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Review Commentary

Non-cross-linked and cross-linked poly(alkylmethyldiallylammonium halides): synthesis and aggregation behavior

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ABSTRACT: Hydrophobically modified polyelectrolytes (polysoaps) are a unique class of water-soluble polymers containing distinct hydrophobic and hydrophilic regions. Above a certain concentration, polysoaps form intramolecular and intermolecular aggregates in aqueous solution. They have attracted much attention not only for their ability to mimic some functions demonstrated by biopolymers but also for their important industrial applications. This review highlights some interesting features of novel non-cross-linked and cross-linked poly(alkylmethyldiallylammonium halides) that have been described in recent years. © 1998 John Wiley & Sons, Ltd.

KEYWORDS: poly(alkylmethyldiallylammonium halides); aggregation behavior; polyelectrolytes; polysoaps

INTRODUCTION

For a long time scientists have been intrigued by proteins and by their ability to fulfil so many functions, including catalysis of a wide diversity of reactions. Various functions are known to be based on their ability to form highly organized molecular assemblies. Hydrophobic effects play a pivotal role in the formation of these assemblies.[1] In this respect they resemble amphiphiles and their tendency to undergo self-assembly processes.[1] Hydrophobically modified polyelectrolytes (polysoaps), which possess distinct hydrophobic and hydrophilic regions, provide a challenging subject for investigation[2–27] not only for their own intrinsic interest but also for their similarities to biomacromolecules, particularly with respect to folding processes. Polysoaps have been regarded as useful model systems for globular proteins because they can mimic some functions exhibited by more complicated biopolymers in aqueous solution.[12–20,23] Above a certain concentration, defined as the critical aggregate concentration (CAC), polysoaps associate to form intramolecular and intermolecular aggregates. Hydrophobically modified polyelectrolytes are a unique class of water-soluble polymers which have attracted considerable attention, owing to their outstanding solution properties and numerous practical applications.

It has long been known that polysoaps in aqueous solution form hydrophobic microdomains, with compact coils of alkyl side-chains surrounded by soluble head groups. Like micelles formed by conventional surfactants, these hydrophobic microdomains solubilize normally water-insoluble organic molecules such as alkanes and arenes.[2] Solubilization of the organic molecules into these hydrophobic microdomains is of particular interest owing to numerous potential applications such as drug delivery.

Since the pioneering work of Strauss and Jackson,[2] polysoaps have been the focus of many studies and they have provided an extremely versatile addition to the growing field of molecular self-assembly.[18–38] These types of amphiphilic macromolecules exhibit unusual aqueous solution behavior, arising from hydrophobic association processes that occur in order to minimize water–hydrophobe contact. Such associations determine the macromolecular conformation, which, in turn, controls the rheological properties of their aqueous solutions. Polysoaps have found important industrial applications[39–41] as water thickeners in diverse fields, e.g. tertiary oil recovery, fluid modification and frictional drag reduction. They can also be used as alternatives for conventional surfactants as flocculants in the treatment of waste-water.[40]

Development of hydrophobically modified polyelectrolytes

Polysoaps gained particular attention in polymer chemistry at the beginning of the 1950s when the spontaneous

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formation and physical properties of surfactant aggregates in aqueous solution were under active research.[2] Detailed studies concerning the transition from polyelectrolyte to polysoap were carried out by Strauss and co-workers[3,4,5] with series of poly-4-vinylpyridine derivatives quaternized with *n*-dodecyl bromide and the remainder with ethyl bromide. It was found that poly-4-vinylpyridine derivatives with an *n*-dodecyl group content smaller than a critical value have a loosely coiled chain structure typical of polyelectrolytes, whereas poly-4-vinylpyridine derivatives with larger contents of *n*-dodecyl groups possess a highly compact shape typical of polysoaps. All the poly-4-vinylpyridine derivatives containing *n*-dodecyl groups also showed a tendency toward intermolecular association. To obtain more quantitative information concerning the molecular dimensions and the aggregate formation of these macromolecules, light scattering studies were carried out, which suggested intramolecular aggregation of *n*-dodecyl groups belonging to the same polysoap molecule in aqueous solution.[5] However, many intriguing questions remained. In particular, the relationships between the chemical structure of a polysoap and its propensity for aggregation are still not fully established.

Poly(methacrylic acid), reported by Katchalsky and co-workers,[6–8] was found to exhibit a marked pH-induced conformational transition from polyelectrolyte to polysoap, which is absent in poly(acrylic acid).[9] At $pH < 3$, the free polymerized acid is formed, and the polymer collapses into a tight hydrophobic coil. However, above pH 4, the polymer coil tends to open. At $pH > 8$, the carboxylic groups are completely ionized, and the poly(methacrylic acid) chain is stretched out to molecular dimensions typical of normal polyelectrolyte[3] due to the repulsion between the carboxylate groups. A similar conformational transition from polyelectrolyte to polysoap induced by a change in pH was also found for poly(ethacrylic acid) by Fichter and Schonert[10] and Nitta *et al.*[11]

In 1967, Dubin and Strauss[12,13] reported extensive studies on the hydrolyzed copolymers of maleic anhydride and *n*-alkyl vinyl ethers which undergo conformational transitions resembling those occurring in biopolymers. These copolymers are transformed into anionic polyelectrolytes by partial or total ionization of the carboxylic groups of the maleic acid moieties. An interesting feature is that the hydrophobic microdomains formed by the copolymers with alkyl side-chains varying between *n*-butyl and *n*-octyl groups may be reversibly destroyed or created by changes in the pH of the medium. For methyl and ethyl side-chains, the copolymers behave like normal hydrophilic polyelectrolytes and undergo a progressive conformational expansion when the degree of neutralization α of the carboxylic groups is increased. For alkyl side-chains $\geq$ n-butyl, however, the increase in results in a conformational transition whereby the copolymer coil changes from a compact globular conformation at low α to the normal extended conformation at higher α. The transition takes place within a fairly narrow range of α, centered around a critical value of the neutralization degree of the carboxylic groups which increases with alkyl chain length. For alkyl side-chains $\geq$ *n*-decyl, the copolymers appear to retain a fairly compact conformation in the whole range of α. From a variety of experimental techniques, including potentiometry, calorimetry and fluorescence, it has been established that the compact coil is stabilized by hydrophobic interactions between the alkyl side-chains.[12–15] Long-range electrostatic interactions become predominant at high degrees of ionization, and the compact conformation is converted into an extended coil form. Furthermore, Hsu and Strauss[16] determined the average number of alkyl chains per hydrophobic microdomain formed by these copolymers in aqueous solution by fluorescence probing. In 1970, the pH-induced conformational transition from polyelectrolyte to polysoap was also observed for copolymers of maleic acid and styrene by Sakurada *et al.*,[17] and the transition was shown to be similar to that for poly(methacrylic acid).

On the basis of the work of Strauss and his colleagues, Kunitake and co-workers[18–20] made detailed studies of the catalytic effects on decarboxylation reactions of 6-nitrobenzisoxazole-3-carboxylate anion using a series of poly-4-vinylpyridine derivatives quaternized with *n*-octyl, *n*-dodecyl, *n*-octadecyl and *n*-docosyl bromides and the remainder with ethyl bromide. The catalytic efficiency of these polysoaps is related to the formation of hydrophobic microdomains in aqueous solution. They concluded that poly-4-vinylpyridine derivatives containing *n*-octyl groups provide an optimum balance of water solubility and polymer hydrophobicity in the series of polysoaps.[20]

Recently, Anton and Laschewsky[21] reported the synthesis of novel polysoaps with well defined chemical compositions by thiol/en addition reactions of diolefin surfactant monomers and dithiols. Structural variations of the dithiols provide main chains with different lengths and polarities in their repeat units. The use of the thiol/en addition in polymerization processes in highly polar, protic solvents is attractive for the synthesis of water-soluble polymers such as polyelectrolytes. However, the different solubilities of the starting materials still pose problems in obtaining high molecular weight polythioethers.[21]

Fluoroalkylated amphiphiles are known to have unique properties, such as greater hydrophobicity, constrained conformational states and chemical inertness, that set them apart from more common hydrocarbon surfactants. The synthesis of fluoroalkylated amphiphiles has been the subject of considerable interest in both fundamental studies and applications. Recently, Sawada *et al.*[22] synthesized a series of novel fluoroalkylated polysoaps possessing five-membered ring structures by reaction of diallylammonium chloride with fluoroalkanoyl peroxides

under conditions similar to those used with diallylammonium chloride. These novel fluoroalkylated polysoaps can reduce the surface tension of water more effectively than non-fluorinated poly(diallylammonium chlorides).[22] Furthermore, these fluoroalkylated cationic polysoaps are readily soluble not only in water but also in organic solvents such as methanol, ethanol and dimethyl sulfoxide.

Along with a number of experimental studies, the aggregates of polysoaps have recently been the subject of considerable theoretical interest.[23] The number of hydrophobic groups incorporated within the macromolecules has been suggested to play an important role in determining the polysoap conformations in aqueous solution. These theoretical treatments of polysoaps have also addressed the phenomenon of the strongly reduced CAC values when the addition of surfactants into polysoap solution results in the formation of mixed micelles.[23]

Although many hydrophobically modified polyelectrolytes have been reported, much less attention has been focused on the control of their association properties.[5–22] Furthermore, structure–property relationships in aqueous solution have not been well established. The purpose of the present review is to highlight some interesting features of non-cross-linked and cross-linked poly(alkylmethyldiallylammonium halides) that have recently been described.

SYNTHESIS

Development of cyclopolymerization

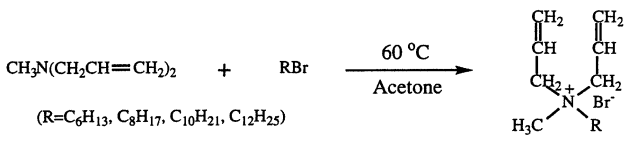
In 1949, Butler and Bunch[42] reported the homolytic polymerization of diallyldiethylammonium bromide. The resulting polymeric material contained no unreacted double bonds and was soluble in water. Interestingly, the polymers could be degraded and were found to contain cyclic structures along the polymer backbone. To explain these results, Butler and co-workers[43,44] proposed a polymerization mechanism that involved alternating intramolecular and intermolecular chain propagation. Later, the ring-forming polymerization mechanism was called cyclopolymerization.

Since the initial investigation by Butler and Bunch,[42] these cyclopolymerizations have been the subject of much interest.[43–49] Radical initiation has been the most widely employed method of promoting cyclopolymerization and the mechanism has been studied extensively.[50–53] Initially, cyclopolymers formed from radical-initiated polymerization of 1,6-dienes were assigned structures based upon a linear network of six-membered rings linked by methylene units. The mechanism for the formation of six-membered rings was based upon the hypothesis that the more stable intermediate radical during polymerization would be a secondary radical. Therefore, radical initiation would proceed via an intermediate secondary radical which then, through a series of alternating intra- and intermolecular steps, would react to form a linear polymer containing six-membered rings.[43,44] This structure was consistent with the high solubility of the polymers which contained no residual unsaturation. Numerous later studies, however, have shown that diene cyclopolymerization can lead to polymers containing a variety of ring sizes, including five-, six- and higher membered rings.[54–58] Extensive studies showed that the polymer formed from diallyldimethylammonium chloride is composed predominantly of five-membered rings linked mainly via a 3,4-*cis* configuration.[56] Detailed studies by using electron spin resonance also indicated that copolymers possessing five-membered ring structures are formed by the free-radical cyclopolymerization of diallylamine derivatives.[57,58]

The scope of the cyclopolymerization reaction is broad, encompassing a large number of dienes and a variety of initiation modes, and has resulted in the formation of new polymers, including macromolecules which are of industrial and medical importance. Some excellent reviews have been published in this field.[52,53]

Synthesis of alkylmethyldiallylammonium halide monomers[24,28–30]

The primary target monomers in our studies were the alkylmethyldiallylammonium halides, which cyclopolymerize to yield a copolymer with pendant alkyl side-chains. Because these compounds are not commercially available, except for dimethyldiallylammonium chloride, we devised a synthetic procedure for obtaining this class of compounds. Methyldiallylamine was prepared from diallylamine according to a published procedure.[59] Dimethyldiallylammonium bromide was obtained from methyldiallylamine and methyl bromide in diethyl ether at room temperature.[60] Alkylmethyldiallylammonium bromides were synthesized via reactions of methyldiallylamine with the corresponding alkyl bromide in acetone (Scheme 1). In our monomer synthesis, the methyl group is first attached to the organic framework carrying the polymerizable group, followed by a single reaction which connects the hydrophobic groups to the monomers and simultaneously generates the ionic structure. This two-step process proved to be very convenient, and the purity of the products is satisfactory.[24,28,30] The materials required for this synthesis are readily available and



Scheme 1.

Scheme 2.

Table 1. Cyclo(co)polymerization of alkylmethyldiallylammonium halides in the absence and presence of *N,N′*-methylenebisacrylamide in aqueous solution[a]

(Co)polymer	*x*/*y* (mol/mol)[b]	*q* (%, w/w)[c]	Yield (%)	Water solubility
PolC-1-Br	100/0	0.00	51	Soluble
PolC-1-Cl	100/0	0.00	51	Soluble
CopolC1-6-Br	60/40	0.00	37	Soluble
CopolC1-8-Br	60/40	0.00	33	Soluble
CopolC1-10-Br	89/11	0.00	35	Soluble
CopolC1-12-Br	88/12	0.00	32	Soluble
CopolC1-12-Cl	89/11	0.00	75	Soluble
CL-PolC-1-Br	100/0	0.40	58	Soluble
CL-PolC-1-Br	100/0	1.0–4.0	37–50	Gel
CL-PolC-1-Cl	100/0	0.40	76	Soluble
CL-PolC-1-Cl	100/0	1.0–4.0	68–74	Gel
CL-CopolC1-6-Br	60/40	0.20	45	Soluble
CL-CopolC1-6-Br	61/39	0.40	42	Soluble
CL-CopolC1-6-Br	62/38	0.80	43	Soluble
CL-CopolC1-6-Br	80/20	0.40	44	Soluble
CL-CopolC1-6-Br	42/58	0.40	33	Soluble
CL-CopolC1-8-Br	61/39	0.20	41	Soluble
CL-CopolC1-8-Br	60/40	0.40	39	Soluble
CL-CopolC1-8-Br	59/41	0.80	47	Soluble
CL-CopolC1-8-Br	78/22	0.40	36	Soluble
CL-CopolC1-8-Br	40/60	0.40	35	Insoluble
CL-CopolC1-10-Br	89/11	0.20	37	Soluble
CL-CopolC1-10-Br	88/12	0.40	44	Soluble
CL-CopolC1-10-Br	90/10	0.80	48	Soluble
CL-CopolC1-10-Br	79/21	0.40	52	Soluble
CL-CopolC1-10-Br	68/32	0.40	47	Soluble
CL-CopolC1-12-Br	89/11	0.10	57	Soluble
CL-CopolC1-12-Br	90/10	0.20	48	Soluble
CL-CopolC1-12-Br	90/10	0.40	53	Soluble
CL-CopolC1-12-Br	89/11	0.80	49	Soluble
CL-CopolC1-12-Br	96/4	0.40	44	Soluble
CL-CopolC1-12-Br	84/16	0.40	41	Soluble
CL-CopolC1-12-Br	78/22	0.40	45	Soluble
CL-CopolC1-12-Br	90/10	1.0–4.0	35–43	Gel
CL-CopolC1-12-Cl	89/11	0.20	80	Soluble
CL-CopolC1-12-Cl	90/10	0.40	78	Soluble
CL-CopolC1-12-Cl	89/11	0.80	75	Soluble
CL-CopolC1-12-Cl	95/5	0.40	78	Soluble
CL-CopolC1-12-Cl	79/21	0.40	67	Soluble

[a] Ammonium peroxodisulfate as initiator.
[b] Compositions of copolymers.
[c] *N,N′*-Methylenebisacrylamide.

inexpensive, and the synthesis consists of simple reactions that give high yields[28,30] of multigram quantities of monomers. Also, this route provides access to a wide variety of derivatives simply by changing one of the starting materials.[30] *n*-Dodecylmethydiallylammonium chloride was prepared from *n*-dodecylmethyldiallylammonium bromide in methanol using an ion-exchange column.[29]

Synthesis of non-cross-linked and cross-linked (co)polymers[24,28–30]

Following the pioneering work of Butler and Bunch,[42] we were able to synthesize a family of novel non-cross-linked and cross-linked poly(alkylmethyldiallylammonium halides) by radical-induced cyclocopolymerization of alkylmethyldiallylammonium halides in the absence and in the presence of a small amount of *N,N′*-methylenebisacrylamide using ammonium peroxodisulfate as initiator in aqueous solution under nitrogen (Scheme 2). In a series of polymerization reactions, the monomer ratio and content of cross-linking agent were varied. The resulting solutions were dialyzed against deionized water using dialysis tubes at room temperature to remove unreacted monomers and oligomers. We obtained the non-cross-linked and cross-linked (co)polymers by subsequently freeze-drying the final solutions. The results are given in Table 1. The molecular weights of the non-cross-linked and cross-linked copolymers are believed not to be significantly different from those of the non-cross-linked and cross-linked homopolymers, re-

spectively, on the basis of the same polymerization conditions. Since these non-cross-linked and cross-linked copolymers differed only in the number of CH_2 groups in the alkyl side-chain, they offered the opportunity to probe their properties as a function of varying hydrophobic effects.

As expected the water solubility of the cross-linked (co)polymers is strongly influenced by the content of the cross-linking agent. An increase in the cross-linking agent content leads to a decrease in water solubility, presumably resulting from a decrease of the macromolecular flexibility in the cross-linked (co)polymers.[28–30] Solubility in water was restricted to cross-linked (co)polymers for which the content of the cross-linking agent is in the range 0.10–0.80% (w/w). When the content of cross-linking agent exceeded 1.00% (w/w), the cross-linked (co)polymers formed a polymer gel in aqueous solution (Table 1). In addition, the water solubility of the non-cross-linked and cross-linked copolymers is also dependent on the content of the alkyl groups in the macromolecules. For example, CL-CopolC1-8-Br is insoluble in water when the content of *n*-octyl groups exceeds 60% (mol/mol). All water-soluble non-cross-linked and cross-linked (co)polymers were characterized by their IR and ^{1}H NMR spectra which show the absence of C=C double bond absorption bands and resonances, respectively. The macromolecules clearly contain monomer units with five-membered rings cross-linked without and with *N*,*N*′-methylenebisacrylamide on the basis of their IR and ^{1}H NMR spectroscopic data,[28–30] which are in agreement with those reported in the literature for structurally related model polymers.[56] All non-cross-linked and cross-linked copolymers containing the same alkyl side-chain (Table 1) showed the same ^{1}H NMR resonances but exhibited only small difference in integrations of the alkyl proton absorptions.[28–30] The copolymer compositions (*x*/*y*), which are presumed to be random, were obtained from their ^{1}H NMR spectra by careful integration of relevant alkyl proton absorptions and were in good agreement with the feed ratio of monomers in the polymerization reactions.[28–30]

Rheological Behavior in Aqueous Solution[28–31]

Viscometry is a convenient and reliable method for probing the formation of compact coils of amphiphilic macromolecules in aqueous solution.[3–5] Strauss and co-workers[3,4] reported that the viscosity of poly-4-vinylpyridine derivatives quaternized with *n*-dodecyl bromide shows a more than 100 fold decrease as the content of *n*-dodecyl groups is varied from 0 to 37.9 mol%. Moreover, it was found that the reduced viscosity changes drastically in the range 10–13 mol% *n*-dodecyl group content in the polysoaps.[3,4] Similar viscosity behavior was also found by Kunitake and co-workers[19,20] for poly-4-vinylpyridine derivatives quaternized with *n*-octyl or *n*-octadecyl bromide but the transition composition varied with the alkyl chain length. The drastic viscosity changes occurred at 40–50 mol% for poly-4-vinylpyridine derivatives containing *n*-octyl groups and *ca* 5 mol% for those containing *n*-octadecyl groups. These results were explained in terms of the molecular dimensions and interactions of the polysoap molecules, and provide a significant insight into polysoap behavior in aqueous solution.

The reduced viscosity of (CL)-PolC-1-Cl and (CL)-PolC-1-Br in aqueous solution was found to decrease strongly with increasing polymer concentration. This is indicative of highly extended molecular dimensions typical of normal polyelectrolyte behavior as a result of increased electrostatic repulsions between ionized groups.[28,29] However, the incorporation of *n*-dodecyl side-chains into the polyelectrolytes greatly influences the reduced viscosity of non-cross-linked and cross-linked copolymers in aqueous solution, as shown in Fig. 1. At low concentration, (CL)-CopolC1-12-Cl exhibits lower reduced viscosities in aqueous solution than (CL)-PolC-1-Cl, which indicates the presence of compact coil comformations brought about by intramolecular micelle formation.[3–5] The conformational transition to compact coils was found to be strongly dependent on the *n*-dodecyl group content in the macromolecules as expected for an aggregation process largely dictated by hydro-

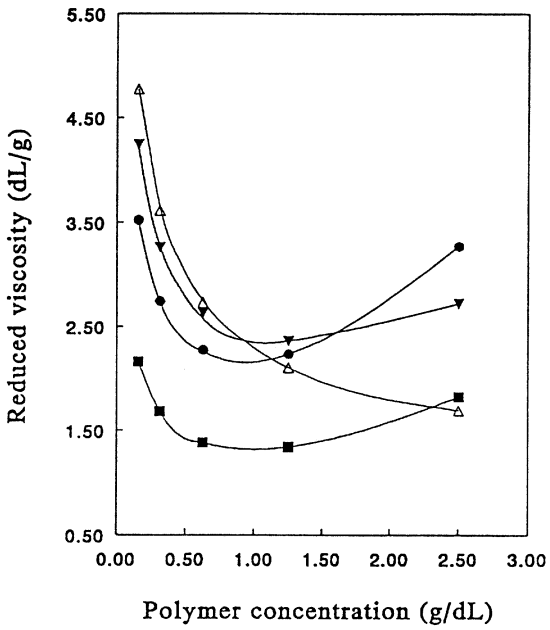


Figure 1. Effects of the *n*-dodecyl group content on the reduced viscosity of cross-linked copolymers in aqueous solution at 30°C: △, CL-PolC-1-Cl (*q*, 0.40%); ▼, CL-CopolC1-12-Cl (*x*/*y*, 95/5; *q*, 0.40%); ●, CL-CopolC1-12-Cl (*x*/*y*, 90/10; *q*, 0.40%); ■CL-CopolC1-12-Cl (*x*/*y*, 79/21; *q*, 0.40%). (Taken from Refer. 29.)

phobic interactions.[1] At higher concentrations, (CL)-CopolC1-12-Cl showed an increase in the reduced viscosity consistent with intermolecular aggregation by hydrophobic interactions between the *n*-dodecyl groups in different macromolecules.[3–5] Similar rheological behavior was also found for both (CL)-CopolC1-12-Br and (CL)-CopolC1-10-Br in aqueous solutions.[28,30]

The reduced viscosity of aqueous solutions of (CL)-CopolC1-8 and (CL)-CopolC1-6, which decreased strongly with increasing copolymer concentration, was only weakly sensitive to changes in the *n*-octyl and *n*-hexyl group contents, indicative of highly extended macromolecular chains similar to those of polyelectrolyte in the concentration region studied.[30]

Consistent with a decrease of the macromolecular flexibility, all cross-linked (co)polymers exhibited larger reduced viscosities than the corresponding non-cross-linked (co)polymer analogues and the reduced viscosity increased with increasing content of the cross-linking agent.[28–30]

HYDROPHOBIC MICRODOMAINS IN AQUEOUS SOLUTION[24,28–31]

One of the most common and convenient methods for probing the formation of hydrophobic microdomains involves monitoring the spectroscopic properties of a hydrophobic dye in the presence of increasing concentrations of amphiphiles.[61–66] Varadaraj and co-workers[62,63] employed the solvatochromic pyridinium-*N*-phenoxide betaine dye to probe the formation of hydrophobic microdomains for a series of hydrophobically modified polyacrylamides in aqueous solution. Recently, the hydrophobic dye Orange OT has also been used to measure the critical micellar concentration (cmc) of glycosylated and non-glycosylated bile acids in aqueous solution.[64] As reported by Klotz *et al.*,[65,66] the absorption spectrum of the solvatochromic probe Methyl Orange can also be employed to probe the formation of hydrophobic microdomains because binding of the dye to hydrophobic regions is accompanied by a substantial shift of the long-wavelength absorption maximum (λ_{max}) to shorter wavelengths.[19,20]

In order to compare the relative hydrophobicities of the binding sites of the microdomains, we measured the λ_{max} of Methyl Orange in the presence of non-cross-linked and cross-linked (co)polymers as a function of polymer concentration in aqueous solution at pH 9.4 and 30 °C (Fig. 2). In the presence of PolC-1-Br no spectral changes were found in the concentration region investigated, indicating that Methyl Orange resides in an aqueous environment. In the low concentration range between *ca* 10^{-5} and 10^{-3} unit mol l^{-1}, CopolC1-12-Br and (CL)-CopolC1-12-Br showed striking spectral shifts which are attributed to the formation of hydrophobic microdomains induced by the presence of Methyl Orange (see later).[31]

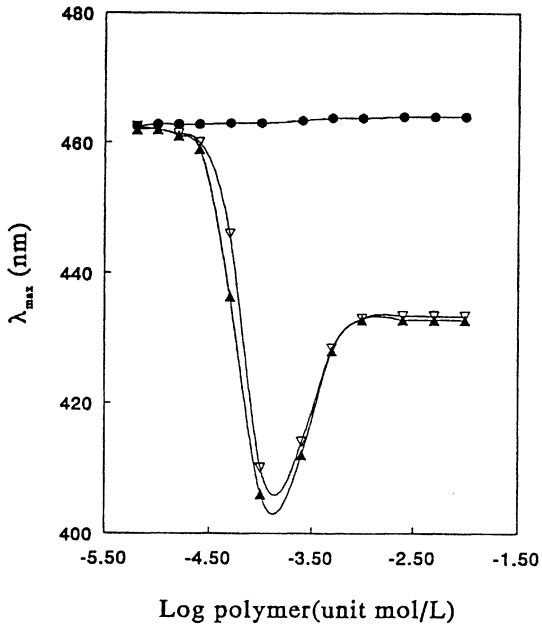


Figure 2. Position of the long-wavelength absorption maximum of Methyl Orange in aqueous solutions in the presence of non-cross-linked and cross-linked (co)polymers at pH 9.4 and 30 °C: ▲, CL-CopolC1-12-Br (*x*/*y*, 90/10; *q*, 0.20%); ▽, CopolC1-12-Br (*x*/*y*, 88/12); ●, PolC-1-Br. (Taken from Ref. 31.)

At concentrations above 1.0×10^{-3} unit mol l^{-1}, substantial spectral shifts are observed, revealing that Methyl Orange is now bound at hydrophobic binding sites in hydrophobic aggregates of CopolC1-12-Br and (CL)-CopolC1-12-Br in aqueous solution. The spectral data (λ_{max}) that refer to relatively high concentrations for all non-cross-linked and cross-linked (co)polymers are given in Table 2. (CL)-CopolC1-12-Cl and (CL)-CopolC1-10-Br induced also considerable spectral shifts and their magnitude increased with an increase in the alkyl group content in the macromolecules.[29,30] By contrast, (CL)-CopolC1-8-Br induced only modest spectral shifts with increasing *n*-octyl group content. No spectral shifts of Methyl Orange to shorter wavelength were observed in the presence of (CL)-CopolC1-6-Br.[30] These data reveal that (CL)-CopolC1-12-Cl, (CL)-CopolC1-12-Br and (CL)-CopolC1-10-Br with sufficiently long alkyl side-chains form hydrophobic microdomains in aqueous solution. (CL)-CopolC1-8-Br apparently shows much less efficient intramolecular micellization and no hydrophobic microdomains are formed in the case of (CL)-CopolC1-6-Br in the concentration region investigated.[30]

FLUORESCENCE SPECTROSCOPIC STUDIES[25,33–35]

Fluorescence probe techniques are powerful tools in

Table 2. Photophysical and kinetic results for non-cross-linked and cross-linked poly(alkylmethyldiallylammonium halides) in aqueous solution

(Co)polymer	*x*/*y* (mol/mol)	*q* (%, w/w)	λ_{max}(nm)[a,b]	I_1/I_3[c]	k_d/k_w[d]
PolC-1-Br	100/0	0.00	464	1.89	3[e]
CL-PolC-1-Br	100/0	0.40	464	1.89	4[e]
PolC-1-Cl	100/0	0.00	464	1.90	3[e]
CL-PolC-1-Cl	100/0	0.40	464	1.90	3[e]
CopolC1-6-Br	60/40	0.00	465	1.81	6
CL-CopolC1-6-Br	60/40	0.20	465	1.81	6
CL-CopolC1-6-Br	61/39	0.40	465	1.79	7
CL-CopolC1-6-Br	62/38	0.80	465	1.80	7
CL-CopolC1-6-Br	80/20	0.40	465	1.82	4
CL-CopolC1-6-Br	42/58	0.40	465	1.75	9
CopolC1-8-Br	60/40	0.00	455	1.74	134
CL-CopolC1-8-Br	61/39	0.20	454	1.73	180
CL-CopolC1-8-Br	60/40	0.40	452	1.73	214
CL-CopolC1-8-Br	59/41	0.80	453	1.75	178
CL-CopolC1-8-Br	78/22	0.40	464	1.80	11
CopolC1-10-Br	89/11	0.00	438	1.61	305
CL-CopolC1-10-Br	89/11	0.20	437	1.60	331
CL-CopolC1-10-Br	88/12	0.40	437	1.61	299
CL-CopolC1-10-Br	90/10	0.80	442	1.62	278
CL-CopolC1-10-Br	79/21	0.40	436	1.54	593
CL-CopolC1-10-Br	68/32	0.40	436	1.52	699
CopolC1-12-Br	88/12	0.00	432	1.55	585
CL-CopolC1-12-Br	89/11	0.10	432	1.55	672
CL-CopolC1-12-Br	90/10	0.20	431	1.54	755
CL-CopolC1-12-Br	90/10	0.40	432	1.55	686
CL-CopolC1-12-Br	89/11	0.80	433	1.56	467
CL-CopolC1-12-Br	96/4	0.40	435	1.59	446
CL-CopolC1-12-Br	84/16	0.40	430	1.53	789
CL-CopolC1-12-Br	78/22	0.40	430	1.52	966
CopolC1-12-Cl	89/11	0.00	433	1.55	1456
CL-CopolC1-12-Cl	89/11	0.20	431	1.54	1578
CL-CopolC1-12-Cl	90/10	0.40	432	1.55	1429
CL-CopolC1-12-Cl	89/11	0.80	432	1.56	1337
CL-CopolC1-12-Cl	95/5	0.40	435	1.60	746
CL-CopolC1-12-Cl	79/21	0.40	430	1.52	1850

[a] Methyl Orange, 2.5×10^{-5} M; λ_{max}, 462.5 nm in aqueous solution at pH 9.4 and 30 °C.
[b] Polymer concentration, 2.5×10^{-3} unit mol l^{-1}.
[c] Polymer concentration, 2.5×10^{-2} unit mol l^{-1}.
[d] First-order rate constants for decarboxylation of 6-NBIC; polymer concentration, 5.0×10^{-2} unit mol l^{-1}; $k_w = 7.35 \times 10^{-6}$ s^{-1} in water at 30 °C.
[e] Polymer concentration, 2.5×10^{-2} unit mol l^{-1}.

detecting aggregate formation of small molecules and macromolecules and interactions between macromolecules and conventional surfactants in aqueous solutions.[67–71] The fluorescence spectrum of the probe molecule pyrene provides information on the micropolarity of the microenvironment at the binding sites for the probe.[67,68] The spectrum shows several vibronic peaks, and the ratio I_1/I_3 of the intensities of the first and third vibronic peaks has been taken as a sensitive indicator of the micropolarity of the pyrene microenvironment.[69,70] In pure water at low pyrene concentrations (2.0×10^{-6} M) this ratio I_1/I_3 is 1.90.[31,67–71] If pyrene binds to hydrophobic binding sites in supramolecular assemblies, I_1/I_3 is reduced by a factor characteristic of the particular microenvironment where the pyrene molecule sits.

We measured the ratio I_1/I_3 of pyrene fluorescence in aqueous solution in the presence of non-cross-linked and cross-linked (co)polymers as a function of polymer concentration (Fig. 3). The fluorescence ratio I_1/I_3 for all non-cross-linked and cross-linked (co)polymers at high polymer concentrations are given in Table 2. In aqueous solutions of (CL)-PolC-1-Cl and (CL)-PolC-1-Br, the fluorescence spectrum of pyrene was similar to that found in pure water in the concentration range studied, consistent with the notion that no hydrophobic microdomains are formed in these systems. At low concentrations, all non-cross-linked and cross-linked copolymers also showed a high I_1/I_3 similar to that in pure water, indicating that pyrene is neither associated with nor solubilized in the random coil of the macromolecules but is solubilized in the aqueous solution. A sudden and large decrease in I_1/I_3 was observed for (CL)-CopolC1-12-Br and (CL)-CopolC1-10-Br on further

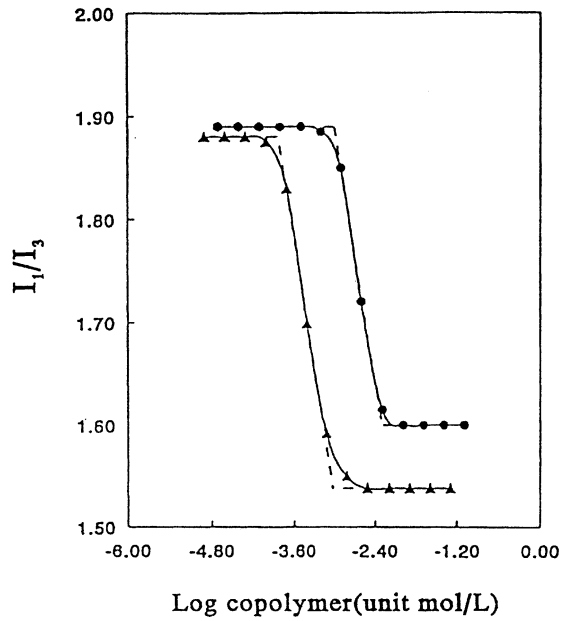


Figure 3. Ratio I_1/I_3 of pyrene fluorescence in aqueous solutions of cross-linked copolymers as a function of copolymer concentration at 25°C: ▲, CL-CopolC1-12,-Br (*x*/*y*, 90/10; *q*, 0.20%) ●, CL-CopolC1-10-Br (*x*/*y*, 89/11; *q*, 0.20%). (Taken from Ref. 36.)

increasing the copolymer concentration (Fig. 3).[33,34] These low I_1/I_3 values are indicative of the binding of pyrene at binding sites located in a relatively non-polar microenvironment in the hydrophobic microdomains. The magnitude of I_1/I_3 upon complete binding of pyrene to the hydrophobic microdomains decreases with increase in the alkyl group content. Interestingly, (CL)-CopolC1-12-Cl was found to demonstrate similar aggregation behavior to (CL)-CopolCl-12-Br.[35] Presumably both polysoaps with chloride and with bromide counterions have the same propensity for intramolecular and intermolecular aggregation processes.

Consistent with the observations based on UV–visible spectroscopy, only a modest decrease in I_1/I_3 was observed at relatively high copolymer concentrations for (CL)-CopolC1-8-Br and no steady value of I_1/I_3 was reached in the concentration range investigated, indicating that no extensive hydrophobic microdomains are formed in aqueous solution.[33] Only weakly cooperative and small decreases in I_1/I_3 were obtained for (CL)-CopolC1-6-Br and there was clearly no sharp transition in I_1/I_3 in the concentration range studied, indicative of the absence of formation of hydrophobic microdomains.[33]

MACROMOLECULAR FLEXIBILITY AND AGGREGATION TENDENCY[36]

The critical aggregation concentration (CAC) may be taken as an indicator of the aggregation tendency of small molecules and macromolecules in aqueous solution.[69,72,73] It has been generally observed that the aggregation tendency of structurally related macromolecules is strongly counteracted by a reduced macromolecular flexibility.[3–5,18–20] However, this widely accepted rule is apparently not applicable for the non-cross-linked and cross-linked polysoaps examined in our study.

Critical aggregation concentration (CAC) of polysoaps[26,27,33–35]

One of the methods for determining the CAC involves plotting the fluorescence ratio I_1/I_3 of pyrene against the polysoap concentration, as illustrated in Fig. 3.[33,69] In aqueous solutions of (CL)-CopolC1-12-Cl, (CL)-CopolC1-12-Br and (CL)-CopolC1-10-Br there is a sharp decrease in I_1/I_3 over a narrow range of polysoap concentrations, indicative of a cooperative intramolecular aggregation process. For practical reasons, the CAC may be taken as the polysoap concentration at which I_1/I_3 reaches a steady value.[33–35] At the CAC, the hydrophobic microdomains are fully formed and completely bind strongly hydrophobic cosolutes such as pyrene. (CL)-CopolC1-8-Br and (CL)-CopolC1-6-Br exhibited no steady I_1/I_3 value with increasing copolymer concentration owing to the absence of efficient formation of hydrophobic microdomains in aqueous solution.[33] Therefore, in this case, the CAC cannot be obtained from the fluorescence spectroscopic results. Under identical experimental conditions, a smaller CAC value signifies a greater propensity for aggregation of the macromolecules.[72,73]

Effects of macromolecular flexibility on the CAC[36]

We examined the effects of the cross-linking agent content (q) as a macromolecular flexibility modifier on the CAC for (CL)-CopolC1-12-Cl, (CL)-CopolC1-12-Br and (CL)-CopolC1-10-Br in aqueous solution. The results are given in Table 3 and the specific effects of the macromolecular flexibility on the aggregate tendency can be demonstrated by the ratio of CAC_q to CAC_0 for the polysoaps with and without cross-linking agent, repectively.

We found that (CL)-CopolC1-12-Cl, (CL)-CopolC1-12-Br and (CL)-CopolC1-10-Br all show the same change in their aggregation tendency accompanying an increase in the content of the cross-linking agent. The decrease in the macromolecular flexibility that results from an increase in the cross-linking agent content leads to an increase in the aggregation tendency which reaches a maximum at 0.20% cross-linking agent content. The propensity for aggregation then decreases with a further decrease in the macromolecular flexibility (Table 3).

Table 3. Effect of cross-linking agent content on the CAC for (CL)-CopolC1-12-Cl (*x*/*y*, 90/10), (CL)-Copol1-12-Br (*x*/*y*, 90/10) and (CL)-CopolC1-10-Br (*x*/*y*, 89/11) at 25 °C and on the polysoap-catalyzed decarboxylation of 6-NBIC in aqueous solution

Polysoap	Cross-linking agent[a] (%, w/w)	CAC $\times 10^3$ (M)	CAC_q/CAC_0[b]	$k_d \times 10^3$ (s^{-1})[c,d]	k_d^q/k_d^{0e}
CopolC1-12-Cl	0.00	1.26	1.00	10.70	1.00
CL-CopolC1-12-Cl	0.20	0.83	0.66	11.60	1.08
CL-CopolC1-12-Cl	0.40	1.12	0.89	10.50	0.98
CL-CopolC1-12-Cl	0.80	1.58	1.25	9.83	0.92
CopolC1-12-Br	0.00	1.74	1.00	4.30	1.00
CL-CopolC1-12-Br	0.10	1.65	0.95	4.94	1.15
CL-CopolC1-12-Br	0.20	0.91	0.52	5.55	1.29
CL-CopolC1-12-Br	0.40	1.54	0.89	5.04	1.17
CL-CopolC1-12-Br	0.80	2.18	1.25	3.43	0.80
CopolC1-10-Br	0.00	6.76	1.00	2.86	1.00
CL-CopolC1-10-Br	0.20	4.16	0.61	3.11	1.09
CL-CopolC1-10-Br	0.40	5.37	0.79	2.80	0.98
CL-CopolC1-10-Br	0.80	10.20	1.51	2.56	0.89

[a] *N*,*N*′-Methylenebisacrylamide.
[b] CAC_q and CAC_0, for cross-linked and non-cross-linked polysoaps, respectively.
[c] k_d, first-order rate constants for the polysoap-catalyzed decarboxylation of 6-NBIC in aqueous solution at pH 11.3 and 30 °C.
[d] (CL)-CopolC1-12-Cl and (CL)-CopolC1-12-Br, 5.0×10^{-2} unit mol l^{-1}; (CL)-CopolC1-10-Br, 1.0×10^{-1} unit mol l^{-1}.
[e] k_d^q and k_d^0, first-order rate constants in the presence of cross-linked and non-cross-linked polysoaps, respectively.

Apparently our results are at variance with those of previous studies[3–5,18–20] which suggested that macromolecules with higher macromolecular flexibility possess a greater aggregation tendency than those with lower macromolecular flexibility. We contend that this specific effect is caused by increased intramolecular micellization in the macromolecules. Intramolecular micellization of cross-linked polysoaps is facilitated by effective contacts between the alkyl side-chains belonging to the same macromolecules at lower cross-linking agent contents. Increased cross-linking of polysoap molecules is expected to decrease intermolecular aggregation because of decreased macromolecular motion of such cross-linked polysoaps in aqueous solution.

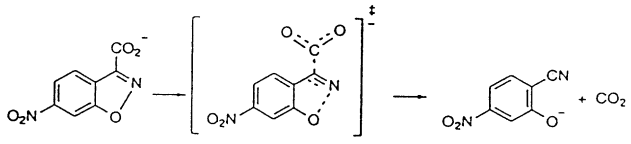
We note that the relationships between macromolecular flexibility and aggregation tendency of non-cross-linked and cross-linked polysoaps are fully consistent with differences in their catalytic effects on the unimolecular decarboxylation of 6-NBIC (see later).[28–30]

UNIMOLECULAR DECARBOXYLATION OF 6-NBIC CATALYZED BY NON-CROSS-LINKED AND CROSS-LINKED (CO)POLYMERS[24,28–30,32]

The unimolecular decarboxylation of the 6-nitrobenzisoxazole-3-carboxylate anion (6-NBIC) is notable for its remarkable sensitivity to the reaction medium (Scheme 3).[74–80] Kemp and co-workers[74–76] examined solvent effects on the decarboxylation rate of 6-NBIC. It was proposed that the rate is mainly influenced by hydrogen bonding of the carboxylate ion with protic solvents and the stabilization of the transition state in dipolar aprotic solvents. Recent analysis of solvent effects on this reaction clearly revealed the importance of hydrogen bonding and ion pairing effects as the major contributing factors in determining the decarboxylation rates.[77–80] The unimolecular decarboxylation of 6-NBIC provides a popular probe for exploring micellar,[81–87] polymer[19,20,88–92] and antibody catalysis.[93–95] The rate accelerations can be largely ascribed to partial dehydration of the carboxylate function of the initial state in the hydrophobic microenvironment at the binding site of 6-NBIC.[77–80] The catalysis of the decarboxylation of 6-NBIC by cationic micelles can be enhanced by addition of electrolytes, and it is sensitive to changes in micellar structure and charge density.[81] The micelle-catalyzed decarboxylation reactions of 6-NBIC have been regarded as useful models for electrostatic and hydrophobic interactions in biological systems to provide information regarding the mechanism of regulation of reactions occurring on membranes.[81–86]

Effects of counterion and alkyl side-chain length on the decarboxylation of 6-NBIC[28–30]

The pseudo-first-order rate constants for the unimolecular decarboxylation of 6-NBIC catalyzed by non-cross-linked and cross-linked (co)polymers were measured as a function of polymer concentration in aqueous solution at pH 11.3 and 30 °C. Representative results are presented in Fig. 4 which show the effects of counterion and alkyl



Scheme 3.

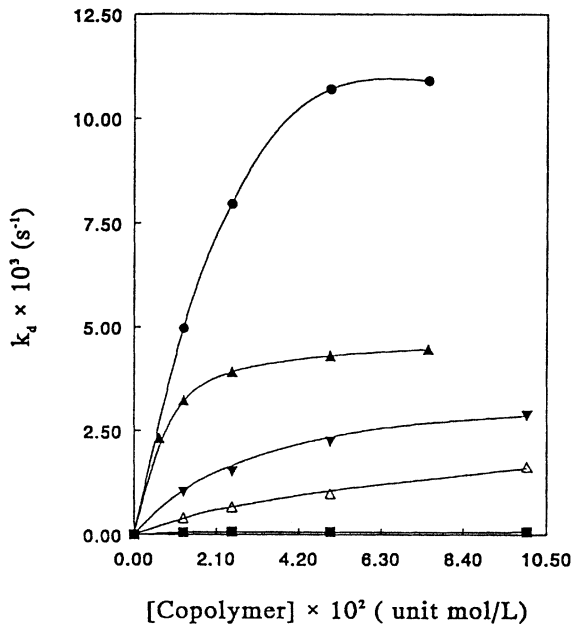


Figure 4. Rate constants for the unimolecular decarboxylation of 6-NBIC catalyzed by non-cross-linked copolymers in aqueous solution as a function of the counterion and the alkyl chain length at pH 11.3 and 30 °C: ●, CopolC1-12-Cl (*x/y*, 89/11); ▲, CopolC1-12-Br (*x/y*, 88/12); ▼, CopolC1-10-Br (*x/y*, 89/11); △, CopolC1-8-Br (*x/y*, 60/40); ■, CopolC1-6-Br (*x/y*, 60/40). (Taken from Ref. 28, 29, 30.)

side-chain length. The kinetic data at high polymer concentrations for all non-cross-linked and cross-linked (co)polymers are given in Table 2. (CL)-PolC-1-Cl and (CL)-PolC-1-Br only showed a small rate enhancement, in conformity with the absence of hydrophobic microdomains. Earlier, we concluded that both CopolC1-12-Cl and CopolC1-12-Br have a similar aggregation behavior in aqueous solution due to similar intramolecular and intermolecular interactions by the *n*-dodecyl groups in the macromolecules. Surprisingly, CopolC1-12-Cl was found to exhibit a much higher catalytic efficiency for the decarboxylation of 6-NBIC than the corresponding CopolC1-12-Br (Fig. 4).[28,29] The increased catalytic effects are attributed to the smaller chloride counterion binding to the cationic groups as compared with the bromide counterion at the periphery of the hydrophobic microdomains leading to increased initial state destabilization.[29] CopolC1-10-Br also exhibited remarkable catalytic efficiency. However, modest rate enhancements were obtained for CopolC1-8-Br when the content of the *n*-octyl group was increased to 40% (mol/mol), in accord with the notion that no extensive hydrophobic microdomains are formed in aqueous solution. CopolC1-6-Br induced only small rate enhancements in the concentration range studied, indicative of the absence of formation of hydrophobic microdomains.[30] We conclude that in the series of non-cross-linked and cross-linked copolymers, the rate acceleration for the decarboxylation of 6-NBIC increases in the order (CL)-CopolC1-12-Cl > (CL)-CopolC1-12-Br > (CL)-CopolC1-10-Br > (CL)-Copol C1-8-Br > (CL)-CopolC1-6-Br.

Effects of cross-linking agent content on the decarboxylation of 6-NBIC[28–30]

The results in Table 3 reveal that the cross-linking agent content significantly affects the rate of decarboxylation of 6-NBIC. The ratio of k_d^q to k_d^0, which are first-order rate constants for the polysoaps with and without cross-linking agent, respectively, can indicate the effect of macromolecular flexibility on the decarboxylation of 6-NBIC. (CL)-CopolC1-12-Cl, (CL)-CopolC1-12-Br and (CL)-CopolC1-10-Br were all found to exhibit a maximum rate constant for the decarboxylation of 6-NBIC at 0.20% (w/w) cross-linking agent, consistent with earlier conclusions regarding the effects of macromolecular flexibility on the aggregation tendency of cross-linked polysoaps. The increased catalytic effects that result from an increase in the cross-linking agent content may be ascribed to an increase in intramolecular micellization in the macromolecules. Consistent with the notion that the three-dimensional macromolecular structures of these cross-linked copolymers permit more efficient intramolecular micellization than that of non-cross-linked copolymers, we also found that CL-CopolC1-8-Br exhibits a slight rate maximum at about 0.4% (w/w) cross-linking agent.[30] This is consistent with the idea that hydrophobic interactions are favored by the geometry of the three-dimentional structures with appropriate cross-linking in macromolecular systems.[36]

AGGREGATE FORMATION OF CATIONIC POLYSOAPS BELOW THEIR CAC INDUCED BY LOW CONCENTRATIONS OF ORGANIC ADDITIVES[31]

For a number of years, ionic surfactants have been known to interact strongly with oppositely charged polyelectrolytes and to form mixed micelles at surfactant concentrations much lower than the cmc of the surfactant.[96] Although the polyelectrolyte–surfactant complex is stabilized mainly by electrostatic attractions, hydrophobic interactions between the surfactant alkyl tail and polymer backbone appear to play an important role. For a number of anionic polyelectrolytes, it has been found that the interaction is cooperative and that its strength increases much with the surfactant chain length and hydrophobicity of the polymers.[96,97] Shimizu *et al.*[98] reported that an increased hydrophobicity of the polymers strengthens the polyelectrolyte–surfactant interaction but at the same time decreases the cooperativity of the binding process. Moreover, the flexibility and charge density of the polyelectrolyte chain also influence the

association. In 1991, Iliopoulos *et al.*[99] found that polyelectrolytes containing a small fraction of very hydrophobic groups, e.g. octadecyl chains, can associate even with surfactants of the same charge. In this case the attractive hydrophobic interactions overcome the unfavorable electrostatic repulsions between the polymer backbone and the surfactant ionic heads. Recently, Magny *et al.*[100] determined the total aggregation number and the number of polymer alkyl groups per mixed micelle formed by hydrophobically modified poly(sodium acrylate) with cationic surfactants by steady-state and time-resolved fluorescence methods. They found that there is an extensive intramolecular contribution of the alkyl groups to mixed micelle formation.[100] Another important consequence of the surfactant binding to the oppositely charged polyelectrolyte is the occurrence of associative phase separation as described by Piculell and Lindman.[101] A concentrated phase containing polyelectrolyte and surfactant is in equilibrium with a dilute solution with excess polymer or surfactant.

Earlier, the striking spectral shifts (λ_{max}) of Methyl Orange that occur at low polysoap concentrations (*ca* 1.0×10^{-4} unit mol l^{-1}) (Fig. 2) were attributed to aggregate formation of cationic polysoaps induced by low concentrations of anionic Methyl Orange. These results warrant more detailed studies. As indicated earlier, reduced viscosities and fluorescence data for pyrene may provide further insight into the conformational transitions of polysoaps induced by interactions with the additives. We have made an attempt to measure the reduced viscosity and the ratio I_1/I_3 of pyrene in aqueous solution of cationic polysoaps in the presence of low concentrations of organic additives, with particular emphasis on the charge type and the alkyl side-chain length of organic additives.

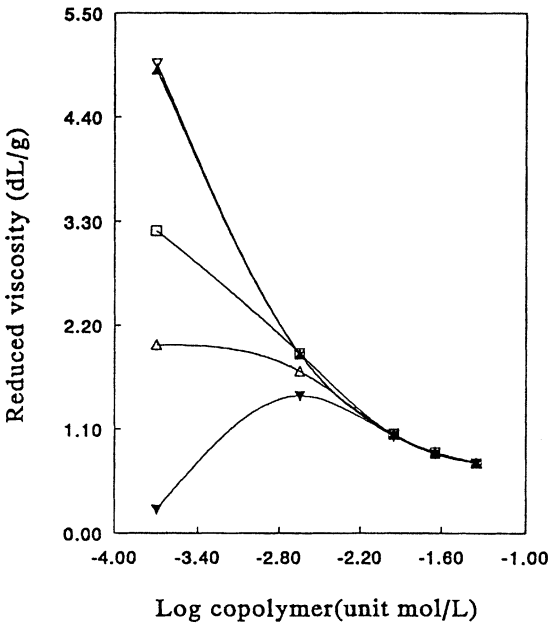


Figure 5. Reduced viscosities (η_{sp}/c) of CL-CopolC1-12-Br (*x/y*, 90/10; *q*, 0.20%) in aqueous solutions in the absence and presence of low concentrations of organic additives at 30 °C: ▽, in water; ▲, in the presence of CTAB (2.5×10^{-5} M); □, in the presence of SBS (2.5×10^{-5} M); △, in the presence of Methyl Orange (2.5×10^{-5} M); ▼, in the presence of Methyl Orange (2.5×10^{-4} M). (Taken from Ref. 33.)

Measurements of reduced viscosity[31]

We determined the reduced viscosity of CL-CopolC1-12-Br in the presence of anionic, cationic and non-ionic additives and the results are shown in Figure 5. Large reductions of the reduced viscosity were found in the presence of Methyl Orange, indicating that compact coils are already present at a concentration of CL-CopolC1-12-Br far below its CAC. Consistent with the UV–visible spectroscopic results, at higher polysoap concentrations the preferred polysoap conformation changed into that characteristic of pure water and the specific effect of Methyl Orange was completely diminished. Cetyltrimethylammonium bromide (CTAB) and *n*-dodecyltrimethylammonium bromide (DTAB) did not affect the reduced viscosity whereas the non-ionic surfactant heptaethylene glycol *n*-dodecyl ether (HEGDE) exerted only a minor effect.[31] By contrast, a low reduced viscosity was observed in the presence of sodium dodecyl sulfate (SDS), while a modest reduction of the reduced viscosity was found in the presence of sodium benzenesulfonate (SBS) and sodium hexyl sulfate (SHS). Sodium methyl sulfate (SMS) had no effect on the reduced viscosity of CL-CopolC1-12-Br.[31] We conclude that the induction of aggregation of cationic polysoaps below their CAC is governed by both electrostatic and hydrophobic interactions. The formation of a compact coil becomes more favorable in the order SMS < SHS < Methyl Orange < SDS.

Fluorescence spectroscopic studies[31]

In an aqueous solution of CL-CopolC1-12-Br at 2.0×10^{-4} unit mol l^{-1}, the ratio I_1/I_3 of pyrene was found to be 1.90 (see earlier). A similar value for I_1/I_3 was obtained in 2.5×10^{-5} M solutions of SDS, SHS, SMS, DTAB and HEGDE, indicating the absence of hydrophobic association. However, in the same solution of CL-CopolC1-12-Br but in the presence of 2.5×10^{-5} M SDS, the ratio I_1/I_3 is reduced to 1.54, revealing that an anionic surfactant below its normal cmc is able to induce the formation of hydrophobic microdomains which provide binding sites for host molecules such as pyrene. Consistent with the observations based on the reduced viscosity, a modest decrease in I_1/I_3 was observed for SHS, whereas solutions of SMS, DTAB and

Table 4. Ratio I_1/I_3 of pyrene fluorescence in aqueous solutions of CL-CopolC1-12-Cl (*x/y*, 79/21; *q*, 0.4% w/w) in the absence and presence of sodium chloride at 25 °C

Polysoap concentration (unit mol l^{-1})	[NaCl] (M)	I_1/I_3[a]	$(I_1/I_3)_0 - (I_1/I_3)_s$[b]
2.0×10^{-5}	0.00	1.89	0.00
	0.01	1.86	0.03
	0.10	1.80	0.09
	1.00	1.71	0.18
4.0×10^{-5}	0.00	1.89	0.00
	0.01	1.86	0.03
	0.10	1.80	0.09
	1.00	1.71	0.18
8.0×10^{-5}	0.00	1.86	0.00
	0.01	1.84	0.02
	0.10	1.77	0.09
	1.00	1.69	0.17
1.6×10^{-4}	0.00	1.74	0.00
	0.01	1.72	0.02
	0.10	1.67	0.07
	1.00	1.59	0.15

[a] Pyrene, 2.0×10^{-6} M.
[b] $(I_1/I_3)_0$ and $(I_1/I_3)_s$ in the absence and presence of NaCl, respectively.

HEGDE exhibited the same I_1/I_3 as found for pure water.[31]

Ion-Induced Hydrophobic Aggregates of Cross-Linked Polysoaps below Their CAC[37,38]

It is well known that the conformations of proteins can be significantly affected by added salts. Salt effects on the association of small-molecule and macromolecular amphiphiles are currently a topic of great interest.[102–106] Extensive studies have shown that an increase in hydrophobic association effects on addition of salting-out agents may lead to changes in the aggregate morphology from spheres to rods and to vesicles.[102] Recently, Zhang and Eisenberg[107,108] reported that the stretching of hydrophobic chains of macromolecular amphiphiles is greatest when they are located within spherical aggregates and it decreases as the aggregate morphology changes from spheres to rods, and decreases further as vesicles are formed. In view of the intense current interest in salt effects on the conformation of amphiphilic macromolecules, it seemed desirable to improve our understanding of this phenomenon by examining salt effects on polysoap aggregation. These effects are generally explained by assuming that the addition of salts causes a contraction of the expanded macromolecules by suppression of Coulombic repulsions between the ionic groups in the main chain.[3–5,12,13] We suggest that this interpretation may be oversimplified. We propose that a major influence of added salts involves salting-out effects that increase hydrophobic association of the polysoaps. Dissolution of salts in water is often accompanied by a volume contraction due to electrostriction of water in the ionic hydration spheres.[109–116] Therefore, there is less empty space for hydrocarbon species and less water for the formation of hydrophobic hydration spheres. Both effects lead to increasing hydrophobic association.[109–116]

Direct fluorescence spectroscopic evidence for salting-out effects on the aggregation of cross-linked polysoaps[37]

We examined the effects of salts on the solubility of (CL)-CopolC1-12-Cl in water above the CAC. An aqueous solution of CL-CopolC1-12-Cl at 1.0×10^{-3} unit mol l^{-1} becomes turbid when the concentration of sodium chloride is increased above 1.0 M.[37] This decrease in the solubility of the polysoap is consistent with previous observations that NaCl tends to salt-out proteins and hydrophobic organic solutes in water.[109–116]

We examined the salting-out effects of NaCl on the hydrophobic association of CL-CopolC1-12-Cl below its CAC in aqueous solution by measuring the ratio I_1/I_3 of pyrene fluorescence (Table 4). This ratio was found to decrease significantly when the concentration of NaCl was increased from 0 to 1.00 M, revealing that pyrene is bound at binding sites located in a relatively hydrophobic microenvironment in aqueous solution. Apparently the formation of hydrophobic microdomains of CL-CopolC1-12-Cl is induced by NaCl below the CAC. These specific hydrophobic effects can be quantified by the values of $(I_1/I_3)_0 - (I_1/I_3)_s$, for cross-linked polysoaps at

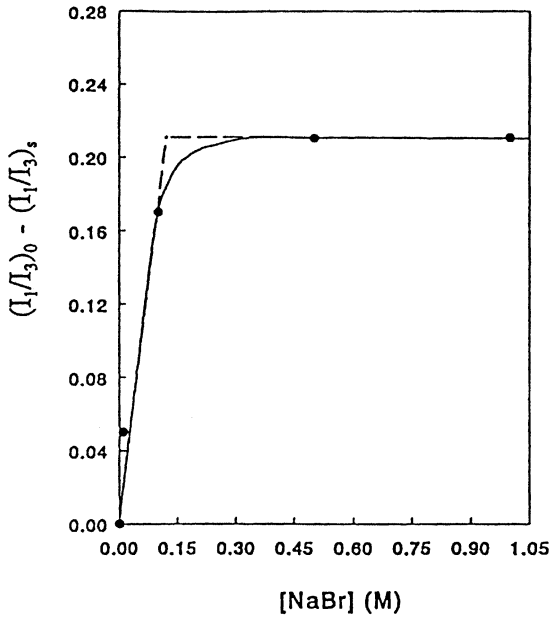


Figure 6. Values of $(I_1/I_3)_0 - (I_1/I_3)_s$ of pyrene in aqueous solutions of CL-CopolC1-10-Br (*x/y*, 79/21; *q*, 0.40%) at 4.0×10^{-5} unit mol l^{-1} as a function of NaBr concentration at 25 °C.

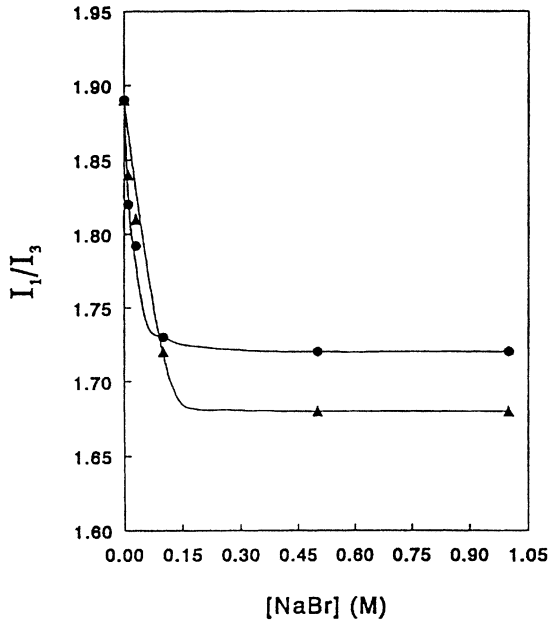


Figure 7. Ratio I_1/I_3 of pyrene fluorescence in aqueous solution of cross-linked polysoaps at 4.0×10^{-5} unit mol l^{-1} as a function of NaBr concentration at 25°C: ●, CL-CopolC1-12-Br (*x*/*y*, 78/22; *q*, 0.40%), ▲, CL-CopolC1-10-Br (*x*/*y*, 79/21; *q*, 0.40%).

a particular concentration in the absence and presence of the salting-out agent.[37]

Critical salt concentration (CSC) of cross-linked polysoaps[37,38]

The control of aggregate formation of cross-linked polysoaps by added NaBr was also established for both CL-CopolC1-10-Br and CL-CopolC1-12-Br below their CAC[33,34] in aqueous solution. The values of $(I_1/I_3)_0 - (I_1/I_3)_s$ for CL-CopolC1-10-Br as a function of NaBr concentration are plotted in Fig. 6 and show a sharp increase in $(I_1/I_3)_0 - (I_1/I_3)_s$ over a narrow range of NaBr concentrations. The values of $(I_1/I_3)_0 - (I_1/I_3)_s$ reach a steady value at a salt concentration which may be termed the critical salt concentration (CSC). At the CSC, hydrophobic microdomains in aqueous solutions of CL-CopolC1-10-Br are fully induced by added salt and completely bind strongly hydrophobic cosolutes such as pyrene. These results appear to suggest that salt-controlled conformation changes of proteins may be akin to the aggregation of the cross-linked polysoaps as controlled by added salts.

Ion-induced reversed hydrophobic effects of cross-linked polysoaps[37,38]

Values for I_1/I_3 of pyrene in aqueous solution of CL-CopolC1-12-Br and CL-CopolC1-10-Br at 4.0×10^{-5} unit mol l^{-1} in the presence of NaBr are presented in Fig. 7. Below 0.10 M NaBr, CL-CopolC1-12-Br showed a larger increase of hydrophobic association than CL-CopolC1-10-Br, in accord with the relative hydrophobicities of the respective alkyl side chains. Surprisingly, CL-CopolC1-10-Br was found to exhibit lower I_1/I_3 values than CL-CopolC1-12-Br at [NaBr] $\geq$ 0.10 M, indicating that under these conditions CL-CopolC1-10-Br provides a more hydrophobic microenvironment than CL-CopolC1-12-Br for pyrene binding. Apparently there is an inverse variation of hydrophobic association with the hydrophobicity of the alkyl side-chain in the cross-linked polysoaps. The same reverse hydrophobic effects were also obtained at 8.0×10^{-5} unit mol l^{-1} when more than 0.10 M NaBr was added.[37] We contend that the reverse hydrophobic effects at [NaBr] $\geq$ 0.10 M originate from differences in the structural characteristics of hydrophobic microdomains formed by CL-CopolC1-10-Br and CL-CopolC1-12-Br as induced by the presence of NaBr. Presumably, specific NaBr-induced salting-out effects, in combination with side chain-independent changes in counterion binding, lead to changes in the compact conformation with concomitant alteration of the hydrophobicity of the binding sites for the apolar fluorescent probe.

CONCLUSIONS

This review has attempted to summarize some recent results pertaining to the aggregation of non-cross-linked and cross-linked poly(alkylmethyldiallylammonium halides) in aqueous solution. The aggregation behavior of these (co)polymers has been characterized extensively by a range of techniques. The formation of hydrophobic microdomains by cross-linked polysoaps induced by organic additives and salts below their CAC provides further evidence for the versatility which is offered by aqueous solutions of cross-linked polysoaps. The first ion-induced reversed hydrophobic effects of cross-linked polysoaps with the hydrophobicity of the amphphilic macromolecules have now been identified. Polysoaps are expected to attract much further attention, particularly because these macromolecular amphiphiles appear to provide interesting possibilities for detailed molecular design.

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