauss, U. P., Gershfeld, N. L. and Crook, E. H. *J. Phys. Chem.* 1956, **60**, 577

19 Strauss, U. P.and Chershfield, N. L. *J. Phys. Chem.* 1954, **58**, 747

20 Binana-Limbelé, W. and Zana, R. *Macromolecules* 1990, **23**, 2731

21 Binana-Limbelé, W. and Zana, R. *Macromolecules* 1987, **20**, 1331

22 Strauss, U. P. and Schlesinger, M. S. *J. Phys. Chem.* 1978, **82**, 1627

23 Strauss, U. P. and Schlesinger, M. S. *J. Phys. Chem.* 1978, **82**, 571

24 Strauss, U. P. and Vesnaver, G. *J. Phys. Chem.* 1975, **79**, 2428

25 Strauss, U. P. and Vesnaver, G. *J. Phys. Chem.* 1975, **79**, 1558

26 Baldwin, M. G. *J. Polym. Sci.* 1965, **A3**, 703

27 McCormick, C. L., Hoyle, C. E. and Clark, M. D. *Polymer* 1992, **33**, 243

28 Ito, K., Ono, H. and Yamashita, Y. *J. Coll. Sci.* 1964, **19**, 28

29 Zdanowicz, V. S. and Strauss, U. P. *Macromolecules* 1993, **26**, 4770

30 Hurter, P. N. and Hatton, T. A. *Langmuir* 1992, **8**, 1291

31 Hu, Y., Kramer, M. C., Boudreaux, C. J. and McCormick, C. L. *Macromolecules* 1995, **28**, 7100

32 Lianos, P., Viriot, M. L. and Zana, R. *J. Phys. Chem.* 1984, **88**, 1098

33 Siverstein, R. M., Bassler, G. C. and Morrill, T. C. in 'Spectrometric Identification of Organic Compounds', 4th Edn., Wiley, New York, 1981, p. 326

34 Dubin, P. L. and Strauss, U. P. *J. Phys. Chem.* 1970, **74**, 2842

35 Dubin, P. L. and Strauss, U. P. *J. Phys. Chem.* 1967, **71**, 2757

36 Zachariasse, K. A., Phuc, N. V. and Kozankiewicz, B. *J. Phys. Chem.* 1981, **85**, 2676

37 Lianos, P. and Zana, R. *J. Phys. Chem.* 1980, **84**, 3339

38 Mazer, N. A., Benedek, G. B. and Carey, M. C. *J. Phys. Chem.* 1976, **80**, 1075

39 Morishima, Y., Tsuji, M., Seki, M. and Kamachi, M. *Macromolecules* 1993, **26**, 3299

40 Morishima, Y., Tsuji, M., Kamachi, M. and Hatada, K. *Macromolecules* 1992, **25**, 4406

41 McCormick, C. L., Hoyle, C. E. and Clark, M. D. *Macromolecules* 1990, **23**, 3124

42 Seo, T., Take, S., Akimoto, T., Hamada, K. and Iijima, T. *Macromolecules* 1991, **24**, 4801

43 Carroll, B. J. *J. Colloid Interface Sci.* 1981, **79**, 126

44 Binana-Limbelé, W. and Zana, R. *Macromolecules* 1987, **20**, 1331

45 Kramer, M. C., Welch, C. G., Steger, J. R. and McCormick, C. L. *Macromolecules* (in press)

46 McCormick, C. L., Hoyle, C. E. and Clark, M. D. *Macromolecules* 1991, **24**, 2397