^{13}C NMR ($(CD_3)_2SO$) δ 142.3 (C2), 139.7 (oxime-CH), 137.1 (Ph-quaternary C), 128.8 (C5), 128.3, 127.7, and 127.6 (each Ph-C), 83.6 (C4), 75.3 (CH_2N), 70.1 ($PhCH_2$); low-resolution ACE mass spectra CI(CH_4) m/z 358.0 (MH^+), 310.0 ($MH^+ - CH_2O - H_2O$), 91.1 ($PhCH_2^+$). Anal. Calcd for $C_{12}H_{12}IN_3O_2$: C, 40.36; H, 3.39; N, 11.77. Found: C, 39.93; H, 3.33; N, 11.53.

1-[(Benzyloxy)methyl]imidazole-5-carboxaldehde Ethylene Acetal (15). A solution of **10** (292 mg, 0.76 mmol) in 5 mL of anhydrous THF was cooled to -78 °C and was treated with butyllithium (611 μL of a 1.41 M solution in hexanes, 0.86 mmol). The reaction mixture was stirred for 5 h at -78 °C, allowed to warm to room temperature, and was quenched with saturated aqueous NH_4Cl (10 mL). The product was isolated by extraction (EtOAc) and purified by radial chromatography (5% CH_3OH/CH_2Cl_2) to afford 150 mg (76%) of **15** as a yellow oil. The compound was characterized by its NMR and mass spectral properties: ^1H NMR ($CDCl_3$) δ 7.64 (s, 1, H2), 7.38-7.27 (m, 5, PhH), 7.18 (s, 1, H4), 6.05 (s, 1, acetal-CH), 5.42 (s, 2, CH_2N), 4.47 (s, 2, $PhCH_2$), 4.04-3.97 (m, 4, CH_2CH_2); ^{13}C NMR ($CDCl_3$) δ 139.5 (C2), 136.2 (Ph-quaternary C), 129.8 (C4), 128.5, 128.0 and 127.8 (each Ph-C), 127.7 (C5) 97.2 (acetal-CH), 74.0 (CH_2N), 70.0 ($PhCH_2$), 64.8 (CH_2CH_2) (correlations observed in the long-range (10-Hz optimized) ^1H-^{13}C Hetcor NMR spectrum were *H2*/CH_2N, *H2*/*C4*, Ph-*H*/Ph-quaternary *C*, *H4*/*C2*, CH_2N/*C2*, $PhCH_2$/CH_2N, $PhCH_2$/Ph-*C*H, $PhCH_2$/Ph-quaternary *C*. A difference-spectra NOE (dNOE) experiment performed by irradiating the CH_2N proton resonance revealed an NOE interaction between these protons and the H2, acetal-CH, and $PhCH_2$ protons); low-resolution FAB mass spectrum m/z 261.2 (MH^+), 231.2 ($MH^+ - CH_2O$). Anal. Calcd for $C_{14}H_{16}N_2O_3$: C, 64.60; H, 6.20; N, 10.76. Found: C, 63.85; H, 6.16; N, 10.38.

Treatment of **10** with butyllithium at -78 °C for 15 min followed by quench with D_2O gave a material which, by ^1H NMR analysis, was a mixture of [2-^2H]-**15** and unlabeled **15**. Similar results were obtained when the halogen-metal exchange reaction was conducted at -100 °C for 15 min.

Attempted C4 Formylation of 13. A solution of **10** (170 mg, 0.44 mmol) in 5 mL of anhydrous THF under argon was cooled to -78 °C and was treated dropwise with butyllithium (611 μL of a 1.41 M solution in hexanes, 0.86 mmol). The reaction mixture was stirred for 10 min at -78 °C and then was treated dropwise with anhydrous DMF (0.2 mL, 2.5 mmol). The mixture was stirred at -78 °C for 35 min, then was allowed to warm to room temperature and was quenched with saturated aqueous NH_4Cl (10 mL). The products were isolated by extraction (EtOAc) and purified by radial chromatography (5% CH_3OH/CH_2Cl_2) to afford 32 mg (25%) of 1-[(benzyloxy)methyl]imidazole-2,5-dicarboxaldehyde 5-ethylene acetal (**16**) as a yellow oil, 47 mg (26%) of 1-[(benzyloxy)methyl]-4-iodoimidazole-2,5-dicarboxaldehyde 5-ethylene acetal (**17**) as a yellow solid, and 7 mg (6%) of **15** as a yellow oil. **16**: ^{H} NMR ($CDCl_3$) δ 9.81 (s, 1, CHO), 7.37 (s, 1, H4), 7.35-7.25 (m, 5, PhH), 7.18 (s, 1, H4), 6.19 (s, 1, acetal-CH), 6.03 (s, 2, CH_2N), 4.55 (s, 2, $PhCH_2$), 4.05-4.00 (m, 4, CH_2CH_2); ^{13}C NMR ($CDCl_3$) δ 182.8 (CHO), 144.7 (C2), 136.6 (Ph-quaternary C), 135.8 (C5), 131.1 (C4), 128.5, 128.0 and 127.7 (each Ph-C), 96.7 (acetal-CH), 73.7 (CH_2N), 71.1 ($PhCH_2$), 65.2 (CH_2CH_2); low-resolution ACE mass spectrum CI(CH_4) m/z 289.1 (MH^+), 259.1 ($MH^+ - CH_2O$), 91.1 ($PhCH_2^+$). **17**: mp 101-102 °C (Et_2O/hexanes); ^1H NMR ($CDCl_3$), δ 9.76 (s, 1, CHO), 7.38-7.25 (m, 5, PhH), 6.05 (s, 1, acetal-CH), 5.98 (s, 2, CH_2N), 4.57 (s, 2, $PhCH_2$), 4.11-4.00 (m, 4, CH_2CH_2); ^{13}C NMR ($CDCl_3$), δ 181.8 (CHO), 146.5 (C2), 136.7 (Ph-quaternary C), 128.6 (C5), 128.4, 128.0 and 127.8 (each Ph-C), 97.7 (acetal-CH), 89.0 (C4), 73.8 (CH_2N), 71.1 ($PhCH_2$), 65.5 (CH_2CH_2); low-resolution ACE mass spectra CI(CH_4) m/z 385.1 ($MH^+ - CH_2O$), 91.1 ($PhCH_2^+$). **15**: ^1H NMR ($CDCl_3$) identical with that of the sample prepared intentionally from **10**.

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemcial Society, for partial support of this research. We thank Mr. Hussein Baarah for his assistance in the preparation of starting materials and Prof. Nelson J. Leonard for kindly permitting one of us (M.P.G.) to conduct some initial experiments in his laboratory at the University of Illinois in Urbana.

Supplementary Material Available: Experimental procedures and data for **1a** and **2a**; ^1H and ^{13}C NMR spectra of **2b**, **7**, **16**, and **17**; short- and long-range 2D ^1H-^{13}C heteronuclear NMR shift correlation spectra for **9**, **10**, and **15** (15 pages). Ordering information is given on any current masthead page.

Synthesis and Catalytic Properties of Hydrophobically Modified Poly(alkylmethyldiallylammonium bromides)

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Received November 26, 1990

A series of hydrophobically modified homo- and copolymers of the poly(alkylmethyldiallylammonium bromide) type has been prepared by free-radical cyclo(co)polymerization of alkylmethyldiallylammonium bromide monomers in aqueous solution. Depending on the length of the alkyl side chain (varied between C_1 and C_{12}) and the conformational freedom of the polymeric main chain, polysoap behavior was found as indicated by the hypsochromic shift of the long-wavelength absorption band of Methyl Orange, noncovalently bound to the macromolecule. The formation of a compact coil results in the presence of hydrophobic microdomains. Polysoap formation, akin to intramolecular micellization, is also revealed by appreciable catalytic effects on the unimolecular decarboxylation of 6-nitrobenzisoxazole-3-carboxylate at pH 11.3 and 30 °C.

Physicochemical studies, including viscosity measurements and fluorescence probing, have revealed that polyelectrolytes carrying sufficiently hydrophobic side chains often form compact coils in aqueous solution.[1,2] In a process which may be termed intramolecular micellization, a number of the side chains aggregate and form hydrophobic microdomains primarily stabilized by hydrophobic interactions. This type of polyelectrolytes has recently been characterized as "polysoaps".[3] Although the exact

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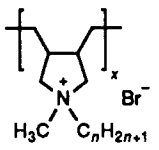
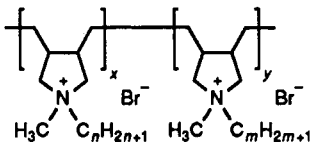
size of these domains has only been determined for few systems,[2] they are large enough to allow solubilization of apolar aromatic and aliphatic molecules.[4] These properties open interesting possibilities for a wide range of industrial applications.[5] In addition, catalytic properties comparable to those of surfactant micelles may be anticipated.[4,6,7] Herein, we report the synthesis of a series of homo- and copolymers by cyclo(co)polymerization of alkylmethyldiallylammonium bromides[8-10] in which the alkyl group is varied from methyl to *n*-dodecyl. Water solubility was found to be a limiting factor in the study of several of these macromolecules. Depending on the magnitude



Pol C-*n*



Copol C *n*-*m* (*x*/*y*)

of *n* and *m*, several of the (co)polymers showed polysoap behavior. In aqueous solution, these polysoaps were efficient catalysts for the unimolecular decarboxylation of 6-nitrobenzisoxazole-3-carboxylate.[11]

Experimental Section

Materials. Methyldiallylamine was synthesized by an Eschweiler–Clarke alkylation reaction.[12] Dimethyldiallylammonium bromide was obtained according to a standard procedure.[13] Using a similar procedure, the other alkylmethyldiallylammonium bromides were obtained by reaction of methyldiallylamine (3 M solution in anhydrous acetone) with a small excess of the appropriate alkyl bromide at room temperature. Reaction times varied from 4 to 30 days. After evaporation of the solvent in vacuo, the products were washed with anhydrous ether and finally dried under reduced pressure at 50 °C for at least 8 h.

^{1}H NMR spectra of the monomers and (co)polymers were taken on a VXR 300-MHz instrument using TMS as an external reference. All spectra were taken in D_2O as the solvent at the temperature of the probe.

Dimethyldiallylammonium bromide (1): reaction time 1 day; yield 98%; amorphous, very hygroscopic material;[14,15] ^{1}H NMR δ 2.93 (s, 6 H), 3.78–3.85 (d, 4 H), 5.55–5.68 (m, 4 H), 5.87–6.05 (m, 2 H) ppm.

Methyl-*n*-butyldiallylammonium bromide (2): reaction time 4 days; yield 42%; mp 176–177 °C; ^{1}H NMR δ 0.85 (t, 3 H), 1.02–1.35 (m, 2 H), 1.60–1.75 (m, 2 H), 2.88 (s, 3 H), 3.09–3.17 (m, 2 H), 3.80 (d, 4 H), 5.55–5.68 (m, 4 H), 5.85–6.01 (m, 2 H) ppm. Found: C, 53.14; H, 8.93; N, 5.64; Br, 32.17. $C_{11}H_{22}NBr$ requires: C, 53.23; H, 8.93; N, 5.64; Br, 32.19.

Methyl-*n*-pentyldiallylammonium bromide (3): reaction time 8 days; yield 48%; mp 120.5–122 °C; ^{1}H NMR δ 0.81–1.00 (t, 3 H), 1.18–1.35 (m, 4 H), 1.65–1.75 (m, 2 H), 2.89 (s, 3 H), 3.11–3.16 (m, 2 H), 3.80 (d, 4 H), 5.55–5.65 (m, 4 H), 5.85–6.01 (m, 2 H) ppm. Found: C, 54.70; H, 9.22; N, 5.30; Br, 30.75. $C_{12}H_{24}NBr$ requires: C, 54.96; H, 9.22; N, 5.34; Br, 30.47.

Methyl-*n*-heptyldiallylammonium bromide (4): reaction time 18 days; yield 60%, wax;[15] ^{1}H NMR δ 0.82 (t, 3 H), 1.15–1.35 (m, 8 H), 1.65–1.80 (m, 2 H), 3.23 (s, 3 H), 3.25–3.35 (m, 2 H), 4.15–4.30 (m, 4 H), 5.65–6.05 (m, 6 H) ppm. Found: C, 57.60; H, 9.55; N, 4.76. $C_{14}H_{28}NBr$ requires: C, 57.90; H, 9.72; N, 4.82.

Methyl-*n*-octyldiallylammonium bromide (5): reaction time 20 days; yield 51%, wax;[15] ^{1}H NMR δ 0.63 (t, 3 H), 0.95–1.20 (m, 10 H), 1.50–1.65 (br s, 2 H), 3.03 (s, 3 H), 3.14–3.19 (m, 2 H), 4.04 (d, 4 H), 5.45–5.90 (m, 6 H) ppm.

Methyl-*n*-dodecyldiallylammonium bromide (6): reaction time 30 days; yield 42%, oil;[15] ^{1}H NMR δ 0.71 (t, 3 H), 1.05–1.24 (m, 18 H), 1.55–1.70 (m, 2 H), 3.09 (s, 3 H), 3.15–3.25 (m, 2 H), 4.09–4.15 (d, 4 H), 5.55–5.95 (m, 6 H) ppm. Found: Br, 22.21. $C_{19}H_{38}NBr$ requires: Br, 22.17.

(Co)polymerizations. Aqueous solutions (50%, w/w) of the monomers were polymerized for 3 days at 65 °C in the presence of 1% (w/w) commercial grade *tert*-butyl hydroperoxide. Copol C 1-12 was also prepared using ammonium persulfate as the initiator according to a standard procedure.[16] In the copolymerizations the monomer feed ratio was varied. The obtained (co)polymers were purified by dialysis (Servapore dialysis tubing 29 mm) for at least 48 h at room temperature and were subsequently freeze-dried.

Despite the rather broad resonances, the (co)polymers could be characterized by their ^{1}H NMR spectra. These spectra showed no allyl resonances. The ^{1}H and ^{13}C NMR (coupled and decoupled, 1,4-dioxane as the reference) spectra of Pol C-1 in D_2O were analyzed in detail. These spectra were in agreement with those measured by Lancaster et al.[9] and ruled out the presence of six-membered ring structures in the macromolecule. Proton resonances corresponding to pyrrolidinium rings which are, respectively, cis and trans substituted by the interconnecting $-CH_2CH_2-$ groups could be easily identified. The cis/trans ratio (about 7:1) is similar to that found previously[9] and does not vary substantially for the (co)polymers described in the present study. Peak assignments were fully confirmed by a ^{13}C–^{1}H heteronuclear chemical shift correlation (HETCOR) experiment.[17] On the basis of these results, the ^{1}H NMR resonances of the other (co)polymers could be easily assigned and were completely reconcilable with the proposed structures. Copolymer compositions were obtained via careful integration of relevant peaks and are accurate to within ca. 1 unit mol %. Apart from the broad ^{1}H NMR resonances, the intrinsic viscosities also indicate the polymeric rather than oligomeric nature of the materials.

Poly(dimethyldiallylammonium bromide) (Pol C-1): yield 40%. This material has been prepared previously.[18] In water we find $[\eta]$ = 0.77 dL·g^{-1}. For this polymer[19] $[\eta] = (1.12 \times 10^{-4}) \cdot M^{0.82}$, and we find M = 57 300.

Poly(methyl-*n*-pentyldiallylammonium bromide) (Pol C-5): yield 48%; $[\eta]$ = 0.46 dL·g^{-1}; ^{1}H NMR δ 0.75 (t, CH_3), 1.16 (s, CH_2), 1.38 (s, CH_2), 2.10 (br s, CH (ring, trans)), 2.50 (br s, CH (ring cis)), 2.85–3.3 (m, CH_3, CH_2(N), CH_2 (ring, cis/trans)), 3.7 (br s, CH_2 (ring, cis/trans)) ppm.

Poly(dimethyldiallylammonium-*co*-methyl-*n*-dodecyldiallylammonium) dibromide (87/13) (Copol C 1-12, 87/13): feed ratio 90/10; yield 50%; $[\eta]$ = 0.58 dL·g^{-1}; ^{1}H NMR δ 0.7 (CH_3), 1.10 (CH_2), 1.35 (CH_2), 2.12 (CH (ring, trans)), 2.53 (CH (ring, cis)), 3.0–3.25 (CH_3, CH_2(N), CH_2 (ring, cis/trans)), 3.68 (CH_2 (ring, cis/trans)) ppm.

Poly(methyl-*n*-butyldiallylammonium-*co*-methyl-*n*-dodecyldiallylammonium) dibromide (97/3) (Copol C 4-12, 97/3): feed ratio 95/5; yield 23%; ^{1}H NMR δ 0.8 (CH_3), 1.0–1.75 (CH_2), 2.12 (CH (ring, trans)), 2.54 (CH (ring, cis)), 2.88–3.40 (CH_3, CH_2(N), CH_2 (ring, cis/trans)), 3.72 (CH_2 (ring, cis/trans)) ppm.

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Poly(methyl-*n*-pentyldiallylammonium-*co*-methyl-*n*-dodecyldiallylammonium) dibromide (98/2) (Copol C 5-12, 98/2): feed ratio 95/5; yield 33%; ^{1}H NMR δ 0.75 (CH_3), 1.05–1.78 (CH_2), 2.10 (CH (ring, trans)), 2.53 (CH (ring, cis)), 2.88–3.35 (CH_3, CH_2(N), CH_2 (ring, cis/trans)), 3.75 (CH_2 (ring, cis/trans)) ppm.

Poly(dimethyldiallylammonium-*co*-methyl-*n*-octyldiallylammonium) dibromide (61/39) (Copol C 1-8, 61/39): feed ratio 60/40; yield 38%; $[\eta]$ = 0.31 dL·g^{-1}; ^{1}H NMR δ 0.98 (CH_3), 1.30–2.02 (CH_2), 2.42 (CH (ring, trans)), 2.81 (CH (ring, cis)), 3.14–3.58 (CH_3, CH_2(N), CH_2 (ring, cis/trans)), 3.75 (CH_2 (ring, cis/trans)) ppm.

Poly(dimethyldiallylammonium-*co*-methyl-*n*-heptyldiallylammonium) dibromide (52/48) (Copol C 1-7, 52/48): feed ratio 50/50; yield 41%; $[\eta]$ = 0.33 dL·g^{-1}; ^{1}H NMR δ 0.97 (CH_3), 1.20–2.0 (CH_2), 2.38 (CH (ring, trans)), 2.78 (CH (ring, cis)), 3.00–3.60 (CH_3, CH_2(N), CH_2 (ring, cis/trans)), 3.92 (CH_2 (ring, cis/trans)) ppm.

Copol C 1-7, 63/37 (feed ratio 60/40, yield 34%) and Copol C 1-7, 75/25 (feed ratio 70/30, yield 51%) showed essentially the same ^{1}H NMR resonances as Copol C 1-7, 52/48, albeit with small differences in integration.

States of Matter and Water Solubilities. Monomer 1 is an amorphous solid, 2 and 3 are crystalline materials, 4 and 5 are waxlike, and 6 is an oil. They are all water soluble. The (co)polymers are amorphous materials. Homopolymers Pol C-1 and Pol C-5 are water soluble, Pol C-7 is swellable in water, whereas Pol C-8 and Pol C-12 are insoluble in water.[20] Relatively small variations in copolymer composition greatly affect the solubility in water. Copol C 1-12, 87/13 is soluble, Copol C 1-12, 80/20 is not. Copol C 4-12, 97/3, Copol C 5-12, 98/2, Copol C 1-7, 52/48, Copol C 1-7, 63/37, Copol C 1-7, 75/25, Copol C 1-8, 61/39, Copol C 1-8, 68/32, and Copol C 1-8, 77/23 are soluble. Copol C 1-8, 50/50 is insoluble.

Viscosity Measurements. These experiments were performed using a Scott AVS 400 viscosimeter at 25 °C. Intrinsic viscosities $[\eta]$ were obtained from linear plots of $\eta_{sp}\cdot c^{-1}$ and ln $\eta_r\cdot c^{-1}$ vs (co)polymer concentration.

Cmc Values. The cmc of monomer 6 (6.1×10^{-3} M, 25 °C) was determined using pyrene as a fluorescence probe.[21] The break in the plot of the ratio I_1/I_3 vs total monomer concentration probes the onsett of micellization. I_1 and I_3 are the intensities of the first and third vibronic peaks in the emission spectrum of pyrene. Excitation and emission wavelengths were 335 and 372 nm, respectively. The solutions were made up by weight in double-distilled water saturated with pyrene (3×10^{-7} M).

Aggregation Numbers. These were measured for micelles formed from 6 in water and in aqueous salt solutions at 25 °C using the procedure of Turro et al.[22] (Table II). We used bis(2,2′-bipyridyl)(4,4′-didecyl-2,2′-bipyridyl)ruthenium(II) perchlorate (1.18×10^{-3} M) as a probe and 9-methylanthracene (2.16×10^{-2} M) as a quencher. Excitation and emission wavelengths were 453 and 626 nm, respectively. All fluorescence spectra were recorded on a SLM-Aminco SPF-500c spectrophotometer equipped with a thermostated cell compartment.

UV–Vis Spectroscopy. UV–vis absorption spectra of Methyl Orange (2.5×10^{-5} M) in the presence of the polysoaps (($1.0–3.0) \times 10^{-3}$ unit M) were recorded on a Perkin-Elmer λ5 spectrophotometer at 30 °C in aqueous solutions adjusted to pH 9.4 with a 0.02 M sodium borate buffer.

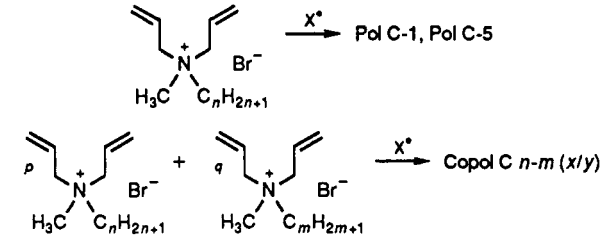
Kinetic Experiments. The kinetic probe 6-nitrobenzisoxazole-3-carboxylate (6-NBIC) was prepared according to a standard procedure.[23] First-order rate constants for the decarboxylation of 6-NBIC were determined at 30.0 ± 0.1 °C by monitoring the increase in absorption using a Perkin-Elmer λ5 spectrophotometer equipped with a data station. All reactions were followed for at least 4 half-lives, and the rate constants were calculated by the Guggenheim method. In a typical experiment 8 μL of a freshly prepared stock solution of 6-NBIC (14×10^{-2} M) was added to 2.5 mL of the aqueous polysoap solution (pH 11.3) in the thermostated cell.

Table I. Position of the Long-Wavelength Absorption Band of Methyl Orange in Aqueous (Co)polymer Solutions at 30 °C and pH 9.4

(co)polymer	concentration, unit M	λ_{max}, nm
–	–	462
Pol C-1	2.43×10^{-3}	462
Pol C-5	2.28×10^{-3}	464
Copol C 1-12 (87/13)	3.61×10^{-3}	422
Copol C 4-12 (97/3)	2.77×10^{-3}	424
Copol C 5-12 (98/2)	2.60×10^{-3}	423
Copol C 1-8 (61/39)	2.93×10^{-3}	440
Copol C 1-8 (68/32)	3.04×10^{-3}	440
Copol C 1-8 (77/23)	3.23×10^{-3}	441
Copol C 1-7 (52/48)	1.29×10^{-3}	440
Copol C 1-7 (63/37)	1.00×10^{-3}	440
Copol C 1-7 (75/25)	9.51×10^{-4}	450

Results and Discussion

Synthesis. The (co)polymers could be easily synthesized by free-radical cyclo(co)polymerization of alkylmethyldiallylammonium bromide monomers in aqueous solution:[8–10]



The macromolecules are presumed to consist of 5-membered rings, in accord with their ^{1}H NMR spectroscopic data. Structural aspects of these polymers have been the subject of much discussion.[8–10,18,24] For Pol C-1 the molecular weight was 57 300 (see the Experimental Section), while the intrinsic viscosities of solutions of the other (co)polymers suggest comparable molecular weights. The composition of the, presumably random, copolymers (x/y) was determined from their ^{1}H NMR spectra. This ratio x/y was usually not very different from the feed ratio p/q. As anticipated, the water solubility of the (co)polymers is critically dependent on n (homopolymers) and n/m (copolymers). The same parameters govern the propensity for formation of hydrophobic microdomains (vide infra).

Hydrophobic Microdomains. Polysoap behavior, involving intramolecular side-chain aggregation to form hydrophobic microdomains in a compact coil conformation, can be probed using sufficiently hydrophobic dyes. These dyes bind to the domains in aqueous solution, thereby undergoing a shift in their UV/vis absorption spectra. We have measured the position of the long-wavelength absorption band of Methyl Orange[20,25] (2.5×10^{-5} M, λ_{max} 462 nm) in the presence of 10^{-5}–10^{-2} unit M of (co)polymer in 0.02 M sodium borate buffers (pH 9.4) at 30 °C (Table I, Figure 1). Binding of Methyl Orange in hydrophobic environments is revealed by a hypsochromic shift. Substantial shifts are observed for Copol C 1-12 (87/13), Copol C 4-12 (97/3), and Copol C 5-12 (98/2). Modest spectral shifts occur in the presence of the copolymers C 1-8 and C 1-7 of various compositions, whereas the homopolymers Pol C-1 and Pol C-5 have no effect on the spectrum. For the most hydrophobic copolymers, the binding process takes place over the copolymer concentration range be-

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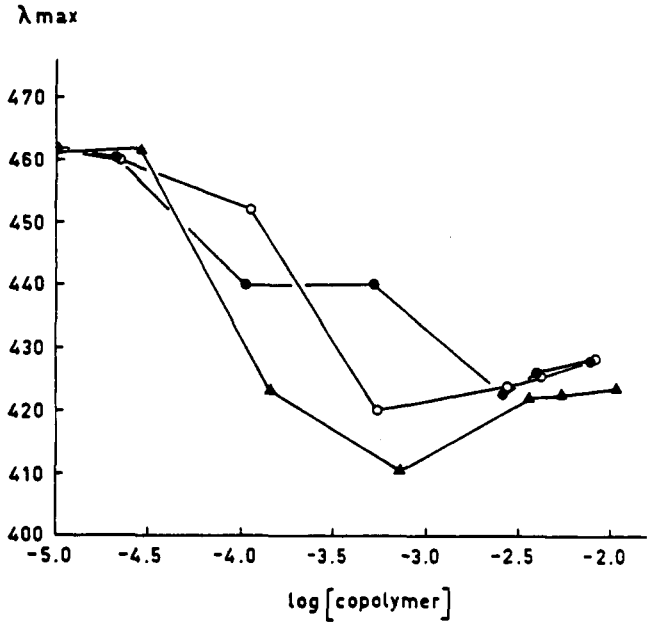
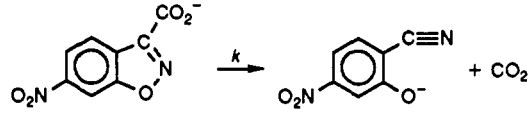


Figure 1. Position of the absorption maximum of Methyl Orange in aqueous polysoap solutions of different concentrations ([copolymer] in unit M); ▲, Copol C 1-12, 87/13; ○, Copol C 4-12, 97/3; ●, Copol C 5-12, 98/2.

tween ca. $10^{-4.5}$ and 10^{-3} unit M. At still higher copolymer concentrations there is a small hyperchromic shift (Figure 1), which may be indicative for the onsett of intermolecular interactions between the macromolecules. These results indicate that within our series of hydrophobically modified polyelectrolytes, only the copolymers carrying an *n*-dodecyl side chain form tightly packed, coiled conformations with relatively "dry" microdomains available for dye solubilization. Much less efficient intramolecular micellization takes place in the case of the Copols C 1-7 and C 1-8.

Polysoap-Catalyzed Decarboxylation of 6-NBIC. The first-order rate constant k for the unimolecular decarboxylation of 6-nitrobenzisoxazole-3-carboxylate (6-NBIC) is very medium dependent.[11] The rate is slow in



water, but rate constants increase dramatically in media which provide less hydrogen-bond stabilization for the initial state and better stabilization of the highly polarizable transition state by London dispersion forces. The decarboxylation of 6-NBIC, which provides a model for biological decarboxylations,[26] has been employed to probe a large variety of reaction media, including micellar and vesicular pseudophases[27,28] as well as hydrophobic microdomains in polymer solutions.[25]

Kinetic parameters for decarboxylation of 6-NBIC in aqueous solution in the presence of various addenda, among them the newly prepared (co)polymers, are summarized in Table II. Monomeric salts, such as Me_4NBr, **4**, and **5** induce small rate enhancements. Micelles formed from **6** induce a large catalytic effect. Rate constants at varying concentrations of **6** around its cmc were analyzed according to the Menger–Portnoy enzyme model for micellar catalysis.[29] The rate constant given in Table II refers to decarboxylation in the micellar pseudophase whereas K_m is the binding constant for binding of 6-NBIC to the micelles. The data show that micelles formed from **6** exhibit a higher catalytic efficiency than CTAB micelles,[27] despite the shorter alkyl chain in the surfactant **6**. Pol C-1 and C-5 induce modest rate enhancements in accord with the data in Table I, which indicate the absence of appreciable formation of hydrophobic microdomains. By contrast, the copolymers C 1-12 (87/13), C 4-12 (97/3), and C 5-12 (98/2) are very efficient catalysts for the decarboxylation, all being better than micellar **6** (Figure 2). Particularly Copol C 1-12 (87/13) induces a huge rate enhancement, which gradually decreases upon elongation

Table II. Kinetic Parameters for the Unimolecular Decarboxylation of 6-NBIC in the Presence of Salts, Micelles, and (Co)polymers at 30 °C and pH 11.3

addendum	$k \times 10^6$, s^{-1}	K_m, M^{-1}	k/k_{H_2O}	r^a
–[b]	7.35			
Me_4NBr[c]	13.0			
4[d]	20.0			
5[d]	15.0			
6[e,f]	2800	69	380	0.999
CTAB[g]	350		48	
Pol C-1[h]	28		3.8	
Pol C-5[h]	76		10.3	
Copol C 1-12 (87/13)[f]	7700	52	1045	0.999
Copol C 4-12 (97/3)[f]	4300	59	585	0.999
Copol C 5-12 (98/2)[f]	2900	80	395	0.995
Copol C 1-8 (61/39)[i]	1300		176	
Copol C 1-8 (68/32)[i]	400		54	
Copol C 1-8 (77/23)[i]	100		14	
Copol C 1-7 (52/48)[j]	150		20	
Copol C 1-7 (63/37)[j]	110		15	
Copol C 1-7 (75/25)[j]	75		10	

[a] Correlation coefficient in the Menger–Portnoy analysis. [b] Aqueous buffer solution.[28] [c] At 1.0 M. [d] At 2.0×10^{-2} M. [e] In micellar solution. Aggregation number: 82 (H_2O), 97 (0.01 M NaBr), 149 (0.1 M NaBr), 154 (0.5 M NaBr). [f] Kinetic parameters according to the Menger–Portnoy model.[29] [g] Taken from ref 31. [h] At 25×10^{-3} unit M. [i] At 40×10^{-3} unit M. [j] At 4×10^{-3} unit M.

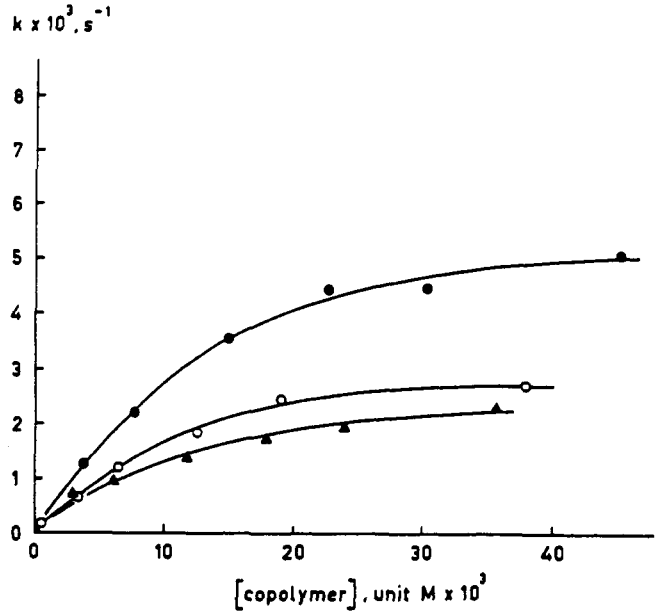


Figure 2. Unimolecular rate constants for the decarboxylation of 6-NBIC (30 °C, pH 11.3) in aqueous solutions of polysoaps; ●, Copol C 1-12, 87/13; ○, Copol C 4-12, 97/3; ▲, Copol C 5-12, 98/2.

(26) Compare: Marlier, J. F.; O'Leary, M. H. *J. Am. Chem. Soc.* **1986**, *108*, 4896.
(27) See, for example: Bunton, C. A.; Minch, M. J.; Hidalgo, J.; Sepulveda, L. *J. Am. Chem. Soc.* **1973**, *95*, 3262.
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of the second alkyl chain. This is unusual, since an increased total hydrophobicity of the side chains involved in domain formation is expected to lead to enhanced catalytic activity. Thus, our results appear to suggest that flexibility of the copolymer chain is a factor that governs microdomain formation.[30] The presence of a (second) *n*-butyl and *n*-pentyl chain in Copol C 4-12 (97/3) and C 5-12 (98/2) allows less efficient compact coil formation as compared with that for Copol C 1-12 (87/13). However, the differences in the molar percentage of the *n*-dodecyl chain in the three copolymers will also affect microdomain formation. Finally, steric effects varying with the length of the second alkyl chain may also modulate the catalytic effect of the polysoap. Interestingly, for the three catalytically most effective copolymers, the K_m values vary only little, which also suggests that most likely several factors are involved in determining the catalytic efficiency. Apart from Copol C 1-8 (61/39), the other copolymers of the Copol C 1-8 and Copol C 1-7 type induce modest or small rate enhancements of the decarboxylation, again in accord with the previous conclusion that these macromolecules do not form extensive microdomains. Therefore, the Menger–Portnoy analysis was not applied for these systems (Table II).

(30) The importance of geometrical constraints in determining the formation of hydrophobic microdomains has been noted before, see: Jager, J. Ph.D. Thesis, Groningen, 1987. For example, poly(methacrylic acid) readily forms compact coils, whereas poly(crotonic acid) does not: Muroga, Y.; Nagasawa, M. *Polym. J.* **1986**, *18*, 15.

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Conclusion

Hydrophobically modified homo- and copolymers of the poly(alkylmethyldiallylammonium bromide) type form hydrophobic microdomains in aqueous solution depending on the length(s) of the alkyl chain(s) and, most likely, the flexibility of the polymer main chain. The polysoaps allow interesting comparisons between intra- and intermolecular micellization processes.

Acknowledgment. Financial support from the Netherlands Technology Foundation (STW) is gratefully acknowledged. We thank T. A. A. Fonteijn for performing highly useful preliminary experiments. We are also much indebted to Mr. Anno Wagenaar for his help in the analysis of the NMR spectra.

Registry No. 1, 14764-64-8; 2, 69419-83-6; 3, 133833-04-2; 4, 133833-05-3; 5, 69419-86-9; 6, 41454-28-8; Pol C-1 (homopolymer), 30870-73-6; Pol C-5 (homopolymer), 133833-10-0; Copol C1-12 (copolymer), 133833-11-1; Copol C5-12 (copolymer), 133833-13-3; Copol C1-7, 133833-15-5; Methyl orange, 547-58-0; 6-nitrobenzisoxazole-3-carboxylate, 42540-91-0.

Supplementary Material Available: ^{1}H NMR spectra of the novel monomers and (co)polymers (16 pages). Ordering information is given on any current masthead page.

Nortopsentins A, B, and C. Cytotoxic and Antifungal Imidazolediylbis[indoles] from the Sponge *Spongosorites ruetzleri*

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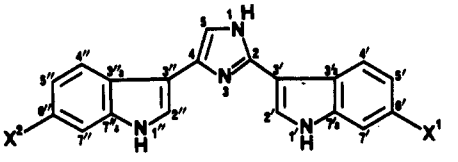
Received October 31, 1990

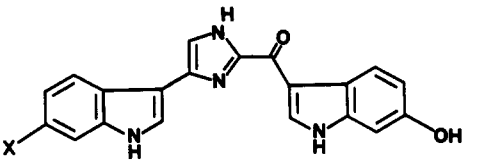
Three novel cytotoxic and antifungal alkaloids, nortopsentins A (1), B (2), and C (3), along with two known compounds, topsentin (4) and bromotopsentin (5), were isolated from the Caribbean deep-sea sponge *Spongosorites ruetzleri*. The structures of the nortopsentins were established mainly on the basis of NMR spectroscopic data. The unique imidazolediylbis[indole] skeleton of the nortopsentins demonstrates a new condensation process in tryptophan metabolism. The nortopsentins exhibited in vitro cytotoxicity against P388 cells and antifungal activity against *Candida albicans*.

The topsentins, discovered recently as antitumor and antiviral agents from marine sponges,[1-3] represent an emerging class of marine bis[indole] alkaloids.[1-8] During our search for bioative marine natural products, we isolated three novel cytotoxic and antifungal compounds belonging to this class, designated as nortopsentins A (1), B (2), and C (3), together with two known compounds, topsentin (4) and bromotopsentin (5), from the deep-sea sponge *Spongosorites ruetzleri* Van Soest and Stentoft, 1988 (order Halichondrida, family Halichondriidae).[9] The unique imidazolediylbis[indole]skeleton of the nortopsentins demonstrates a new condensation process in tryptophan metabolism.[1-8]

S. ruetzleri, one of the four *Spongosorites* sponges reported to produce the topsentins by Tsujii et al.,[2,10] was recollected by Johnson-Sea-Link submersible at a depth of 460 m off Nassau, Bahamas, in March 1987. The



1: X^1 = X^2 = Br
2: X^1 = Br, X^2 = H
3: X^1 = H, X^2 = Br



4: X = H
5: X = Br

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