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Synthesis and Catalytic Properties of Cross-Linked Hydrophobically Associating Poly(alkylmethyldiallylammonium bromides)

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Cross-linked, hydrophobically associating homo- and copolymers were synthesized by free-radical cyclo(co)polymerization of alkylmethyldiallylammonium bromide monomers with a small amount of *N*,*N*′-methylenebisacrylamide in aqueous solution using ammonium persulfate as the initiator. The cross-linked homo- and copolymers showed a increase of their reduced viscosity in water and intrinsic viscosity in 1.0 M sodium chloride solutions upon the controlled introduction of cross-linking *N*,*N*′-methylenebisacrylamide into their chemical structure. Depending on the hydrophobic group content of the cross-linked copolymers, a conformational transition was revealed by viscosity measurements which is accounted for by intramolecular micelle formation and intermolecular aggregation. The hydrophobic microdomains of the cross-linked polysoaps were characterized by hypsochromic shifts of the long-wavelength absorption band of methyl orange as a solvatochromic probe, noncovalently bound to the macromolecule. Catalysis of the unimolecular decarboxylation of 6-nitrobenzisoxazole-3-carboxylate by the cross-linked copolymers was investigated in aqueous solution at pH 11.3 and 30 °C. The cross-linked polysoaps exhibited higher catalytic activities for decarboxylation than the corresponding non-cross-linked copolymer analogues. A maximum in rate constant was found at about 0.2% (w/w) of cross-linking agent in the cross-linked copolymers.

Substantial interest has developed in synthetic, hydrophobically modified polyelectrolytes both as models for enzymic catalysis[1–6] and for potential practical applications.[7,8] In aqueous solution, polyelectrolytes with sufficiently hydrophobic alkyl side chains (polysoaps) retain many of the properties of polymers from which they are derived but the physical–chemical behavior is considerably modified by the presence of the hydrophobic side chains. Hydrophobic interactions between side chains cause contractions in the molecular dimensions due to aggregate formation,[9,10] which may be termed intramolecular micellization. Like micelles formed by ordinary surfactants, these intramolecular microdomains solubilize normally water-insoluble organic molecules.[10,11] Polysoap-catalyzed reactions may mimic reactions occurring on biological membranes and may serve as models for electrostatic and hydrophobic interactions in biological binding processes.[1,3,5,6] The hydrophobic microdomains efficiently catalyze reactions such as the unimolecular decarboxylation of 6-nitrobenzisoxazole-3-carboxylate anion (6-NBIC).[3,5,6,] A major factor determining the rate acceleration may be partial dehydration of the carboxylate function of the initial state.[12]

In the present study, we report the synthesis of a series of novel cross-linked homo- and copolymers by cyclo(co)polymerization of alkylmethyldiallylammonium bromides in which the alkyl group is methyl and *n*-dodecyl and cross-linked with a small amount of *N*,*N*′-methylenebisacrylamide. Viscosity measurements provide direct evidence for the formation of the hydrophobic aggregates in aqueous solutions. The conformational transitions of the cross-linked polysoaps are strongly dependent upon the dodecyl group content. Pseudo-first-order rate constants for the decarboxylation of 6-NBIC catalyzed by cross-linked polysoaps were determined as a function of the detailed structure of the polysoap. The decarboxylation of 6-NBIC is markedly influenced by both the dodecyl group content and the percentage of cross-linking in the polysoaps, indicating that the catalysis is sensitive to changes in the intramolecular aggregate structure.

Experimental Section

Materials and Monomers. Methyldiallylamine was prepared according to the procedure reported in the literature.[13] Dimethyldiallylammonium bromide was synthesized from methyldiallylamine (2 M solution in freshly distilled diethyl ether) and a small excess of liquefied methyl bromide (Fluka) at room temperature by a standard procedure.[14] *n*-Dodecylmethyldiallylammonium bromide was obtained using a similar procedure by reaction of methyldiallylamine (2.5 M solution in distilled acetone) with 1 equiv of distilled *n*-dodecyl bromide (Janssen) at 60 °C. After evaporation of the solvent under reduced pressure, the product was dissolved in deionized water, extracted several times with diethyl ether, and finally freeze-dried for at least 2 days. Methyl orange (Aldrich) was used as received.

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Dimethyldiallylammonium Bromide (DIMDABr) (1): Reaction time 1 day; yield 96%; hygroscopic solid; ^{1}H NMR δ 2.90 (s, 6H), 3.80−3.85 (d, 4H), 5.55−5.65 (m, 4H), 5.85−6.05 (m, 2H) ppm. Analysis: calculated for $C_8H_{16}NBr$ C, 46.62; H, 7.82; N, 6.80; Br, 38.76. Found C, 46.47; H, 7.80; N, 6.77; Br, 38.84.

***n*-Dodecylmethyldiallylammonium Bromide (DMDAABr)[3] (2):** Reaction time 4 days; yield 86%; waxlike solid. Analysis: calculated for $C_{19}H_{38}NBr$ C, 63.32; H, 10.63; N, 3.89; Br, 22.17. Found C, 63.43; H, 10.49; N, 3.86; Br, 22.14.

Cross-Linking (Co)polymerizations. The monomers and deionized water (50%, w/w) were added to a flask equipped with a magnetic stirrer and a nitrogen inlet and outlet. After the monomers were completely dissolved, the monomer solutions were polymerized in the presence of a small amount of *N,N'*-methylenebisacrylamide using commercial grade ammonium persulfate as the initiator at 60 °C under nitrogen. In the cross-linking polymerizations the monomer ratio and content of cross-linking agent were varied. Non-cross-linked (co)polymers were also synthesized under similar polymerization conditions. The obtained reaction mixtures were dialyzed against deionized water using dialysis tubes (Servapore dialysis tubing 29 mm) for 72 h at room temperature. The polymer solutions were subsequently freeze-dried for at least 3 days. The obtained cross-linked (co)polymers were characterized by their IR and ^{1}H NMR spectra. These spectra showed that there are no C=C double bond absorption bands and resonances, respectively, in these products. The ^{1}H NMR spectra were in agreement with those reported in the literature for structurally related polymers.[3,15]

Cross-Linked Poly(dimethyldiallylammonium bromide) (CL-PolC-1): White amorphous solid: ^{1}H NMR δ 1.15 (CH_2), 1.40 (CH_2), 2.10 (CH (ring, trans)), 2.55 (CH (ring, cis)), 3.00−3.20 (CH_3(N), CH_2(N), CH_2 (ring, cis/trans)), 3.65 (CH_2(ring, cis/trans)) ppm.

Cross-Linked Poly(dimethyldiallylammonium-*co*-*n*-dodecylmethyldiallylammonium dibromide) (CL-CopolC1−12): White amorphous solid; ^{1}H NMR δ 0.75 (CH_3), 1.20 (CH_2), 1.45 (CH_2), 2.15 (CH (ring, trans)), 2.60 (CH (ring, cis)), 3.05−3.30 (CH_3(N), CH_2(N), CH_2 (ring, cis/trans)), 3.70 (CH_2(ring, cis/trans)) ppm.

All the CL-CopolC1−12 macromolecules reported in Table 1 showed the same ^{1}H NMR resonances but exhibit small differences in integrations. The molecular weights of the cross-linked copolymers are believed to be not very different from the cross-linked homopolymer on the basis of the same polymerization conditions.

IR and ^{1}H NMR Measurements. The infrared spectra of the cross-linked and non-cross-linked (co)polymers were measured with a Perkin-Elmer 841 infrared spectrophotometer in a KBr disk. ^{1}H -NMR spectra of the monomers and all water-soluble polymers were taken on a VXR 300 MHz instrument using TMS as an external reference. All NMR spectra were taken in D_2O except for methyldiallylamine which was taken in $CDCl_3$.

Viscosity Measurements. The reduced viscosities of aqueous solutions of polysoaps were measured in a capillary viscometer of the Ubbelohde type (Scott AVS 400 viscosimeter) in a constant temperature bath at 30 °C. The intrinsic viscosities were determined in 1.0 M sodium chloride solutions. Constant values of the reduced viscosities (dL/g) were obtained for polymer concentrations between 0.0625 and 1.00 g/dL. The following values were found: PolC-1(3), 0.20; CL-PolC-1(4), 0.36; CopolC1-12(8), 0.12; CL-CopolC1-12(9), 0.17; CL-CopolC1-12(10), 0.21; CL-CopolC1-12(11), 0.28; CL-CopolC1-12(12), 0.32; CL-CopolC1-12(16), 0.31; Cl-CopolC1-12(17), 0.18; CL-CopolC1-12(18), 0.16. Apparently the intrinsic viscosities for the different polymers coincide with these values. All polymer solutions were made up in double-distilled water.

UV−Vis Spectral Measurements. UV−vis absorption spectra of methyl orange were recorded on a Philips PU 8740 UV/vis scanning spectrophotometer in the presence of cross-linked copolymers at 30 °C in aqueous solutions adjusted to pH 9.4 with a 0.02 M sodium borate buffer. The solution of methyl orange (2.5 × 10^{-5} M) was prepared with double-distilled water.

Kinetic Experiments. Fresh stock solutions of 6-nitrobenzisoxazole-3-carboxylate anion (6-NBIC) for kinetic measurements were prepared in methanol. The reaction was initiated by mixing of 2.5 mL of the aqueous solutions of cross-linked copolymers at pH 11.3 in 0.002 M NaOH with 5 μL of the prepared stock solution of 6-NBIC (1.8 × 10^{-1} M) in the thermostated cell. All reactions were followed spectrophotometrically at 410 nm using a Perkin-Elmer λ2 spectrophotometer equipped with a data station. The first-order rate constants (± 1%) for unimolecular decarboxylation of 6-NBIC were determined from measurements for at least six half-lives at 30 ± 0.1 °C.

Results and Discussion

Synthesis. The synthesis of cross-linked (co)polymers by free-radical cyclo(co)polymerization of alkylmethyldiallylammonium bromide with a small amount of *N,N'*-methylenebisacrylamide using ammonium persulfate as initiator in aqueous solution is depicted in Scheme 1. The results are summarized in Table 1. As anticipated, the water solubility of the cross-linked (co)polymers is strongly influenced by the content of the cross-linking agent. Solubility in water was restricted to (co)polymers for which the content of the cross-linking agent is in the range of 0.10−0.80% (w/w). The cross-linked (co)polymers formed a polymer gel in aqueous solution when the cross-linking agent content exceeded 1.0% (w/w) (see Table 1). These materials are strongly hygroscopic and therefore the absorption bands of water at 3440, 2080, and 1640 cm^{-1} could not be eliminated in their IR spectra. In contrast with the infrared spectra of PolC-1(3) and CopolC1−12(8), the polysoaps CL-PolC-1(4) to CL-PolC-1(7) and CL-CopolC1−12(10) to CL-CopolC1−12(18) showed a marked NH absorption band at 1530 cm^{-1} and the strength of the NH absorption band increased with an increase of the cross-linking agent content. The macromolecules contain monomer units with 5-membered rings cross-linked with *N,N'*-methylenebisacrylamide on the basis of their ^{1}H NMR spectroscopic data.[3,15−17] The cross-linked copolymer compositions, which are presumed to be random, were obtained from their ^{1}H NMR spectra by careful integration of relevant peaks.[18] The results for all water-soluble cross-linked copolymers are presented in Table 2. The compositions of these cross-linked copolymers (*x*/*y*) are in good agreement with the feed ratio of monomers in the polymerization reactions.

Viscosity Behavior of Cross-Linked Polysoaps. The reduced viscosities for PolC-1(3), CL-PolC-1(4), CopolC1−12(8), and CL-CopolC1−12(11) in aqueous solutions are plotted in Figure 1 as a function of concentration. They show that the reduced viscosity in aqueous solution increases with decreasing concentration, instead of decreasing linearly to a limiting value. The cross-linked (co)polymers (CL-PolC-1(4) and CL-CopolC1−12(11)) exhibited larger reduced viscosities than non-cross-linked (co)polymer analogues (PolC-1(3) and CopolC1−12(8)). CL-CopolC1−12(11) and CopolC1−12(8) showed lower reduced viscosities in aqueous solution than CL-PolC-1(4) and PolC-1(3), respectively. These results may

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Scheme 1

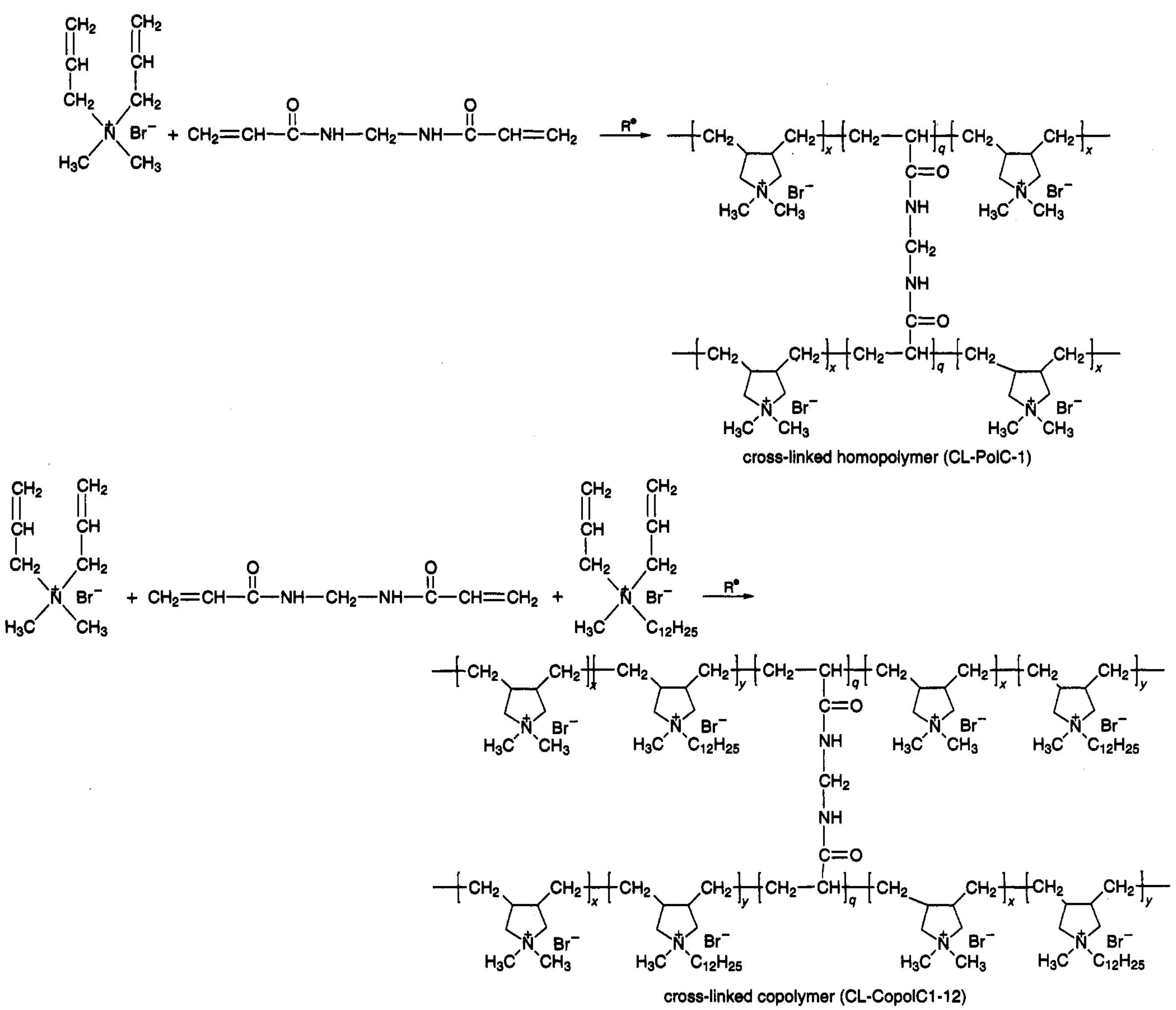

Table 1. Cyclo(co)polymerization of Alkylmethyldiallylammonium Bromide in Aqueous Solution

polymers	DIMDABr[a] (mol)	DMDAABr[b] (mol)	*N,N'*-MbisAM[c] (%, w/w)	APS[d] (mg)	polymerization time (h)	yield (%)	water solubility
PolC-1(3)	0.018	0.000	0.00	74	72	51	soluble
CL-PolC-1(4)	0.018	0.000	0.40	74	72	58	soluble
CL-PolC-1(5)	0.018	0.000	1.00	74	3.0	50	gel
CL-PolC-1(6)	0.018	0.000	2.00	74	1.0	46	gel
CL-PolC-1(7)	0.014	0.000	4.00	58	1.0	37	gel
CopolC1−12(8)	0.018	0.002	0.00	88	72	32	soluble
CL-CopolC1−12(9)	0.018	0.002	0.10	88	72	57	soluble
CL-CopolC1−12(10)	0.018	0.002	0.20	88	72	48	soluble
CL-CopolC1−12(11)	0.018	0.002	0.40	88	72	53	soluble
CL-CopolC1−12(12)	0.018	0.002	0.80	88	72	49	soluble
CL-CopolC1−12(13)	0.018	0.002	1.00	88	18	43	gel
CL-CopolC1−12(14)	0.018	0.002	2.00	88	1.0	40	gel
CL-CopolC1−12(15)	0.018	0.002	4.00	88	0.5	35	gel
CL-CopolC1−12(16)	0.019	0.001	0.40	85	72	44	soluble
CL-CopolC1−12(17)	0.017	0.003	0.40	90	72	41	soluble
CL-CopolC1−12(18)	0.016	0.004	0.40	92	72	45	soluble

[a] Dimethyldiallylammonium bromide. [b] *n*-Dodecylmethyldiallylammonium bromide. [c] *N,N'*-Methylenebisacrylamide. [d] Ammonium persulfate.

be attributed to a conformational transition from polyelectrolyte to polymer micelle.[19-21] The plateaus of the CL-CopolC1−12(11) and CopolC1−12(8) curves may be the result of a competition between intra- and intermolecular micelle formation leading to, respectively, a decrease and an increase in reduced viscosity. In the presence of 1.0 M sodium chloride solution, the cross-

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Table 2. Compositions of Water-Soluble Cross-Linked Copolymers Based on ^{1}H NMR

	feed ratio (%, mol/mol)		found (%, mol/mol)	
copolymers	*n*	*m*	*x*	*y*
CopolC1−12(8)	90	10	88	12
CL-CopolC1−12(9)	90	10	89	11
CL-CopolC1−12(10)	90	10	90	10
CL-CopolC1−12(11)	90	10	90	10
CL-CopolC1−12(12)	90	10	89	11
CL-CopolC1−12(16)	95	5	96	4
CL-CopolC1−12(17)	85	15	84	16
CL-CopolC1−12(18)	80	20	78	22

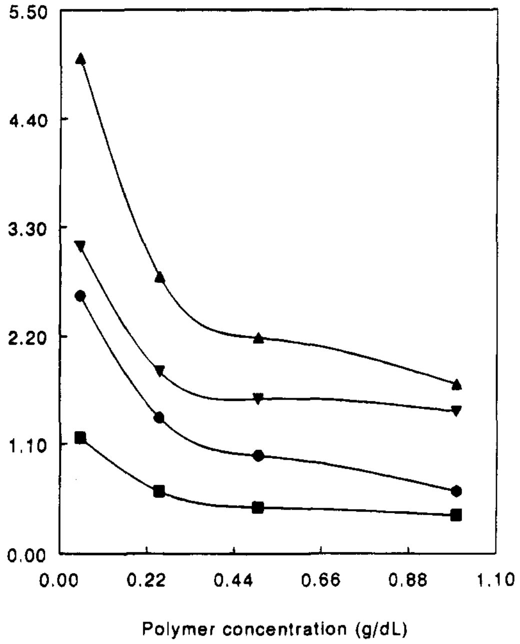

Figure 1. Reduced viscosities (η_{sp}/c) of non-cross-linked and cross-linked (co)polymers in aqueous solution at 30 °C: (▲) CL-PolC-1(4), (▼) CL-CopolC1−12(11), (●) PolC-1(3), (■) CopolC1−12(8).

linked (co)polymer solutions underwent a rather large decrease in reduced viscosity and a normal, linear reduced viscosity plot was obtained (see Experimental Section). Figure 2 shows the effect of cross-linking agent content on the intrinsic viscosity of cross-linked (co)polymers. These data show that intrinsic viscosities for water-soluble cross-linked copolymers with a constant dodecyl group content are largely increased when the content of cross-linking agent is enhanced. The effect of the dodecyl group content on the intrinsic viscosity of cross-linked (co)polymers with a constant content of cross-linking agent is illustrated graphically in Figure 3. A strong decrease in intrinsic viscosity occurs when the dodecyl group content is increased due to the formation of compact coils. The drastic changes in intrinsic viscosity indicate that the conformational transition of cross-linked copolymers is strongly dependent upon the dodecyl group content.

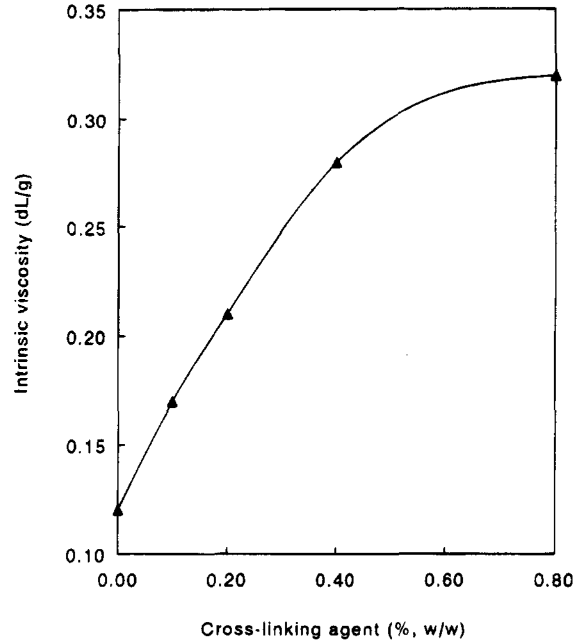

Figure 2. Effect of cross-linking agent content on the intrinsic viscosity (η) of CL-CopolC1−12 (x/y, 90/10) in 1.0 M sodium chloride solution at 30 °C.

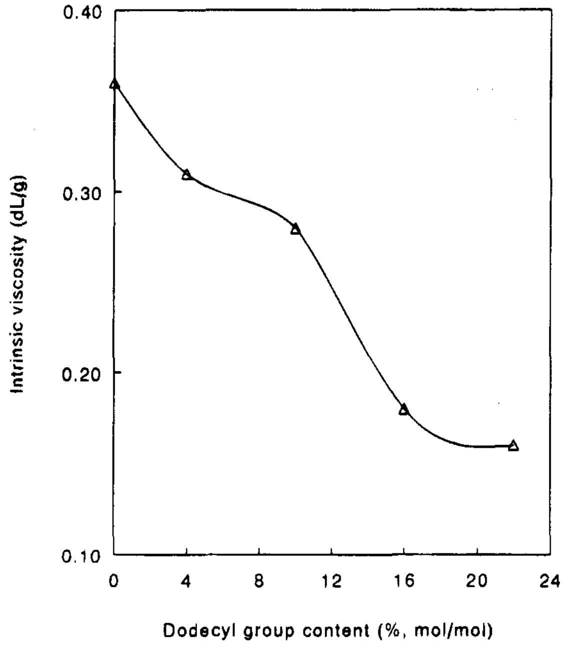

Figure 3. Effect of dodecyl group content on the intrinsic viscosity (η) of CL-CopolC1−12 containing 0.40% (w/w) of cross-linking agent in 1.0 M NaCl solution at 30 °C.

Binding of Methyl Orange to Compact Coils Formed by Cross-Linked Polysoaps. The position of the long-wavelength absorption maximum of methyl orange[3,5,9,22] in aqueous solution has been determined in the presence of cross-linked (co)polymers at pH 9.4 and 30 °C (Figure 4 and Table 3). Methyl orange (2.5×10^{-5} M) shows a λ_{max} at 462.5 nm in aqueous 0.02 M sodium borate buffer solutions (pH 9.4) at 30 °C. The hypsochromic shifts (Table 3) reveal the binding of methyl orange at hydrophobic binding sites in the presence of cross-linked copolymers. Electrostatic interactions may also contribute to the overall binding process. The data refer to relatively high polysoap concentrations where the formation of hydrophobic microdomains is not induced by the presence of the dye.[9] The water-soluble cross-linked copolymers exhibit considerable spectral shifts (except for CL-PolC-1(4)) and the spectral shifts increase with an increasing dodecyl group content. However, the spectral shifts are weakly sensitive to the differences in cross-linking. The data given in Table 3 indicate that

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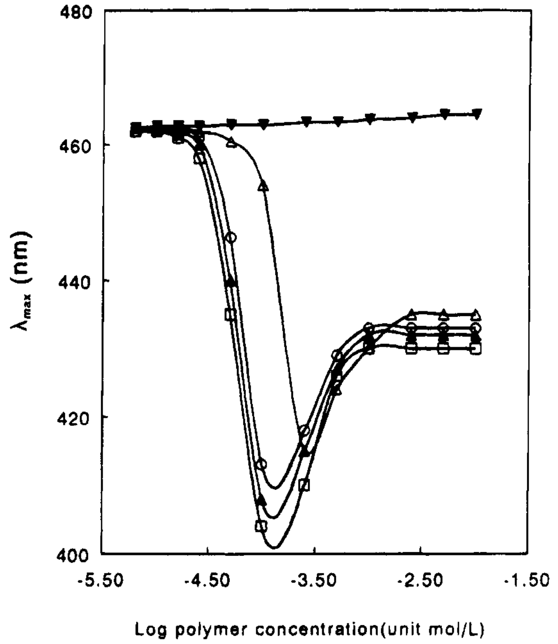


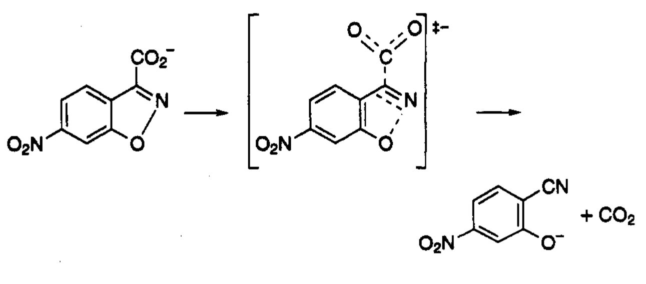
Figure 4. Position of the long-wavelength absorption maximum of methyl orange in aqueous solutions in the presence of cross-linked (co)polymers at pH 9.4 and 30 °C: (▼) CL-PolC-1(4), (△) CL-CopolC1−12(16), (○) CL-CopolC1−12(12), (▲) CL-CopolC1−12(11), (□) CL-CopolC1−12(18).

Table 3. Position of the Long-Wavelength Absorption Maximum of Methyl Orange in Aqueous Solution of Cross-Linked (Co)polymers at pH 9.4 and 30 °C

polymers	concentration (unit mol/L)	λ_{max}[a] (±1) (nm)
PolC-1(3)	2.5×10^{-3}	464
CL-PolC-1(4)	2.5×10^{-3}	464
CopolC1−12(8)	2.0×10^{-3}	432
CL-CopolC1−12(9)	2.1×10^{-3}	432
CL-CopolC1−12(10)	2.2×10^{-3}	431
CL-CopolC1−12(11)	2.2×10^{-3}	432
CL-CopolC1−12(12)	2.1×10^{-3}	433
CL-CopolC1−12(16)	2.4×10^{-3}	435
CL-CopolC1−12(17)	1.0×10^{-2}	430
CL-CopolC1−12(18)	3.0×10^{-2}	430

[a] Methyl orange, 2.5×10^{-5} M; λ_{max} 462.5 in aqueous solution at pH 9.4 and 30 °C.

Scheme 2



only the cross-linked copolymers with sufficient *n*-dodecyl side chains form hydrophobic microdomains in a compact coil conformation.

Catalysis of the Decarboxylation of 6-NBIC by the Cross-Linked Polysoaps. The unimolecular decarboxylation of 6-nitrobenzisoxazole-3-carboxylate anion (6-NBIC, Scheme 2) is extremely slow in an aqueous solution ($k_w = 7.35 \times 10^{-6}$ s^{-1}),[23] and the reaction rate depends greatly on the reaction medium.[24-28] The decarboxylation of 6-NBIC has been extensively used to investigate the microenvironment at binding sites for micellar and vesicular pseudophases[23,25,29] and hydrophobic microdomains in polymer solutions.[3,5,6,30] We have studied the unimolecular decarboxylation of 6-NBIC in the presence of cross-linked (co)polymers in aqueous solution at pH 11.3 and 30 °C. The data given in Figure 5 show that all cross-linked copolymers are very efficient catalysts for decarboxylation of 6-NBIC in aqueous solution. Catalysis by the cross-linked copolymers with a high dodecyl group content exhibits a rapid enhancement of the first-order rate constants (k_d) at low concentrations of polysoap, followed by gradual leveling off with

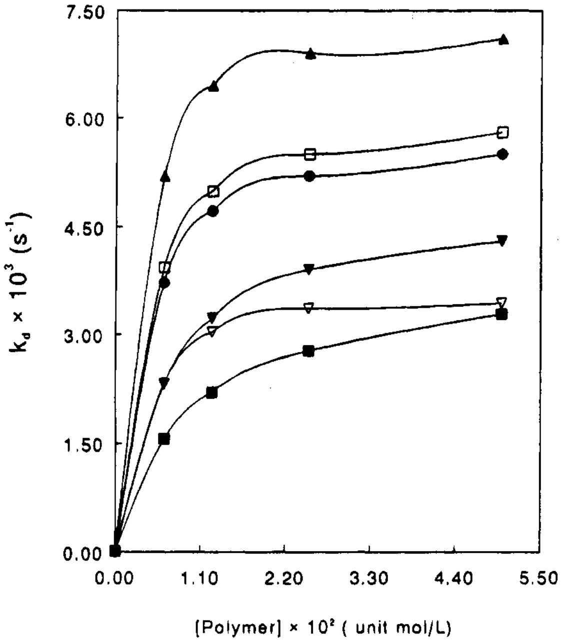


Figure 5. Rate constants for the unimolecular decarboxylation of 6-NBIC in aqueous solutions of cross-linked polysoaps at pH 11.3 and 30 °C: (▲) CL-CopolC1−12(18), (□) CL-CopolC1−12(17), (●) CL-CopolC1−12(10), (▼) CopolC1−12(8), (▽) CL-CopolC1−12(12), (■) CL-CopolC1−12(16).

Table 4. Kinetic Parameters for Unimolecular Decarboxylation of 6-NBIC in Aqueous Solutions in the Presence of Cross-Linked (Co)polymers at pH 11.3 and 30 °C

cross-linked (co)polymer	$k_m \times 10^3$ (s^{-1})	K (M^{-1})	k_m/k_w[a]	γ[b]
CL-PolC-1(4)	3.2×10^{-5} [c]		4	
CopolC1−12(8)	5.18	134	705	0.999
CL-CopolC1−12(9)	5.58	162	759	0.999
CL-CopolC1−12(10)	6.14	262	835	0.999
CL-CopolC1−12(11)	5.66	182	770	0.999
CL-CopolC1−12(12)	3.86	254	525	0.992
CL-CopolC1−12(16)	3.64	114	495	0.980
CL-CopolC1−12(17)	6.58	242	895	0.999
CL-CopolC1−12(18)	7.96	434	1083	0.999

[a] $k_w = 7.35 \times 10^{-6}$ s^{-1} in aqueous solution.[23] [b] Correlation coefficient in the Menger−Portnoy analysis.[31] [c] At 2.5×10^{-2} unit mol/L.

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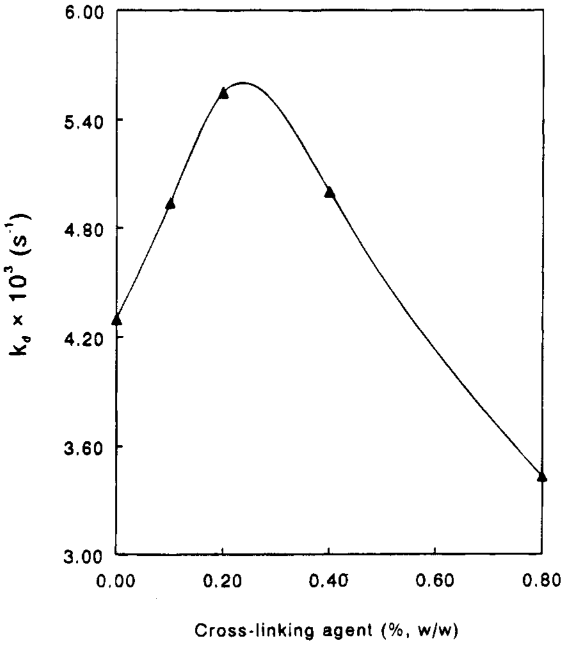

Figure 6. Effect of cross-linking agent content on the rate constant for decarboxylation of 6-NBIC in aqueous solutions of CL-CopolC1−12 (*x*/*y*, 90/10) (5.0×10^{-2} unit mol/L) at pH 9.4 and 30 °C.

increasing concentration. Finally, rate constants reach plateau values. Table 4 shows the kinetic parameters for the unimolecular decarboxylation of 6-NBIC in aqueous solution in the presence of cross-linked copolymers obtained from an analysis in terms of the Menger–Portnoy model.[31] Thus, k_m is the decarboxylation rate constant for the substrate fully bound to the cross-linked polysoap, and *K* is the equilibrium constant for the association of 6-NBIC with cross-linked polysoap. CL-PolC-1(4) only shows a small rate enhancement, indicating that no hydrophobic microdomains are formed in this system. The kinetic data could not be analyzed within the framework of the Menger–Portnoy model,[31] and therefore, the rate constant for high polymer concentration is given. The results given in Figure 6 reveal that the cross-linking agent content significantly affects the rate of decarboxylation of 6-NBIC in aqueous solution. A maximum of the rate constant was observed at about 0.20% (w/w) cross-linking agent content. Apparently the presence of a small amount of cross-linking in CL-CopolC1−12(10) allows more efficient intramolecular micelle formation as compared with that in CopolC1−12(8). The effect of the dodecyl group content of cross-linked copolymers on the decarboxylation rate of 6-NBIC in aqueous solution is presented in Figure 7. As anticipated on the basis of intrinsic visicosity measurements,[20] the reaction rates for decarboxylation of 6-NBIC are drastically enhanced with an increase in the dodecyl group content of cross-linked polysoaps and CL-CoplC1−12(18) shows the highest catalytic efficiency.

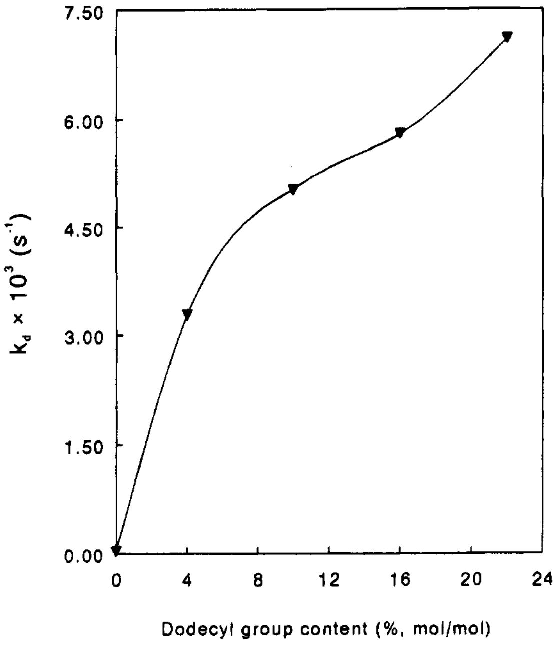

Figure 7. Effect of the dodecyl group content on the rate constant for the decarboxylation of 6-NBIC in aqueous solutions of CL-CopolC1−12 containing 0.40% (w/w) of cross-linking agent (5.0×10^{-2} unit mol/L) at pH 11.3 and 30 °C.

Conclusion

The present study shows that the formation of hydrophobic microdomains in cross-linked poly(alkylmethyldiallylammonium bromides) clearly depends on the structure of the macromolecular chain. The presence of a small amount of cross-linking allows more efficient intramolecular micelle formation as compared with non-cross-linked copolymer analogues. For the cross-linked copolymers, intrinsic viscosities also indicate that the conformational transition of cross-linked copolymers to compact coils is strongly influenced by the dodecyl group content. The decarboxylation of 6-nitrobenzisoxazole-3-carboxylate is efficiently catalyzed by the polysoaps and responds to the detailed structure and aggregation properties of the macromolecules.

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Supplementary Material Available: IR and ^{1}H NMR spectra of the novel cross-linked (co)polymers (11 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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