Fluorescence Spectroscopic Study of the Aggregation Behavior of Non-Cross-Linked and Cross-Linked Poly(alkylmethyldiallylammonium bromides) Having Decyl, Octyl, and Hexyl Side Chains in Aqueous Solution

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Received June 19, 1995. In Final Form: October 6, 1995[⊗]

The conformational state of a series of non-cross-linked and cross-linked poly(alkylmethyldiallylammonium bromides) bearing decyl, octyl, and hexyl side chains ((CL)-CopolC1−10, (CL)-CopolC1−8, and (CL)-CopolC1−6, respectively) in aqueous solutions were investigated by fluorescence spectroscopy using pyrene as a probe. Photophysical studies show that the conformational transition of random coil non-cross-linked and cross-linked copolymers to compact coils is strongly side chain length dependent. (CL)-CopolC1−10 with sufficient *n*-decyl side chains was found to form hydrophobic microdomains in compact coil conformations in aqueous solution. Much less efficient intramolecular micellization was observed for (CL)-CopolC1−8 in a similar concentration range. No conformational transition to compact coils was found in the case of (CL)-CopolC1−6 as indicated by the absence of pyrene binding to the macromolecule. The presence of sodium bromide facilitates the formation of compact coil conformations for (CL)-CopolC1−10 in aqueous solution. There are significant effects of side chain length and alkyl group content on the critical aggregation concentration (cac). The cac for (CL)-CopolC1−10 in aqueous solution decreased strongly with increasing total hydrophobicity of the *n*-decyl side chains in the polysoaps. The cross-linked copolymers CL-CopolC1−10 exhibited lower cac's than the corresponding non-cross-linked copolymer analogues. A minimum in the cac for (CL)-CopolC1−10 in aqueous solution was found at about 0.20% (w/w) cross-linking agent.

Introduction

Synthetic, hydrophobically-modified polyelectrolytes ("polysoaps") have recently become the subject of extensive research.[1−10] The wide interest in macromolecules with various hydrophobic functionalities has led to the preparation of a range of hydrophobically-modified polyelectrolytes which have been shown to possess interesting properties in a variety of fields, e.g., catalysis.[6−10] A family of novel non-cross-linked and cross-linked poly(alkylmethyldiallylammonium halides) containing dodecyl, decyl, octyl and hexyl side chains ((CL)-CopolC1−12, (CL)-CopolC1−12-Cl, (CL)-CopolC1−10, (CL)-CopolC1−8, and (CL)-CopolC1−6, respectively) provides convenient systems to study the role of electrostatic and hydrophobic interactions relevant for adsorption of molecules at hydrophobic/hydrophilic interfaces and the factors that control the reactions between these adsorbed molecules.[8−14] Both (CL)-CopolC1−12 and (CL)-CopolC1−12-Cl induce huge rate enhancements for the unimolecular decarboxylation of 6-nitrobenzisoxazole-3-carboxylate anion (6-NBIC) in aqueous solution. Polysoaps with chloride counterions ((CL)-CopolC1−12-Cl) are more efficient catalysts for the decarboxylation of 6-NBIC than the corresponding polysoaps with bromide counterions ((CL)-CopolC1−12) most likely due to the smaller chloride counterion binding at the periphery of the hydrophobic microdomains leading to increased initial state destabilization.[8,9] (CL)-CopolC1−10 induces a remarkably large rate acceleration for the decarboxylation of 6-NBIC, whereas (CL)-CopolC1−8 induces only modest rate enhancements and a small rate enhancement is observed for (CL)-CopolC1−6.[10] Polysoaps cross-linked by a small amount of *N,N′*-methylenebis(acrylamide) as a cross-linking agent have been found to exhibit higher catalytic activities than the corresponding non-cross-linked copolymer analogues.[8−10] Recently, we described the synthesis of hydrophobically-modified polyacrylamides with *n*-dodecylmethyldiallylammonium bromide (Copol(AM-C12)) and their catalytic effects on the unimolecular decarboxylation of 6-NBIC in aqueous solution.[12] The decarboxylation rate of 6-NBIC was found to be significantly retarded by intermolecular hydrogen bonding of the macromolecules to the carboxylate functionality of 6-NBIC at binding sites in the hydrophobic microdomains. Photophysical studies have provided strong evidence that (CL)-CopolC1−12 and (CL)-CopolC1−12-Cl possess similar aggregate properties in aqueous solution as a result of intra- and intermolecular hydrophobic interactions between the alkyl side chains.[13,14]

Herein we report a detailed characterization of the aggregation behavior for a family of non-cross-linked and cross-linked poly(alkylmethyldiallylammonium bromides) containing decyl, octyl, and hexyl side chains (Scheme 1) in aqueous solution by fluorescence probing. The critical aggregation concentration (cac) is dependent on the alkyl

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⊗ Abstract published in *Advance ACS Abstracts,* January 1, 1996.

(1) *Polymers in Aqueous Media*; Glass, J. E., Ed.; Advances in Chemistry Series 223; American Chemical Society: Washington, DC, 1989.
(2) Dubin, P. L.; Davis, D. D. *Macromolecules* **1984**, *17*, 1294.
(3) Zdanowicz, V. S.; Strauss, U. P. *Macromolecules* **1993**, *26*, 4770.
(4) Yang, Y. J.; Engberts, J. B. F. N. *J. Org. Chem.* **1991**, *56*, 4300.
(5) Hsu, J. L.; Strauss, U. P. *J. Phys. Chem.* **1987**, *91*, 6238.
(6) Kunitake, T.; Shinkai, S.; Hirotsu, S. *J. Org. Chem.* **1977**, *42*, 306.
(7) Shinkai, S.; Hirakawa, S.; Shimomura, M.; Kunitake, T. *J. Org. Chem.* **1981**, *46*, 868.
(8) Wang, G. J.; Engberts, J. B. F. N. *J. Org. Chem.* **1994**, *59*, 4076.
(9) Wang, G. J.; Engberts, J. B. F. N. *Eur. Polym. J.* **1995**, *31*, 409.
(10) Wang, G. J.; Engberts, J. B. F. N. *J. Org. Chem.* **1995**, *60*, 4030.
(11) Wang, G. J.; Engberts, J. B. F. N. *Langmuir* **1994**, *10*, 2583.
(12) Wang, G. J.; Engberts, J. B. F. N. *Langmuir* **1995**, *11*, 3856.
(13) Wang, G. J.; Engberts, J. B. F. N. *Recl. Trav. Chim. Pays-Bas* **1994**, *113*, 390.
(14) Wang, G. J.; Engberts, J. B. F. N. *Gazz. Chim. Ital.*, in press.

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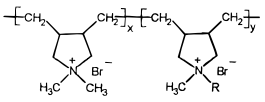
Scheme 1

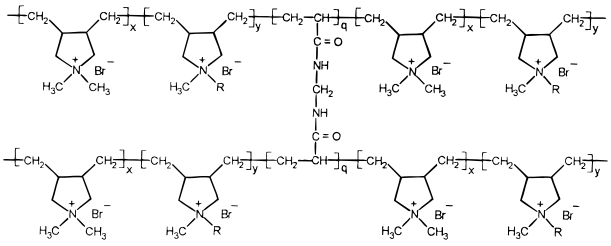


Copolymer

CopolC1-10 (R: $C_{10}H_{21}$)

CopolC1-8 (R: C_8H_{17})

CopolC1-6 (R: C_6H_{13})



Cross-linked copolymer

CL-CopolC1-10 (R: $C_{10}H_{21}$)

CL-CopolC1-8 (R: C_8H_{17})

CL-CopolC1-6 (R: C_6H_{13})

Table 1. Compositions of Poly(alkylmethyldiallylammonium bromides) Cross-Linked with a Small Amount of *N,N′*-Methylenebis(acrylamide)

copolymer	compositions of copolymer,[a] *x/y* (mol/mol)	cross-linking agent, % (w/w)
CopolC1−10(1)	89/11	0.00
CL-CopolC1−10(2)	89/11	0.20
CL-CopolC1−10(3)	88/12	0.40
CL-CopolC1−10(4)	90/10	0.80
CL-CopolC1−10(5)	79/21	0.40
CL-CopolC1−10(6)	68/32	0.40
CopolC1−8(1)	60/40	0.00
CL-CopolC1−8(2)	61/39	0.20
CL-CopolC1−8(3)	60/40	0.40
CL-CopolC1−8(4)	59/41	0.80
CL-CopolC1−8(5)	78/22	0.40
CopolC1−6(1)	60/40	0.00
CL-CopolC1−6(2)	60/40	0.20
CL-CopolC1−6(3)	61/39	0.40
CL-CopolC1−6(4)	62/38	0.80
CL-CopolC1−6(5)	80/20	0.40
CL-CopolC1−6(6)	42/58	0.40

[a] For ^{1}H-NMR, see ref 10.

chain length and the alkyl group content and is significantly influenced by the content of the cross-linking agent in the copolymers. A minimum in the cac for (CL)-CopolC1−10 in aqueous solution is observed at about 0.20% (w/w) cross-linking agent, which coincides with a maximum catalytic efficiency for the unimolecular decarboxylation of 6-NBIC in aqueous solution.[8,10]

Experimental Section

Non-Cross-Linked and Cross-Linked Copolymers and Reagents. The synthesis of the non-cross-linked and cross-linked poly(alkylmethyldiallylammonium bromides) having decyl, octyl, and hexyl side chains has been reported previously.[10] Their compositions and the nomenclature used are shown in Table 1. Aqueous solutions of the copolymers were prepared in double-distilled water. The copolymer concentrations are expressed in unit mol L^{-1}. Pyrene was the same as that used in the previous investigation.[13] Sodium bromide (Janssen) was a commercial compound of reagent grade.

Fluorescence Spectroscopy. Fluorescence spectra of pyrene solubilized in the copolymer solutions were recorded with an SLM-Aminco SPF-500 spectrophotometer equipped with a thermostated cell holder at 25 °C. The stock solution of pyrene (2.0×10^{-6} M) was made up in double-distilled water. The excitation wavelength was 335 nm. The emission spectra were recorded from 360 to 390 nm. The emission bandpass was 5 nm. The ratio I_1/I_3 of the fluorescence intensities of the first and third vibronic peaks was then calculated, which provides a measure for the polarity of the microenvironment of pyrene at binding sites in hydrophobic microdomains.

Results and Discussion

Hydrophobic Microdomains of Non-Cross-Linked and Cross-Linked Copolymers. Fluorescence probes like pyrene have been widely used to probe the microstructure of various types of hydrophobically-modified (co)-polymers and to study the interactions between polymers and conventional surfactants in aqueous solutions. The vibrational structure of the fluorescence bands of pyrene is known to be sensitive to the local polarity of the microenvironment at the binding sites.[23−25] The pyrene fluorescence spectrum in aqueous solution of polysoaps has provided particularly valuable information on the conformational state of the macromolecules in aqueous solution.[13,18] In these studies, the ratio I_1/I_3 of the intensities of the first and third vibronic peaks, which decreases with decreasing polarity of the binding sites in the polysoaps, has been taken as a sensitive indicator for the micropolarity of the pyrene microenvironment.[26−28] In the hydrophobically associating polymers the hydrophobic microdomains, like micelles formed by ordinary surfactants, provide sites for solubilization of the hydrophobic molecule pyrene causing the decrease in the ratio I_1/I_3. Such solubilization sites are absent in the polymer solutions comprised of poly(dimethyldiallylammonium bromide).[13] In order to avoid the formation of pyrene excimers, low pyrene concentrations (2.0×10^{-6} M) should be used. Relevant plots of the fluorescence ratio I_1/I_3 vs copolymer concentrations as a function of *n*-decyl group content for the polysoaps CL-CopolC1−10 are presented in Figure 1. At low concentrations, all CL-CopolC1−10 copolymers show a high I_1/I_3 similar to that in pure water, indicating that pyrene is neither associated with nor solubilized in the CL-CopolC1−10 macromolecules but is solubilized in the aqueous phase. A sudden and large decrease of the ratio I_1/I_3 is observed upon further increasing the copolymer concentration. These low I_1/I_3 values are indicative for binding of pyrene at binding sites located in a relative nonpolar microenvironment in the hydrophobic microdomains. The final magnitude of I_1/I_3 upon complete binding of pyrene to the hydrophobic microdomains decreases with an increase in the *n*-decyl group content, revealing that the micropolarity at the different binding sites is dependent on the aggregate structure of CL-CopolC1−10 in aqueous solution. The polysoap CL-CopolC1−10(6) which possesses the highest

(15) Pankasem, S.; Thomas, J. K.; Snowden, M. J.; Vincent, B. *Langmuir* **1994**, *10*, 3023.
(16) Chu, D. Y.; Thomas, J. K. *J. Am. Chem. Soc.* **1986**, *108*, 6270.
(17) Binana-Limbele, W.; Zana, R. *Macromolecules* **1987**, *20*, 1331.
(18) Binana-Limbele, W.; Zana, R. *Macromolecules* **1990**, *23*, 2731.
(19) Benrraou, M.; Zana, R.; Varoqui, R.; Pefferkorn, E. *J. Phys. Chem.* **1992**, *96*, 1468.
(20) Biggs, S.; Selb, J.; Candau, F. *Langmuir* **1992**, *8*, 838.
(21) Anthony, O.; Zana, R. *Langmuir* **1994**, *10*, 4048.
(22) Effing, J. J.; McLennan, I. J.; Kwak, J. C. T. *J. Phys. Chem.* **1994**, *98*, 2499.
(23) Abuin, E. B.; Scaiano, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 6274.
(24) Kalyanasundaram, K.; Thomas, J. K. *J. Am. Chem. Soc.* **1977**, *99*, 2039.
(25) Lianoes, P.; Lang, J.; Sturm, J.; Zana, R. *J. Phys. Chem.* **1984**, *80*, 283.
(26) Thomas, J. K. *Chem. Rev.* **1980**, *80*, 283.
(27) Yekta, A.; Aikawa, M.; Turro, N. *Chem. Phys. Lett.* **1979**, *63*, 543.
(28) Yang, Y. J.; Engberts, J. B. F. N. *Recl. Trav. Chim. Pays-Bas* **1991**, *110*, 384.

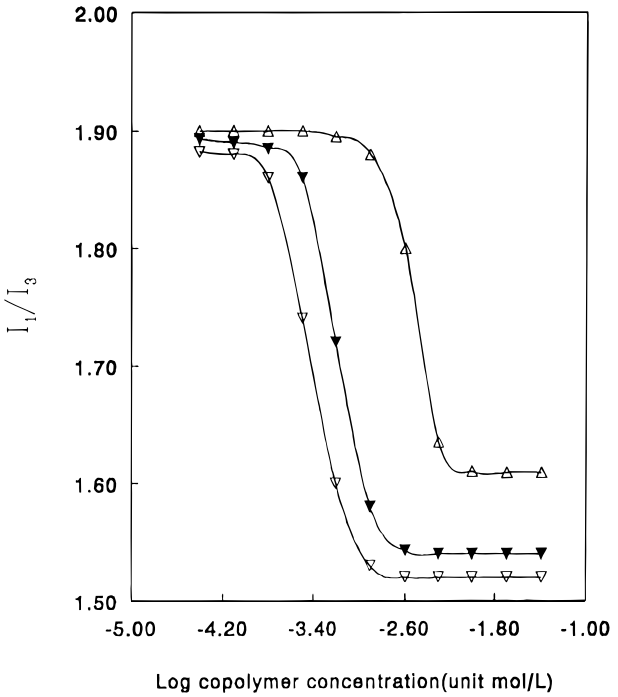


Figure 1. Effect of *n*-decyl group content on the ratio I_1/I_3 of pyrene fluorescence in aqueous solutions of CL-CopolC1−10 at 25 °C: △, CL-CopolC1−10(3); ▼, CL-CopolC1−10(5); ▽, CL-CopolC1−10(6).

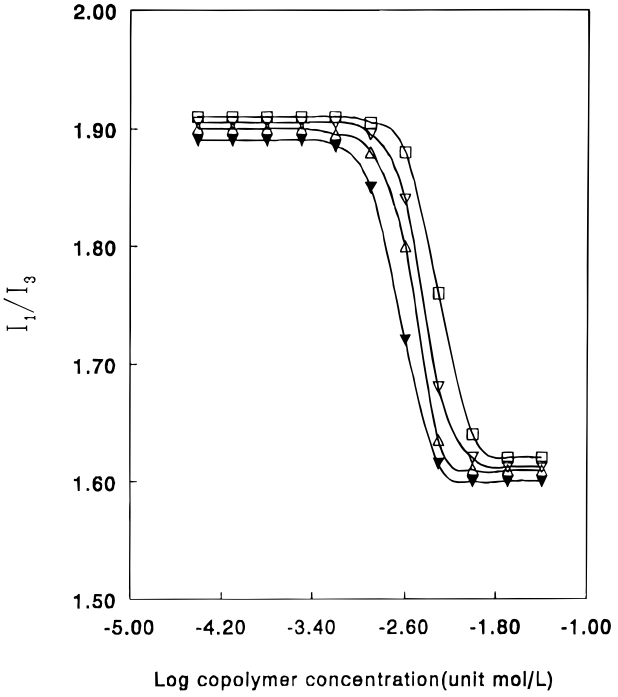


Figure 2. Effect of cross-linking agent content on the fluorescence ratio I_1/I_3 of pyrene in aqueous solutions of CL-CopolC1−10 at 25 °C: □, CL-CopolC1−10(4); ▽, CopolC1−10-(1); △, CL-CopolC1−10(3); ▼, CL-CopolC1−10(2).

number of decyl side chains provides the most hydrophobic environment for pyrene at its binding sites in aqueous solution. The intramolecular micellization of CL-CopolC1−10(3) is clearly less effective than that of CL-CopolC1−10(5) and CL-CopolC1−10(6) due to reduced hydrophobic association.

Figure 2 shows plots of the fluorescence ratio I_1/I_3 vs copolymer concentrations as a function of the cross-linking agent content for CL-CopolC1−10. Apparently, CL-CopolC1−10(2) provides the most hydrophobic environment for pyrene at its binding sites in aqueous solution as compared with that of CopolC1−10(1), CL-CopolC1−10(3), and CL-CopolC1−10(4), indicating that the presence of only a small amount of cross-linking in the macromolecules leads to most efficient intramolecular micellization. This result may be attributed to increased intramolecular hydrophobic interactions in the macromolecules for the copolymers with a small amount of cross-linking. However the aggregation tendency is counteracted by a drastically reduced macromolecular flexibility in the case of excessively cross-linked copolymers leading to less efficient intra- and intermolecular aggregation. It is noted that the shape of the curves for all the polysoaps (CL)-CopolC1−10 (Figures 1 and 2) is practically the same, indicative for similar cooperativities in the formation of intra- and intermolecular aggregates in these systems.

Table 2. The cac and ΔG_A for Non-Cross-Linked and Cross-Linked Polysoaps in Aqueous Solution at 25 °C

polysoap	cac,[a] M	ΔG_A,[b] kcal mol^{-1}
CopolC1−10(1)	6.76×10^{-3}	−2.96
CL-CopolC1−10(2)	4.16×10^{-3}	−3.25
CL-CopolC1−10(3)	5.37×10^{-3}	−3.09
CL-CopolC1−10(4)	1.02×10^{-2}	−2.72
CL-CopolC1−10(5)	1.45×10^{-3}	−3.87
CL-CopolC1−10(6)	8.32×10^{-4}	−4.20

[a] cac, the critical aggregate concentration of polysoaps in aqueous solution, see text. [b] Gibbs energy for microdomain formation calculated from $\Delta G_A = RT$ ln(cac), $T = 298$ K.

The plots of the fluorescence ratio I_1/I_3 vs copolymer concentration represent binding isotherms of pyrene to the hydrophobic microdomains for the non-cross-linked and cross-linked copolymers.[13] The data given in Figure 1 and Figure 2 are rationalized by assuming that pyrene is completely solubilized in hydrophobic regions formed by the aggregates of non-cross-linked and cross-linked copolymers at concentrations above the cac. On the basis of this approach, the cac and the calculated ΔG_A, the change in Gibbs energy involved in the formation of the compact coil conformation, are presented in Table 2. The Gibbs energy change for the transfer of 1 mol of polysoap from solution to the aggregated phase, ΔG_A, is given by $\Delta G_A = RT$ ln(cac). The absolute value of ΔG_A for CL-CopolC1−10(6) is the largest, indicating a greater driving force for intramolecular and intermolecular aggregation than that for the other copolymers.

The fluorescence probing results for (CL)-CopolC1−8 in aqueous solution as a function of copolymer concentration are shown in Figure 3. At quite high copolymer concentrations, only a modest decrease of the fluorescence ratio I_1/I_3 is observed and no steady value in the ratio I_1/I_3 is reached in the concentration range investigated. The pyrene experiences only a modest hydrophobic environment in aqueous solutions of (CL)-CopolC1−8, indicating that no extensive hydrophobic microdomains are formed in aqueous solution. Figure 4 shows similar data for (CL)-CopolC1−6 in aqueous solution as a function of copolymer concentration. There is clearly no sharp transition in the ratio I_1/I_3 at a critical copolymer concentration as observed in the case of (CL)-CopolC1−10. Only weakly cooperative and small decreases in the ratio I_1/I_3 are observed, indicative of the absence of significant intramolecular micelle formation. Table 3 summarizes the results of the fluorescence experiments, and the ratio I_1/I_3 of pyrene at high copolymer concentrations is given for all (CL)-CopolC1−10, (CL)-CopolC1−8, and (CL)-CopolC1−6 macromolecules in aqueous solution. We contend that in the series of non-cross-linked and cross-linked copolymers solely (CL)-CopolC1−10 with sufficient *n*-decyl side chains

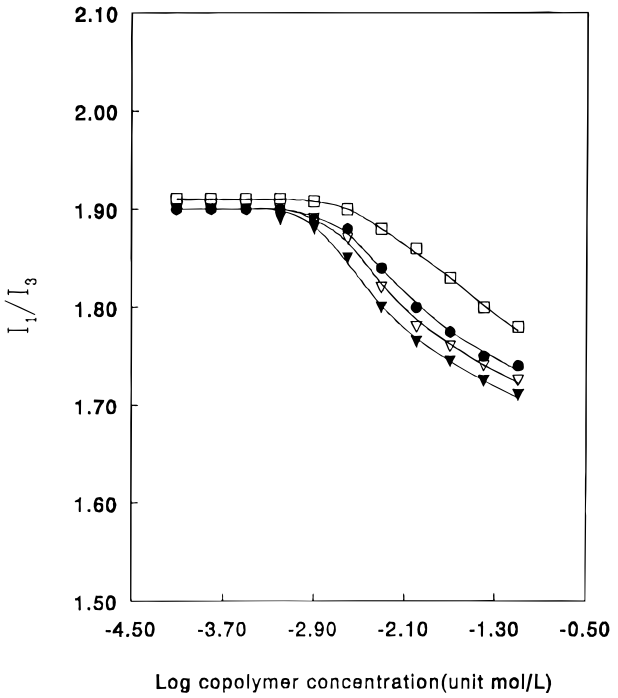


Figure 3. Intensity ratio I_1/I_3 of pyrene fluorescence in aqueous solution in the presence of CL-CopolC1−8 as a function of concentration at 25 °C: □, CL-CopolC1−8(5); ●, CL-CopolC1−8(4); ▽, CopolC1−8(1); ▼, CL-CopolC1−8(2).

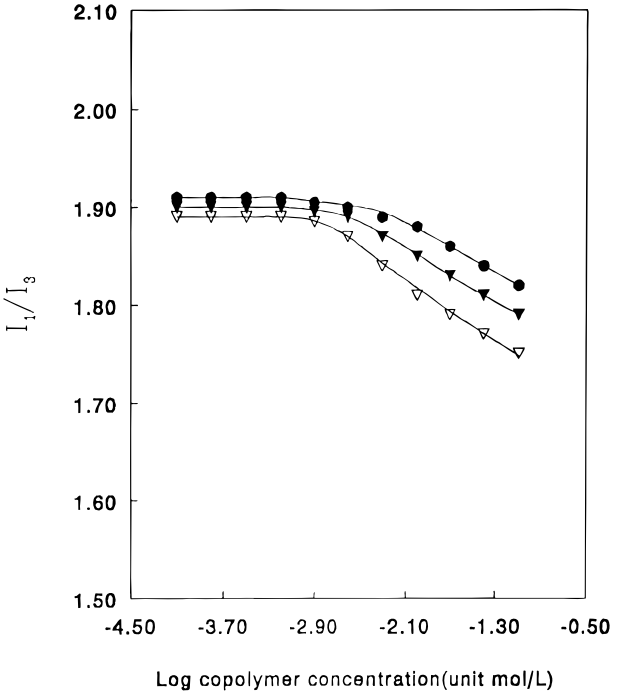


Figure 4. Intensity ratio I_1/I_3 of pyrene flurescence in aqueous solution in the presence of CL-CopolC1−6 as a function of concentration at 25 °C: ●, CL-CopolC1−6(5); ▼, CL-CopolC1−6(3); ▽, CL-CopolC1−6(6).

efficiently forms hydrophobic microdomains in compact coil conformations in aqueous solution. This conclusion is consistent with previous UV spectroscopic and kinetic results.[10]

The conformational state of (CL)-CopolC1−10 in aqueous solution is also influenced by the ionic strength. A typical experimental result is presented in Figure 5, which shows the effect of added sodium bromide on the fluorescence ratio I_1/I_3 of pyrene in aqueous solutions of CL-CopolC1−10(5). The variation of the initial plateau value

Table 3. Pyrene Fluorescence in Aqueous Solutions of the Non-Cross-Linked and Cross-Linked Copolymers at 25 °C

copolymer	concentration (unit mol/L)	I_1/I_3[a]
CopolC1−10(1)	2.0×10^{-2}	1.61
CL-CopolC1−10(2)	2.0×10^{-2}	1.60
CL-CopolC1−10(3)	2.0×10^{-2}	1.61
CL-CopolC1−10(4)	2.0×10^{-2}	1.62
CL-CopolC1−10(5)	2.0×10^{-2}	1.54
CL-CopolC1−10(6)	2.0×10^{-2}	1.52
CopolC1−8(1)	4.0×10^{-2}	1.74
CL-CopolC1−8(2)	4.0×10^{-2}	1.73
CL-CopolC1−8(3)	4.0×10^{-2}	1.73
CL-CopolC1−8(4)	4.0×10^{-2}	1.75
CL-CopolC1−8(5)	4.0×10^{-2}	1.80
CopolC1−6(1)	8.0×10^{-2}	1.81
CL-CopolC1−6(2)	8.0×10^{-2}	1.81
CL-CopolC1−6(3)	8.0×10^{-2}	1.79
CL-CopolC1−6(4)	8.0×10^{-2}	1.80
CL-CopolC1−6(5)	8.0×10^{-2}	1.82
CL-CopolC1−6(6)	8.0×10^{-2}	1.75

[a] Pyrene, 2.0×10^{-6} M.

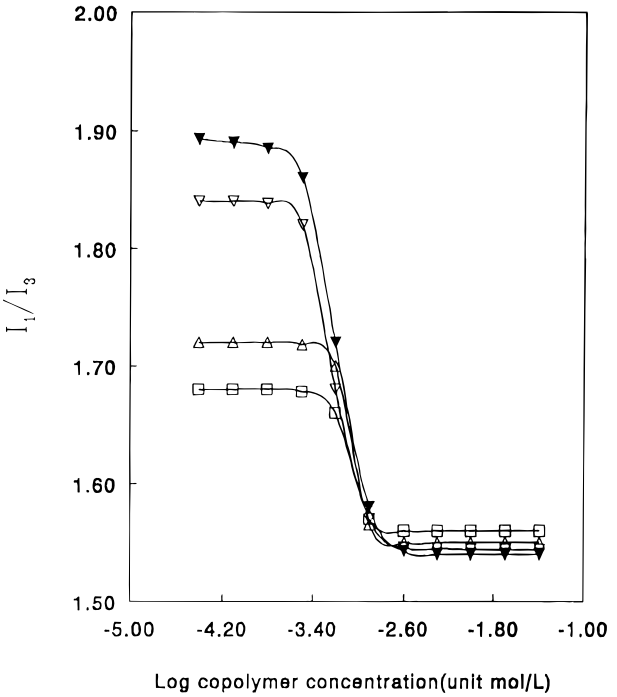


Figure 5. Effect of various concentrations of sodium bromide on the fluorescence ratio I_1/I_3 of pyrene in aqueous solution of CL-CopolC1−10(5) as a function of polysoap concentration at 25 °C: ▼, in the absence of NaBr; ▽, in the presence of 0.01 M NaBr; △, in the presence of 0.1 M NaBr; □, in the presence of 1.0 M NaBr.

of I_1/I_3 before a rapid decrease sets in is particularly instructive. This plateau value in the presence of small concentrations of sodium bromide is close to that found in pure water but is significantly decreased with increasing concentration of sodium bromide at low copolymer concentration. Apparently, CL-CopolC1−10(5) provides a more hydrophobic microenvironment for pyrene binding in the presence of sodium bromide. This may be explained by assuming that addition of sodium bromide causes contraction of the expanded macromolecules at low concentrations by suppression of Coulombic repulsions between the ionic groups,[29,30] which facilitates the in-

(29) Strauss, U. P.; Gershfeld, N. L.; Crook, E. H. *J. Phys. Chem.* **1956**, *60*. 577.
(30) Dubin, P. L.; Strauss, U. P. *J. Phys. Chem.* **1970**, *74*, 2842.

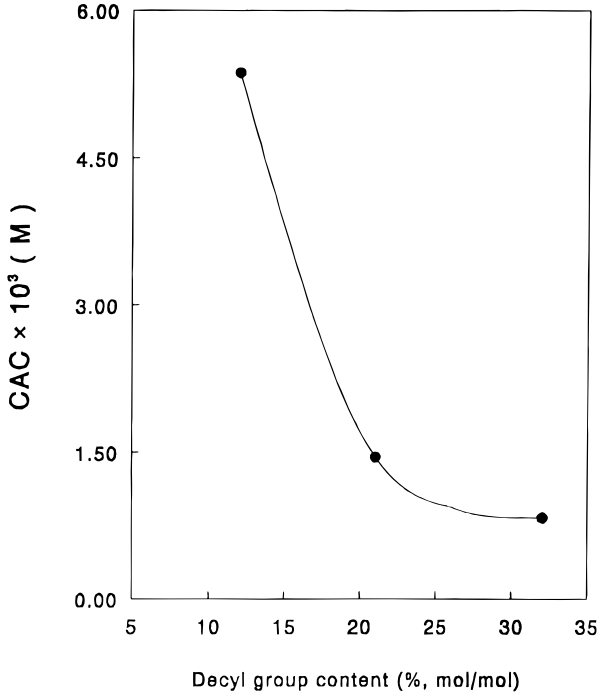


Figure 6. Effect of *n*-decyl group content on the cac for CL-CopolC1−10 containing 0.40% (w/w) of cross-linking agent in aqueous solution at 25 °C.

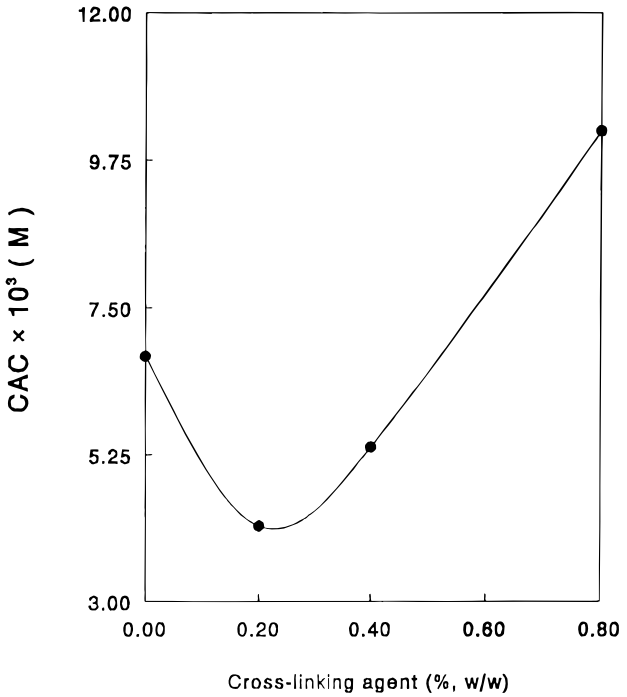


Figure 7. Effect of cross-linking agent content on the cac for (CL)-CopolC1−10 (*x*/*y*, 89/11) in aqueous solution at 25 °C.

tramolecular aggregation of *n*-decyl side chains. Aqueous solutions of CL-CopolC1−10(5) at concentrations above 1.0×10^{-3} unit mol L^{-1} become turbid when the sodium bromide is increased beyond 1.0 mol L^{-1}. The small changes in the fluorescence ratio I_1/I_3 of pyrene at higher concentrations of CL-CopolC1−10(5) probably indicate that pyrene binds into the interior of the microdomains where the fluorescence spectrum of the probe is hardly influenced by the presence of added electrolytes.[13,14]

Critical Aggregation Concentration of Non-Cross-Linked and Cross-Linked Copolymers. In aqueous solutions of (CL)-CopolC1−10, there is a sharp decrease in the fluorescence ratio I_1/I_3 of pyrene over a narrow range of copolymer concentrations (Figure 1 and Figure 2). The ratio I_1/I_3 in copolymer solutions reaches a steady value at a copolymer concentration which may be termed the critical aggregate concentration (cac).[13,16] At the cac, the hydrophobic microdomains in aqueous solutions of polysoaps are fully formed and completely bind strongly hydrophobic cosolutes such as pyrene. (CL)-CopolC1−8 and (CL)-CopolC1−6 exhibit no steady I_1/I_3 value with increasing copolymer concentration owing to the absence of efficient formation of hydrophobic microdomains in aqueous solution. Therefore, in this case, the cac cannot be obtained from the fluorescence spectroscopic results. Figure 6 shows a plot of the cac for CL-CopolC1−10 in aqueous solution vs the *n*-decyl group content. As anticipated for hydrophobic interactions being the main driving force for the formation of the hydrophobic domains, the cac decreases strongly with increasing *n*-decyl group content. CL-CopolC1−10(6) shows the lowest cac as a result of largest total hydrophobicity of the *n*-decyl side chains in the macromolecules. Figure 7 shows the cac plotted against the content of cross-linking agent for (CL)-CopolC1−10 in aqueous solution. The results reveal that the cross-linking agent content significantly affects the cac for (CL)-CopolC1−10 in aqueous solution. A minimum of the cac for (CL)-CopolC1−10 was observed at about 0.20% (w/w) cross-linking agent content, which is consistent with the observed maximum in catalytic efficiency for the unimolecular decarboxylation of 6-NBIC by CL-CopolC1−10 in aqueous solution.[8,10] This pleasing consistency provides strong evidence that the presence of a small amount of cross-linking in (CL)-CopolC1−10 leads to more efficient intramolecular micellization in aqueous solution.

Conclusions

The present work reports detailed fluorescence studies on aggregate behavior of a series of non-cross-linked and cross-linked poly(alkylmethyldiallylammonium bromides) having decyl, octyl, and hexyl side chains ((CL)-CopolC1−10, (CL)-CopolC1−8, and (CL)-CopolC1−6, respectively) in aqueous solutions using pyrene as a probe. The conformational transition of the copolymers to compact coils is strongly dependent on the alkyl side chain length. (CL)-CopolC1−10 with sufficient *n*-decyl side chains forms hydrophobic microdomains in compact coil conformations in aqueous solution. (CL)-CopolC1−8 exhibits much less efficient intramolecular micellization. No conformational transition to compact coils is observed for (CL)-CopolC1−6 in aqueous solution. The critical aggregation concentration (cac) clearly depends on the number and length of the macromolecular chains. The cac for (CL)-CopolC1−10 in aqueous solution decreases strongly with increasing total hydrophobicity of the *n*-decyl side chains in the macromolecules. The cross-linking agent was also found to affect significantly the cac of (CL)-CopolC1−10 and a minimum of the cac for (CL)-CopolC1−10 in aqueous solution was observed at about 0.20% (w/w) cross-linking agent.

Acknowledgment. Financial support from the Netherlands Technology Foundation (STW) is gratefully acknowledged.

LA9504873