Synthesis and Catalytic Properties of Non-Cross-Linked and Cross-Linked Poly(alkylmethyldiallylammonium bromides) Having Decyl, Octyl, and Hexyl Side Chains

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A family of non-cross-linked and cross-linked copolymers containing decyl, octyl, and hexyl groups as side chains ((CL)-CopolC1-10, (CL)-CopolC1-8, and (CL)-CopolC1-6, respectively) were synthesized by radical-initiated cyclocopolymerization of alkylmethyldiallylammonium bromide monomers without and with a small amount of *N,N'*-methylenebisacrylamide as a cross-linking agent in aqueous solution. Their ^{1}H NMR and IR spectra indicated the presence of five-membered rings cross-linked without and with *N,N'*-methylenebisacrylamide in the macromolecules. Viscosity measurements showed that the cross-linked copolymers exhibit a larger reduced viscosity in aqueous solution with increasing cross-linking agent content in the copolymers. For (CL)-CopolC1-10, the conformational transition to compact coils was indicated by changes of the reduced viscosity in dilute aqueous solutions. At higher concentrations, intermolecular aggregation was also revealed and increased with increasing the percentage of cross-linking for CL-CopolC1-10. (CL)-CopolC1-8 and (CL)-CopolC1-6 showed extented molecular dimensions in aqueous solution. The hydrophobic microdomains of the non-cross-linked and cross-linked copolymers were probed by hypsochromic shifts of the long-wavelength absorption band of Methyl Orange as a solvatochromic agent, noncovalently bound to the macromolecule. The unimolecular decarboxylation of 6-nitrobenzisoxazole-3-carboxylate (6-NBIC), catalyzed by these copolymers in aqueous solution, was used as a model reaction to study the influence of polysoap microenviroment on reactivity. Depending on the hydrophobic group content, (CL)-CopolC1-10 led to a remarkably large rate enhancement, whereas (CL)-CopolC1-8 induced only modest rate acceleration for the decarboxylation of 6-NBIC. A small rate enhancement was observed in the presence of (CL)-CopolC1-6. The decarboxylation rate is also sensitive to changes of the percentage of cross-linking in the macromolecules. A maximum in rate constant was found at about 0.2% (w/w) cross-linking agent for CL-CopolC1-10 and at about 0.4% (w/w) for CL-CopolC1-8 in plots of the rate constant vs cross-linking agent content.

Various functions of biological systems in nature are known to be based on the presence of highly organized molecular assemblies.[1-3] The majority of the chemical interactions and reactions occur in the vicinity of boundaries between apolar and polar regions. Hydrophobically-modified polyelectrolytes (polysoaps) are regarded as good models for a globular protein in aqueous solution[4] and provided convenient systems to study the role of electrostatic and hydrophobic interactions relevant for adsorption of molecules at the hydrophobic/hydrophilic interfaces and the factors that control the reactions between these adsorbed molecules.[5,6] The presence of hydrophobic microdomains in the compact conformation of the polysoap plays an essential role in the binding and activity and may lead to large rate enhancements due to a specific microenvironmental effect and an accumulation of the reactants in the pseudophase.[7-8]

The unimolecular decarboxylation of 6-nitrobenzisoxazole-3-carboxylate anion (6-NBIC) is notable for its remarkable sensitivity to the reaction medium.[9] The decarboxylation rate varies by 8 orders of magnitude going from water to dipolar aprotic solvents.[10] As a result of the medium sensitivity, the unimolecular decarboxylation of 6-NBIC has been extensively employed as a popular probe in micelle,[11] bilayer,[12] macrocyclic host,[13] polymer,[6,8] and antibody catalysis.[14] The rate accelerations can be largely ascribed to partial dehydration of

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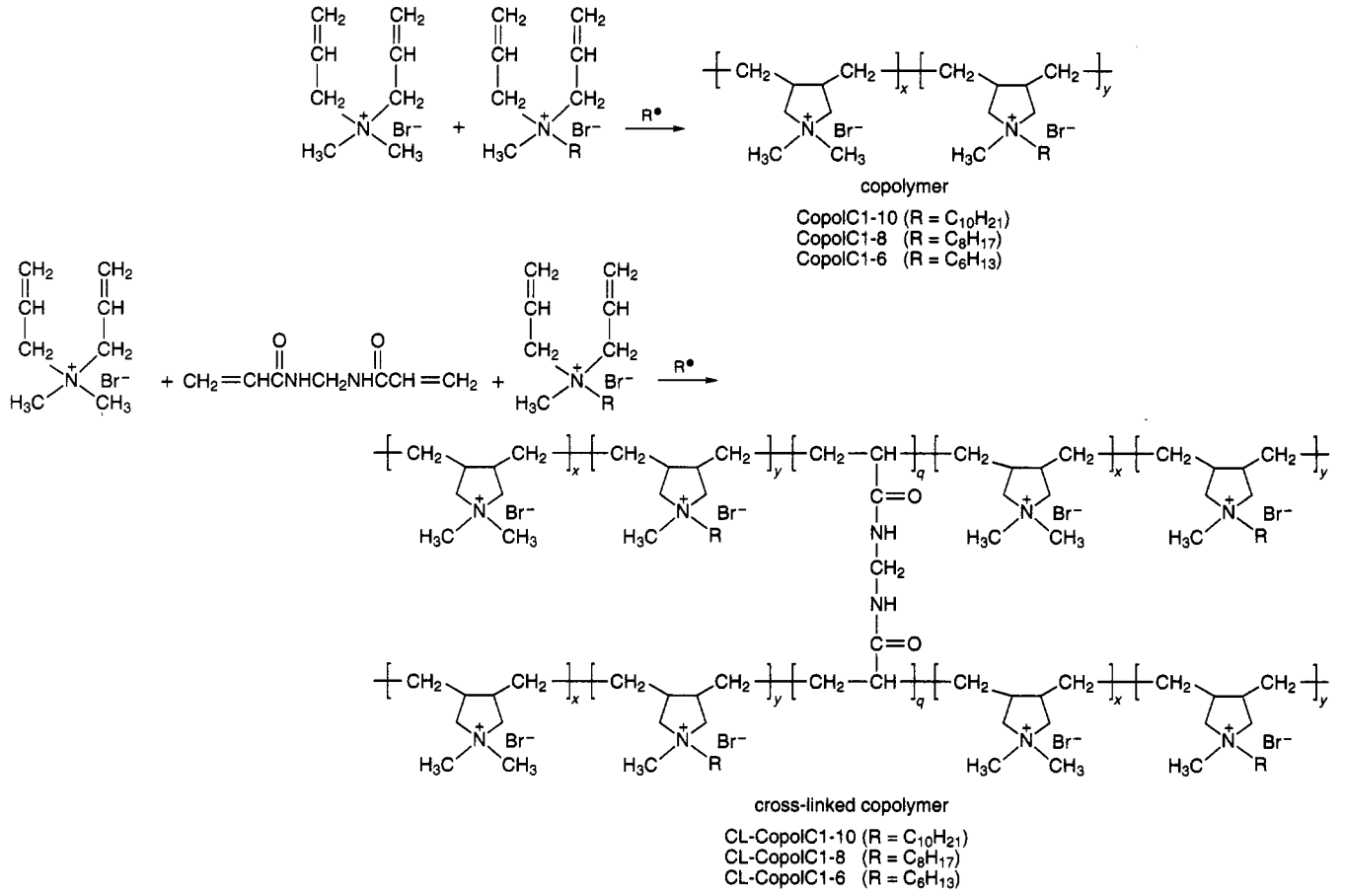
Scheme 1



the carboxylate function of the initial state in the hydrophobic microenvironment.[8,14]

We recently described the catalysis of the unimolecular decarboxylation of 6-NBIC by cross-linked poly(alkylmethyldiallylammonium bromides) and poly(alkylmethyldiallylammonium chlorides) containing dodecyl side chains (CL-CopolC1-12 and CL-CopolC1-12-Cl, respectively) in aqueous solution in which huge rate enhancements were obtained for both polysoaps.[8] CL-CopolC1-12-Cl polysoaps were found to be more efficient catalysts for the unimolecular decarboxylation of 6-NBIC than the corresponding CL-CopolC1-12 due 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.[8b] The formation of the hydrophobic microdomains in aqueous solution of the cross-linked polysoaps is remarkably influenced by the dodecyl group content and the specific structure of the macromolecules.[8,15a]

In the present paper we make an endeavor to provide further insight into the structure–reactivity relation for the rate enhancement of the unimolecular decarboxylation of 6-NBIC in aqueous solution by using systematically tuned polysoaps. To investigate the properties of polysoaps as a function of the side-chain length, we have synthesized a series of novel non-cross-linked and cross-linked poly(alkylmethyldiallylammonium bromides) bearing different alkyl side chains varying from methyl to *n*-decyl. Cross-linking was induced by adding a small amount of *N,N'*-methylenebisacrylamide. Reduced viscosities in aqueous solution have been measured to obtain information concerning the molecular dimensions and the aggregate formation. (CL)-CopolC1-10 shows a clear tendency toward intramolecular and intermolecular aggregation with increasing polymer concentration, whereas (CL)-CopolC1-8 and (CL)-CopolC1-6 exhibit normal polyelectrolyte behavior in aqueous solution. The unimolecular decarboxylation of 6-NBIC catalyzed by non-cross-linked and cross-linked copolymers has been studied as a function of the structure of the macromolecular chain. (CL)-CopolC1-10 is an efficient catalyst for the unimolecular decarboxylation of 6-NBIC in aqueous solution.

Experimental Section

Materials and Reagents. The syntheses of methyldiallylamine, dimethyldiallylammonium bromide, and cross-linked homopolymer poly(dimethyldiallylammonium bromide) (CL-PolC-1(4): cross-linking agent, 0.4% (w/w)) have been described previously.[8a] Methyl Orange was used as received from Aldrich. Ammonium persulfate (Janssen) and *N,N'*-methylenebisacrylamide (Janssen) were commercial compounds of reagent grade. *n*-Decyl bromide, *n*-octyl bromide, and *n*-hexyl bromide were obtained from Janssen and were distilled under vacuum before use.

Synthesis of Monomers. A solution of methyldiallylamine (2.5 M in acetone) was placed in a 250 mL round bottom flask equipped with a magnetic stirring bar. One equivalent of distilled *n*-decyl bromide was added, and the resulting mixture was reacted at 60 °C for 4 days in an oil bath. The solvent was removed by evaporation under reduced pressure. The residue was dissolved in deionized water and extracted several times with diethyl ether to remove unreacted material. Finally, the product solution was freeze-dried for at least 2 days. *n*-Octylmethyldiallylammonium bromide and *n*-hexyl-

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Table 1. Cyclocopolymerization of *n*-Decyllmethyldiallylammonium Bromide and Dimethyldiallylammonium Bromide in the Absence and Presence of *N,N'*-Methylenebisacrylamide in Aqueous Solution

copolymer	DIMDABr[a] (mol)	DeMDAABr[b] (mol)	*N,N'*-MbisAM[c] (%, w/w)	APS[d] (mg)	yield[e] (%)	water solubility
CopolC1-10(1)	0.036	0.004	0.00	174	35	soluble
CL-CopolC1-10(2)	0.036	0.004	0.20	174	37	soluble
CL-CopolC1-10(3)	0.036	0.004	0.40	174	44	soluble
CL-CopolC1-10(4)	0.036	0.004	0.80	174	48	soluble
CL-CopolC1-10(5)	0.032	0.008	0.40	180	52	soluble
CL-CopolC1-10(6)	0.028	0.012	0.40	186	47	soluble

[a] Dimethyldiallylammonium bromide. [b] *n*-Decylmethyldiallylammonium bromide. [c] *N,N'*-Methylenebisacrylamide. [d] Ammonium persulfate. [e] Polymerization time, 72 h.

Table 2. Cyclocopolymerization of *n*-Octylmethyldiallylammonium Bromide and Dimethyldiallylammonium Bromide in the Absence and Presence of *N,N'*-Methylenebisacrylamide in Aqueous Solution

copolymer	DIMDABr[a] (mol)	OMDAABr[b] (mol)	*N,N'*-MbisAM[c] (%, w/w)	APS[d] (mg)	yield[e] (%)	water solubility
CopolC1-8(1)	0.024	0.016	0.00	176	33	soluble
CL-CopolC1-8(2)	0.024	0.016	0.20	176	41	soluble
CL-CopolC1-8(3)	0.024	0.016	0.40	176	39	soluble
CL-CopolC1-8(4)	0.024	0.016	0.80	176	47	soluble
CL-CopolC1-8(5)	0.032	0.008	0.40	168	36	soluble
CL-CopolC1-8(6)	0.016	0.024	0.40	182	35	insoluble

[a] Dimethyldiallylammonium bromide. [b] *n*-Octylmethyldiallylammonium bromide. [c] *N,N'*-Methylenebisacrylamide. [d] Ammonium persulfate. [e] Polymerization time, 72 h.

Table 3. Cyclocopolymerization of *n*-Hexylmethyldiallylammonium Bromide and Dimethyldiallylammonium Bromide in the Absence and Presence of *N,N'*-Methylenebisacrylamide in Aqueous Solution

copolymer	DIMDABr[a] (mol)	HMDAABr[b] (mol)	*N,N'*-MbisAM[c] (%, w/w)	APS[d] (mg)	yield[e] (%)	water solubility
CopolC1-6(1)	0.012	0.008	0.00	94	37	soluble
CL-CopolC1-6(2)	0.012	0.008	0.20	94	45	soluble
CL-CopolC1-6(3)	0.012	0.008	0.40	94	42	soluble
CL-CopolC1-6(4)	0.012	0.008	0.80	94	43	soluble
CL-CopolC1-6(5)	0.016	0.004	0.40	90	44	soluble
CL-CopolC1-6(6)	0.008	0.012	0.40	98	33	soluble

[a] Dimethyldiallylammonium bromide. [b] *n*-Hexylmethyldiallylammonium bromide. [c] *N,N'*-Methylenebisacrylamide. [d] Ammonium persulfate. [e] Polymerization time, 72 h.

methyldiallylammonium bromide were synthesized using a similar procedure by reaction of methyldiallylamine with 1 equiv of distilled *n*-octyl bromide and *n*-hexyl bromide, respectively. For the hygroscopic materials, often no completely satisfactory elemental analyses could be obtained.

***n*-Decylmethyldiallylammonium bromide (DeMDAABr):** yield 91%; waxlike solid; ^{1}H NMR δ 0.80 (t, 3H), 1.20–1.30 (m, 14H), 1.70–1.85 (m, 2H), 2.95 (s, 3H), 3.10–3.20 (m, 2H), 3.90–4.05 (m, 4H), 5.65–5.80 (m, 4H), 5.90–6.10 (m, 2H). Elem. anal., found Br 23.88, $C_{17}H_{34}NBr$ requires Br 24.04.

***n*-Octylmethyldiallylammonium bromide (OMDAABr):** Yield 95%; yellow oil; ^{1}H NMR δ 0.85 (t, 3H), 1.25–1.40 (m, 10H), 1.70–1.85 (m, 2H), 3.00 (s, 3H), 3.20–3.30 (m, 2H), 3.95–4.05 (m, 4H), 5.65–5.80 (m, 4H), 5.95–6.15 (m, 2H).

***n*-Hexylmethyldiallylammonium bromide (HMDAABr):** yield 92%; yellow oil; ^{1}H NMR δ 0.85 (t, 3H), 1.25–1.40 (m, 6H), 1.70–1.85 (m, 2H), 3.00 (s, 3H), 3.20–3.30 (m, 2H), 3.90–4.00 (m, 4H), 5.65–5.80 (m, 4H), 5.95–6.15 (m, 2H).

Cyclocopolymerizations. The monomers were dissolved under a nitrogen atmosphere in deionized water in a flask equipped with a magnetic stirrer to form a 50% weight solution of monomers. The polymerizations were carried out at 60 °C in the presence of a small amount of *N,N'*-methylenebisacrylamide using ammonium persulfate as the initiator under a nitrogen atmosphere, in which the monomer ratio and content of cross-linking agent were varied. The non-cross-linked copolymers were synthesized under similar polymerization conditions but in the absence of cross-linking agent. The resulting polymer solutions were dialyzed against deionized water using dialysis tubes (Servapore dialysis tubing 29 mm) for 3 days at room temperature to remove unreacted monomers and oligomers. The final solutions were freeze-dried for at least 3 days. The structures of non-cross-linked and cross-linked copolymers were characterized by IR and ^{1}H NMR spectroscopy. No absorptions due to C=C bonds were found. The ^{1}H NMR resonances of the non-cross-linked and cross-linked copolymers could be easily assigned when they were compared with spectroscopic data for structurally related model polymers.[8,16]

Non-cross-linked and cross-linked poly(dimethyldiallylammonium-co-*n*-decylmethyldiallylammonium bromides) (CopolC1-10 and CL-CopolC1-10): white amorphous solids; ^{1}H NMR δ 0.75 (CH_3), 1.20 (CH_2), 1.45 (CH_2), 2.20 (CH(ring, trans)), 2.60 (CH(ring, cis)), 3.00–3.30 (CH_3(N), CH_2(N), CH_2(ring, cis/trans)), 3.75 (CH_2(ring, cis/trans)).

Non-cross-linked and cross-linked poly(dimethyldiallylammonium-co-*n*-octylmethyldiallylammonium bromides) (CopolC1-8 and CL-CopolC1-8): white amorphous solids; ^{1}H NMR δ 0.80 (CH_3), 1.15–1.85 (CH_2), 2.25 (CH(ring, trans)), 2.65 (CH(ring, cis)), 3.00–3.40 (CH_3(N), CH_2(N), CH_2(ring, cis/trans)), 3.75 (CH_2(ring, cis/trans)).

Non-cross-linked and cross-linked poly(dimethyldiallylammonium-co-*n*-hexylmethyl diallylammonium bromides) (CopolC1-6 and CL-CopolC1-6): white amorphous solids; ^{1}H NMR δ 0.80 (CH_3), 1.20–1.90 (CH_2), 2.20 (CH(ring, trans)), 2.65 (CH(ring, cis)), 3.05–3.45 (CH_3(N), CH_2(N), CH_2(ring, cis/trans)), 3.75 (CH_2(ring, cis/trans)).

All non-cross-linked and cross-linked copolymers containing the same alkyl side chain reported in Table 4 showed the same ^{1}H NMR resonances but exhibited small differences in integrations. On the basis of the same polymerization conditions, the molecular weights of the non-cross-linked and cross-linked copolymers are believed to be not significantly different from those of the non-cross-linked and cross-linked homopolymers, respectively.

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Table 4. Compositions of Non-Cross-Linked and Cross-Linked Copolymers Based on ^1H NMR

	feed ratio (%, mol/mol)		found (%, mol/mol)	
copolymers	*n*	*m*	*x*	*y*
CopolC1-10(1)	90	10	89	11
CL-CopolC1-10(2)	90	10	89	11
CL-CopolC1-10(3)	90	10	88	12
CL-CopolC1-10(4)	90	10	90	10
CL-CopolC1-10(5)	80	20	79	21
CL-CopolC1-10(6)	70	30	68	32
CopolC1-8(1)	60	40	60	40
CL-CopolC1-8(2)	60	40	61	39
CL-CopolC1-8(3)	60	40	60	40
CL-CopolC1-8(4)	60	40	59	41
CL-CopolC1-8(5)	80	20	78	22
CopolC1-6(1)	60	40	60	40
CL-CopolC1-6(2)	60	40	60	40
CL-CopolC1-6(3)	60	40	61	39
CL-CopolC1-6(4)	60	40	62	38
CL-CopolC1-6(5)	80	20	80	20
CL-CopolC1-6(6)	40	60	42	58

IR and ^1H NMR Measurements. Infrared spectra were obtained with KBr plates using a Perkin-Elmer 841 infrared spectrophotometer. ^1H NMR spectra were recorded on a VXR 300 MHz instrument for the monomers and all water-soluble copolymers with TMS as an external reference. All ^1H NMR spectra were taken in D_2O except for methyldiallylamine which was taken in $CDCl_3$.

Viscosity Measurements. All polymer solutions were prepared using doubly-distilled water. The reduced viscosities of aqueous polymer solutions were determined in a capillary viscometer of the Ubbelohde type (Scott AVS 400 viscosimeter) in a constant temperature bath at 30 °C. Plots of the reduced viscosity against polymer concentration were nonlinear under these conditions.

UV–Visible Spectral Measurements. UV–vis absorption spectra of Methyl Orange in the presence of the non-cross-linked and cross-linked copolymers were measured on a Philips PU 8740 UV/vis scanning spectrophotometer at 30 °C in aqueous solutions adjusted to pH 9.4 with a 0.02 M sodium borate buffer. The stock solution of Methyl Orange (2.5×10^{-5} M) was made up in doubly-distilled water.

Kinetic Experiments. The cuvette was filled with 2.5 mL of an aqueous solution of the copolymers at pH 11.3 in 0.002 M NaOH, and the solution was equilibrated for 10 min in the thermostated cell compartment (30 ± 0.1 °C) of a Perkin-Elmer λ2 spectrophotometer equipped with a data station. A fresh stock solution (5 μL) of 6-nitrobenzisoxazole-3-carboxylate anion (6-NBIC), which was dissolved in methanol (2.0×10^{-1} M), was added by a microsyringe. The reaction mixture was quickly mixed by shaking, and the absorbance at 410 nm was recorded as a function of time. The first-order rate constants (±1%) for the unimolecular decarboxylation of 6-NBIC were obtained from measurements for at least 5–6 half-lives.

Results and Discussion

Synthesis. Radical initiation has been the most widely employed method for promoting cyclopolymerization, and the mechanism has been studied extensively.[17,18] The synthesis of non-cross-linked and cross-linked copolymers by radical-induced cyclocopolymerization of alkylmethyldiallylammonium bromides in the absence and presence of a small amount of *N,N'*-methylenebisacrylamide using ammonium persulfate as initiator in aqueous solution is represented in Scheme 1. In a typical polymerization, the monomer and cross-linking agent content were varied and elevated temperatures were required to effect cyclopolymerization as lower temperatures resulted in reduced copolymer yields. The polymerization results for (CL)-CopolC1-10, (CL)-CopolC1-8, and (CL)-CopolC1-6 are presented in Tables 1, 2 and 3, respectively. All non-cross-linked and cross-linked copolymers are water-soluble except for CL-CopolC1-8(6) in which the content of the *n*-octyl group is increased to 60% (mol/mol). During the free-radical polymerization of alkylmethyldiallylammonium bromides, several reac-

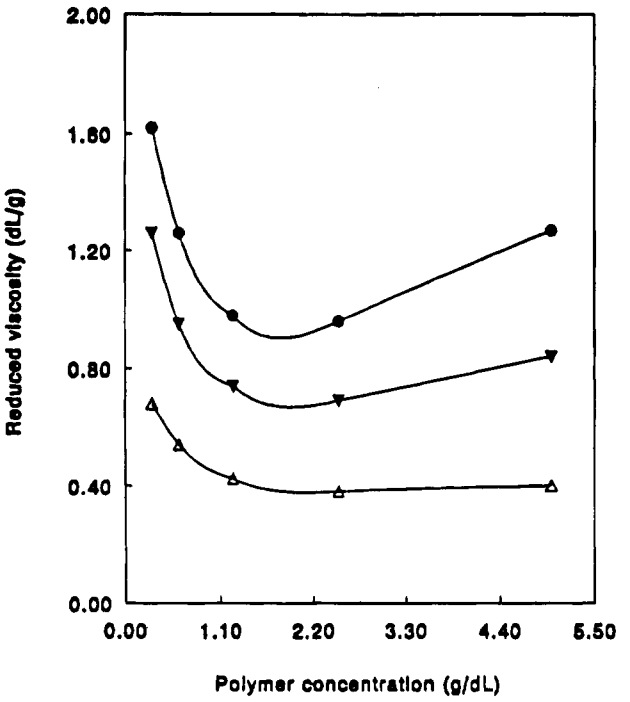

Figure 1. Effect of cross-linking agent content on the reduced viscosity (η_{sp}/c) of CL-CopolC1-10 (*x/y*, 90/10) in aqueous solution at 30 °C: ●, CL-CopolC1-10(4); ▼, CL-CopolC1-10(3); △, CopolC1-10(1).

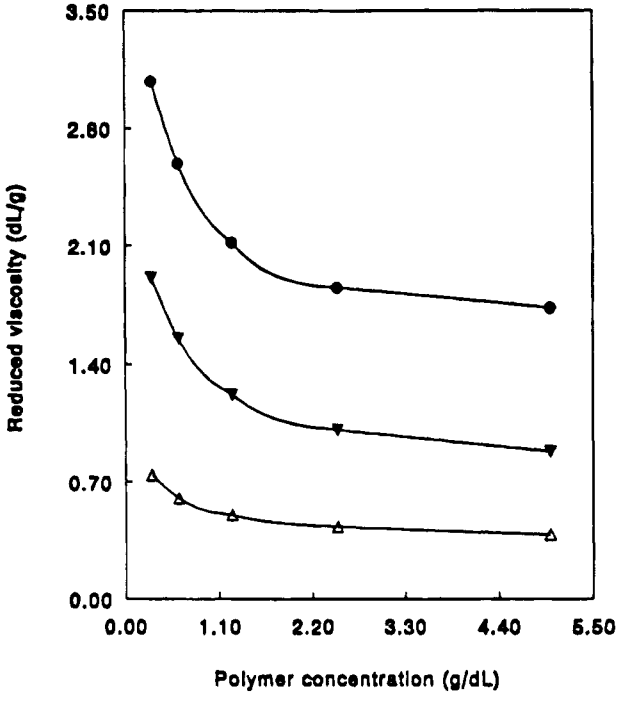

Figure 2. Effect of cross-linking agent content on the reduced viscosity (η_{sp}/c) of CL-CopolC1-8 (*x/y*, 60/40) in aqueous solution at 30 °C: ●, CL-CopolC1-8(4); ▼, CL-CopolC1-8(3); △, CopolC1-8(1).

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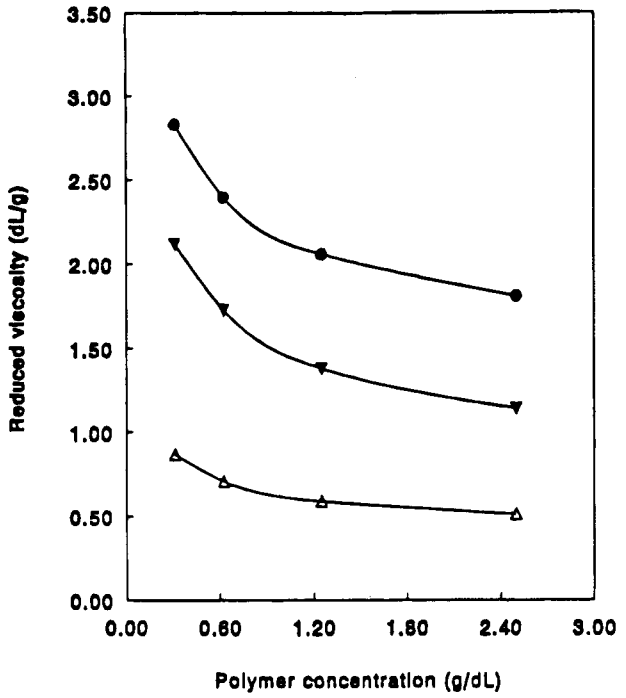

Figure 3. Effect of cross-linking agent content on the reduced viscosity of CL-CopolC1-6 (x/y, 60/40) in aqueous solution at 30 °C: ●, CL-CopolC1-6(4); ▼, CL-CopolC1-6(3); △, CopolC1-6(1).

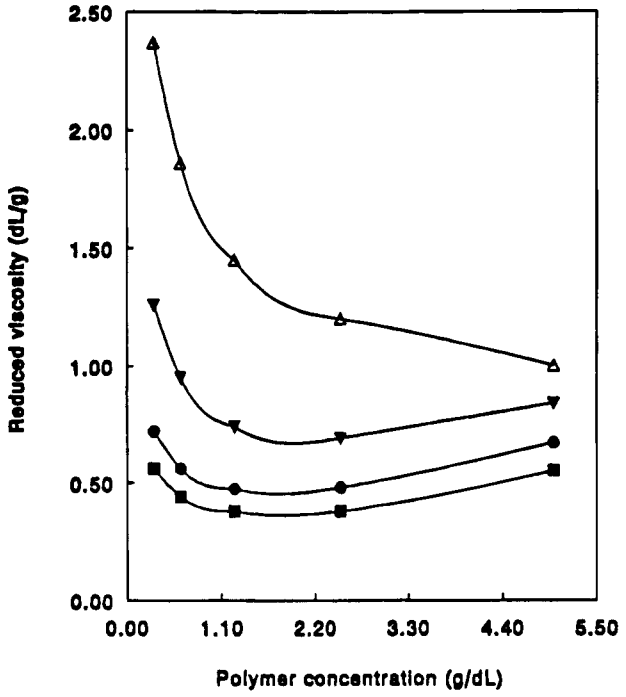

Figure 4. Effect of n-decyl group content on the reduced viscosity (η_{sp}/c) of CL-CopolC1-10 containing 0.40% (w/w) of cross-linking agent in aqueous solution at 30 °C: △, CL-PolC-1(4); ▼, CL-CopolC1-10(3); ●, CL-CopolC1-10(5); ■, CL-CopolC1-10(6).

tion pathways are possible. Reaction of the radical initiator with diene is likely to yield the thermodynamically more stable secondary radical. Ring closure could occur either through an α- or a β-addition process to give either five- or six-membered rings. Although less thermodynamically stable than a secondary radical, a primary radical might also be formed upon radical initiation. Ring closure pathways could then result in either six- or seven-membered rings. To determine the nature of the structural components of the copolymers, the non-cross-linked and cross-linked copolymers were analyzed by infrared and ^{1}H NMR spectroscopy. The infrared spectral data provide only general structural information for the non-cross-linked copolymers (i.e., the presence of NCH_3 groups). However, for the cross-linked copolymers, the NH function present in the macromolecules was observed at 1530 cm^{-1} and the strength of the marked NH absorption band increased with an increase of the cross-linking agent content. These materials are strongly hygroscopic as indicated by the presence of absorption bands of water at 3440, 2080, and 1640 cm^{-1} in their IR spectra. The ^{1}H NMR spectra, which were in agreement with those reported in the literature for structurally related model polymers,[8,16] provide important structural information regarding the composition of the polymers. The macromolecules clearly contain monomer units with five-membered rings cross-linked without and with *N,N'*-methylenebisacrylamide on the basis of their ^{1}H NMR spectroscopic data.[8,16,19] The cross-linked copolymer compositions, which are presumed to be random, were assessed from their ^{1}H NMR spectra by careful integration of relevant peaks.[16] The results are summarized in Table 4. The compositions of (CL)-CopolC1-10, (CL)-CopolC1-8, and (CL)-CopolC1-6 (x/y) are in good agreement with the feed ratio of monomers in the polymerization reactions.

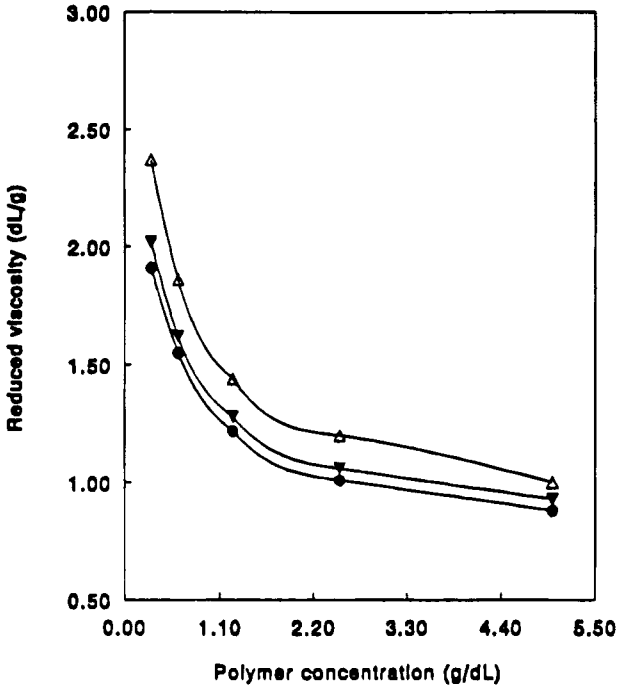

Figure 5. Effect of n-octyl group content on the reduced viscosity of CL-CopolC1-8 containing 0.40% (w/w) of cross-linking agent in aqueous solution at 30 °C: △, CL-PolC-1(4); ▼, CL-CopolC1-8(5); ●, CL-CopolC1-8(3).

Conformational Transition from Polyelectrolytes to Compact Coils. Measurements of reduced viscosity have been extensively used for probing the conformational transition of extended polymer chains to compact coils in aqueous solution.[8,15b,20] Relevant plots of reduced

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(20) (a) Dubin, P. L.; Strauss, U. P. *J. Phys. Chem.* **1970**, *74*, 2842. (b) Strauss, U. P.; Williams, B. L. *J. Phys. Chem.* **1961**, *65*, 1390.

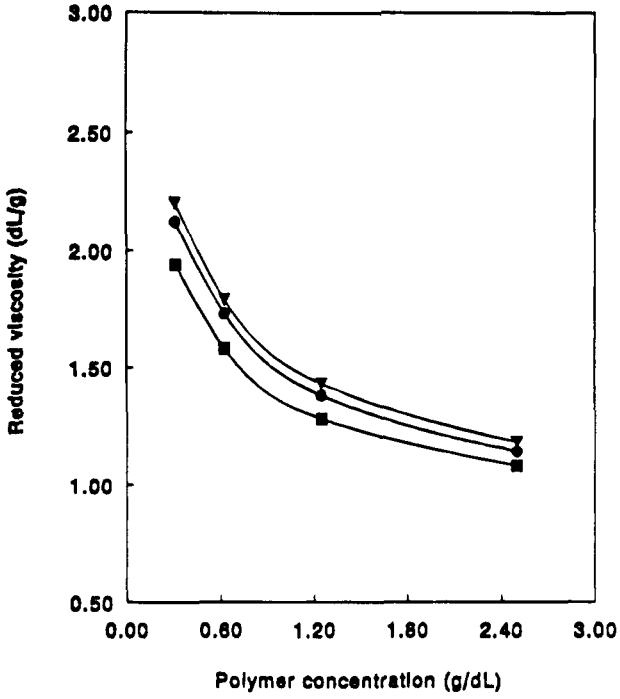


Figure 6. Effect of *n*-hexyl group content on the reduced viscosity of CL-CopolC1-6 containing 0.40% (w/w) of cross-linking agent in aqueous solution at 30 °C: ▼, CL-CopolC1-6(5); ●, CL-CopolC1-6(3); ■, CL-CopolC1-6(6).

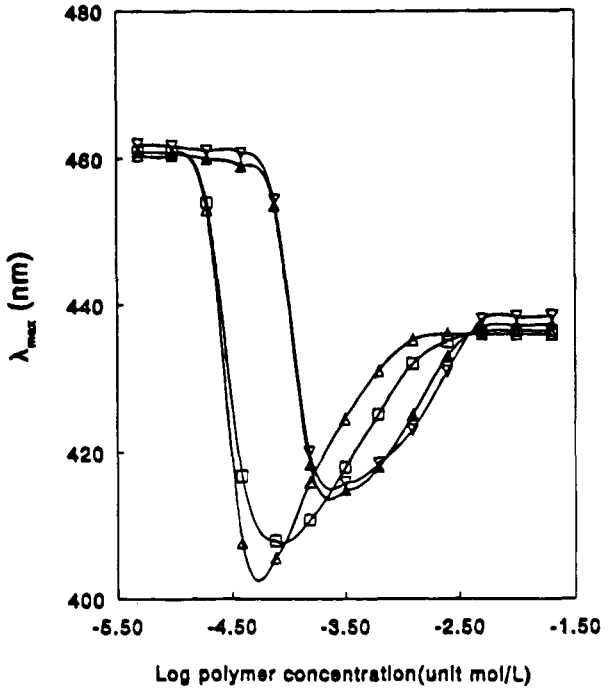


Figure 7. Position of the long-wavelength absorption maximum of Methyl Orange in aqueous solutions in the presence of copolymers at pH 9.4 and 30 °C: ▽, CopolC1-10(1); ▲, CL-CopolC1-10(3); □, CL-CopolC1-10(5); △, CL-CopolC1-10(6).

viscosities vs polymer concentrations as a function of the content of cross-linking agent in CL-CopolC1-10, CL-CopolC1-8, and CL-CopolC1-6 are shown in Figures 1–3.

CL-CopolC1-10, CL-CopolC1-8, and CL-CopolC1-6 exhibit larger reduced viscosities in aqueous solution than the corresponding non-cross-linked copolymer analogue. The reduced viscosity of (CL)-CopolC1-8 and (CL)-CopolC1-6, which is very large at high dilutions due to the extended conformation of the macromolecules, de-

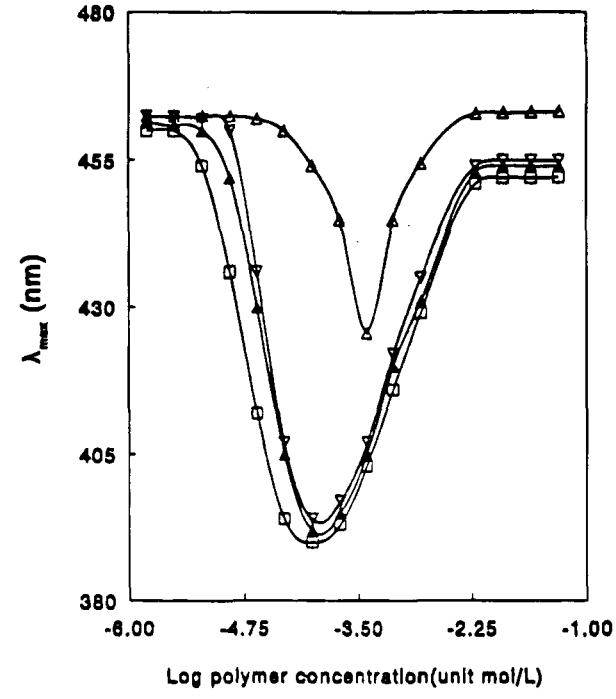


Figure 8. Position of the long-wavelength absorption maximum of Methyl Orange in aqueous solutions in the presence of CL-CopolC1-8 at pH 9.4 and 30 °C: △, CL-CopolC1-8(5); ▽, CopolC1-8(1); ▲, CL-CopolC1−8(2); □, CL-CopolC1-8(3).

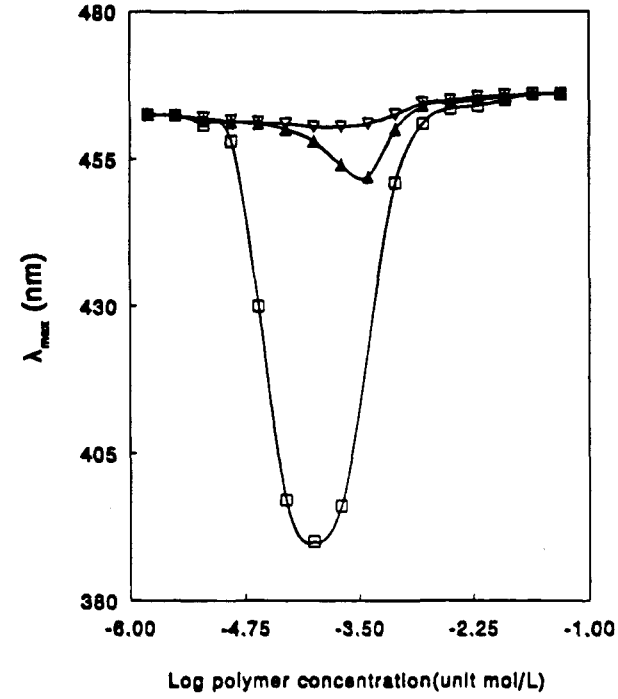


Figure 9. Position of the long-wavelength absorption maximum of Methyl Orange in aqueous solutions in the presence of CL-CopolC1-6 at pH 9.4 and 30 °C: ▽, CopolC1-6(1); ▲, CL-CopolC1-6(3); □, CL-CopolC1-6(6).

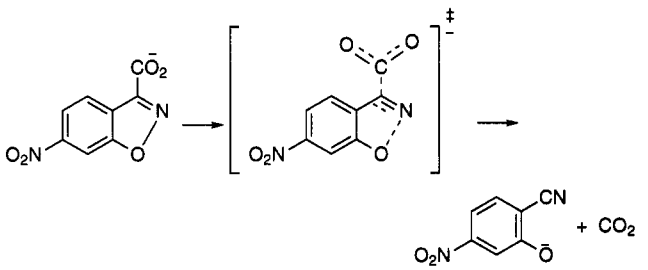
creases with increasing polymer concentration because the electrostatic repulsions between ionized groups are diminished. However, at higher concentration, CL-CopolC1-10 shows an increase of the reduced viscosity in aqueous solution with increasing polymer concentration presumably due to intermolecular aggregation by hydrophobic interactions between decyl groups in different macromolecules.[8] Further support for the intermolecular interactions is provided by the effect of cross-

Table 5. Position of the Long-Wavelength Absorption Maximum of Methyl Orange in Aqueous Solutions of Non-Cross-Linked and Cross-Linked Copolymers at pH 9.4 and 30 °C

copolymer	concn (unit mol/L)	λ_{max}[a] (±1) (nm)
CopolC1-10(1)	1.0×10^{-2}	438
CL-CopolC1-10(2)	1.0×10^{-2}	437
CL-CopolC1-10(3)	1.0×10^{-2}	437
CL-CopolC1-10(4)	1.0×10^{-2}	442
CL-CopolC1-10(5)	2.0×10^{-2}	436
CL-CopolC1-10(6)	2.0×10^{-2}	436
CopolC1-8(1)	1.25×10^{-2}	455
CL-CopolC1-8(2)	1.25×10^{-2}	454
CL-CopolC1-8(3)	1.25×10^{-2}	452
CL-CopolC1-8(4)	1.25×10^{-2}	453
CL-CopolC1-8(5)	1.25×10^{-2}	464
CopolC1-6(1)	2.5×10^{-2}	468
CL-CopolC1-6(2)	2.5×10^{-2}	468
CL-CopolC1-6(3)	2.5×10^{-2}	468
CL-CopolC1-6(4)	2.5×10^{-2}	468
CL-CopolC1-6(5)	2.5×10^{-2}	468
CL-CopolC1−6(6)	2.5×10^{-2}	468

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

Scheme 2



linking agent content in the macromolecules, suggesting that the intermolecular aggregation is clearly dependent upon the detailed structure of the macromolecular chain. Effect of the *n*-decyl group content on the reduced viscosity of the CL-CopolC1-10 with a constant content of cross-linking agent is illustrated graphically in Figure 4. For comparison, the cross-linked homopolymer (CL-PolC-1(4))[8a] containing no hydrophobic side chains is also included in this study. CL-CopolC1-10 exhibits lower reduced viscosities in aqueous solutions than CL-PolC-1(4) at low polymer concentration, which indicates the presence of the compact coil as a result of intramolecular micelle formation.[8,20] Furthermore, on raising the *n*-decyl group content of CL-CopolC1-10, the reduced viscosity is reduced, which suggests that the conformational transition of cross-linked copolymers to compact coils is significantly dependent upon the *n*-decyl group content in the macromolecules.[8] At higher concentration, all CL-CopolC1-10's show a tendency toward intermolecular aggregation brought about by attractions between decyl groups belonging to different macromolecules. The results given in Figure 5 and 6 reveal that the reduced viscosities of (CL)-CopolC1-8 and (CL)-CopolC1-6 are weakly sensitive to changes of the *n*-octyl and *n*-hexyl group contents in the macromolecules. For all (CL)-CopolC1-8 and (CL)-CopolC1-6, the reduced viscosity increases strongly with decreasing polymer concentration, indicative for highly extended molecular chains typical of normal polyelectrolyte behavior.

Hydrophobic Microdomains of Non-Cross-Linked and Cross-Linked Copolymers. The absorption spectrum of the solvatochromic probe Methyl Orange can be employed to probe the formation of hydrophobic microdomains because binding of the dye to hydrophobic

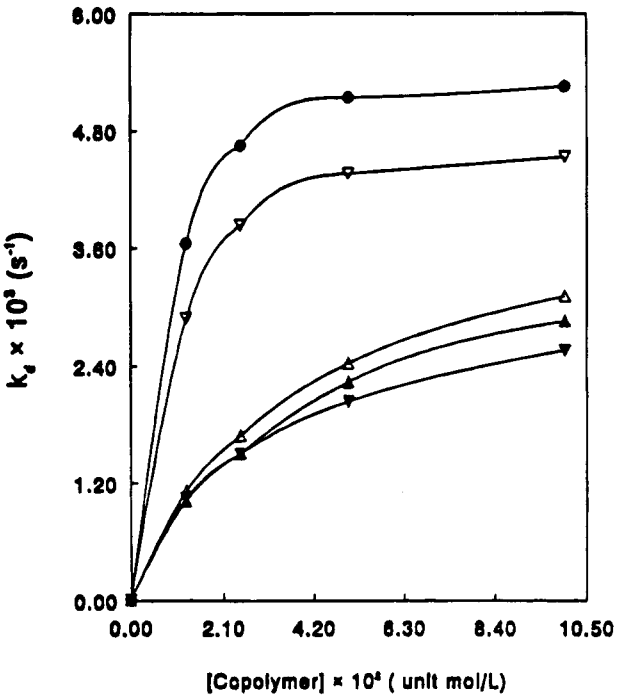


Figure 10. Rate constants for the unimolecular decarboxylation of 6-NBIC in aqueous solutions of non-cross-linked and cross-linked polysoaps at pH 11.3 and 30 °C: ●, CL-CopolC1-10(6); ▽, CL-CopolC1-10(5); △, CL-CopolC1-10(2); ▲, CopolC1-10(1); ▼, CL-CopolC1-10(4).

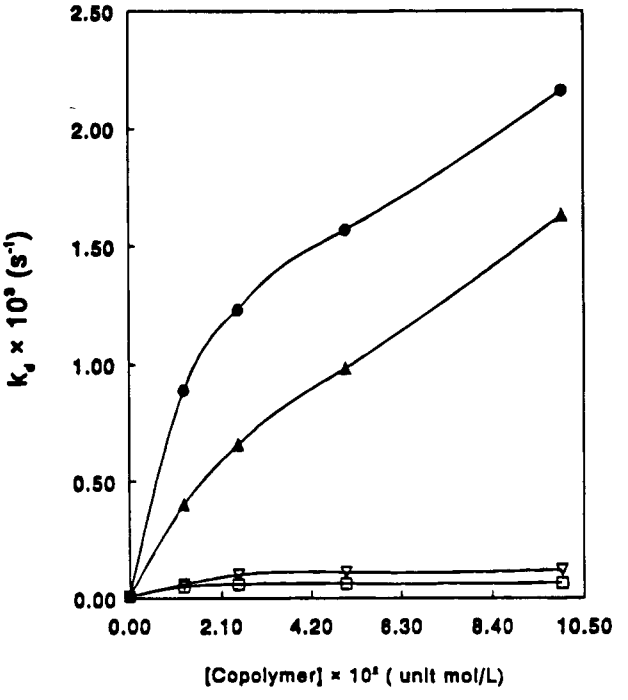


Figure 11. Rate constants for the unimolecular decarboxylation of 6-NBIC in aqueous solutions of the copolymers at pH 11.3 and 30 °C: ●, CL-CopolC1-8(3); ▲, CopolC1-8(1); ▽, CL-CopolC1-8(5); □, CL-CopolC1-6(6).

regions is accompanied by a substantial shift of λ_{max} to shorter wavelengths.[6c,8,21] In order to compare the relative hydrophobicities of the binding sites of copolymers,

(21) Takaghisi, T.; Nakata, Y.; Kuroki, N. *J. Polym. Sci., Polym. Chem. Ed.* **1974**, *12*, 807.
(22) Mooijman, F. R.; Engberts, J. B. F. N. *J. Org. Chem.* **1989**, *54*, 3994.

Table 6. Kinetic Data for Unimolecular Decarboxylation of 6-NBIC Catalyzed by Non-Cross-Linked and Cross-Linked Copolymers Containing Octyl and Hexyl Side Chains in Aqueous Solution at pH 11.3 and 30 °C

copolymer	concn (unit mol/L)	$k_d \times 10^6$ (s^{-1})	k_d/k_w[a]
CopolC1-8(1)	5.0×10^{-2}	984	134
CopolC1-8(1)	1.0×10^{-1}	1630	222
CL-CopolC1-8(2)	5.0×10^{-2}	1320	180
CL-CopolC1-8(3)	5.0×10^{-2}	1570	214
CL-CopolC1-8(3)	1.0×10^{-1}	2160	294
CL-CopolC1-8(4)	5.0×10^{-2}	1310	178
CL-CopolC1-8(5)	5.0×10^{-2}	81	11
CL-CopolC1-8(5)	1.0×10^{-1}	119	16
CopolC1-6(1)	5.0×10^{-2}	43	6
CL-CopolC1-6(2)	5.0×10^{-2}	45	6
CL-CopolC1-6(3)	5.0×10^{-2}	48	7
CL-CopolC1-6(4)	5.0×10^{-2}	50	7
CL-CopolC1-6(5)	5.0×10^{-2}	30	4
CL-CopolC1-6(6)	5.0×10^{-2}	64	9

[a] $k_w = 7.35 \times 10^{-6}$ s^{-1} in aqueous solution at 30 °C.[22]

Table 7. Kinetic Parameters for Unimolecular Decarboxylation of 6-NBIC in Aqueous Solutions in the Presence of Non-Cross-Linked and Cross-Linked Copolymers Carrying a Decyl Side Chain at pH 11.3 and 30 °C

copolymer	$k_m \times 10^3$, s^{-1}	K, M^{-1}	k_m/k_w[a]	γ[b]
CopolC1-10(1)	3.68	30	501	0.995
CL-CopolC1-10(2)	4.09	32	556	0.998
CL-CopolC1-10(3)	3.20	38	435	0.995
CL-CopolC1-10(4)	3.04	42	414	0.998
CL-CopolC1-10(5)	4.97	135	676	0.999
CL-CopolC1-10(6)	5.58	377	759	0.999

[a] k_w=7.35 $\times$ 10^{-6} s^{-1} in aqueous solution.[22] [b] Correlation coefficient in the Menger–Portnoy analysis.[3]

λ_{max} of Methyl Orange was measured in the presence of (CL)-CopolC1-10, (CL)-CopolC1-8, and (CL)-CopolC1-6 at pH 9.4 and 30 °C in aqueous solution (Figures 7–9 and Table 5). The hypsochromic shifts summarized in Table 5 reveal the binding of Methyl Orange to hydrophobic binding sites in the presence of the copolymers. (CL)-CopolC1-10 induced considerable spectral shifts and, as anticipated, the magnitude of the spectral shifts increased with an increase in the *n*-decyl group content. (CL)-CopolC1-8 induced only modest spectral shifts with increasing *n*-octyl group content. No spectral changes of Methyl Orange were observed in the presence of (CL)-CopolC1-6. We contend that solely (CL)-CopolC1-10 with sufficient *n*-decyl side chains forms hydrophobic microdomains in aqueous solution. (CL)-CopolC1-8 apparently shows much less efficient intramolecular micellization in the concentration region investigated. No hydrophobic microdomains are formed in the case of the (CL)-CopolC1-6. In the low concentration range between ca. 10^{-5} and 10^{-3} unit mol/L, all (CL)-CopolC1-10 and (CL)-CopolC1-8 including CL-CopolC1-6(6) show most striking spectral shifts (Figures 7–9), which is attributed to the formation of the hydrophobic microdomains induced by the presence of Methyl Orange.[15b]

Decarboxylation of 6-NBIC Catalyzed by Non-Cross-Linked and Cross-Linked Copolymers. The first-order rate constants (k_d) for the unimolecular decarboxylation of the 6-nitrobenzisoxazole-3-carboxylate anion (6-NBIC, Scheme 2) catalyzed by (CL)-CopolC1-10, (CL)-CopolC1-8, and (CL)-CopolC1-6 have been determined in aqueous solution at pH 11.3 and 30 °C (Figures 10, 11 and Table 6). Previous studies have shown that the cross-linked copolymers containing *n*-dodecyl side chains (CL-CopolC1-12) may induce a rate

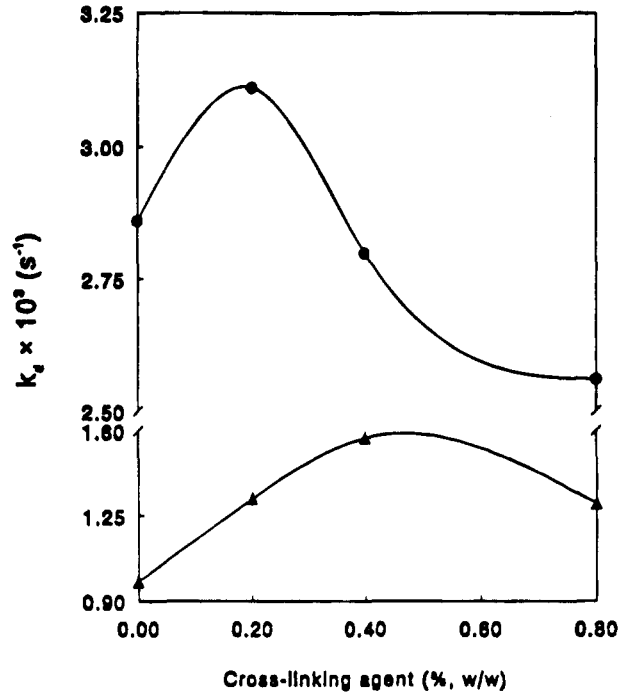


Figure 12. Effect of cross-linking agent content on the rate constant for decarboxylation of 6-NBIC in aqueous solutions of cross-linked copolymers at pH 9.4 and 30 °C: ●, CL-CopolC1-10 (*x*/*y*, 90/10) (1.0×10^{-1} unit mol/L); ▲, CL-CopolC1-8 (*x*/*y*, 60/40) (5.0×10^{-2} unit mol/L).

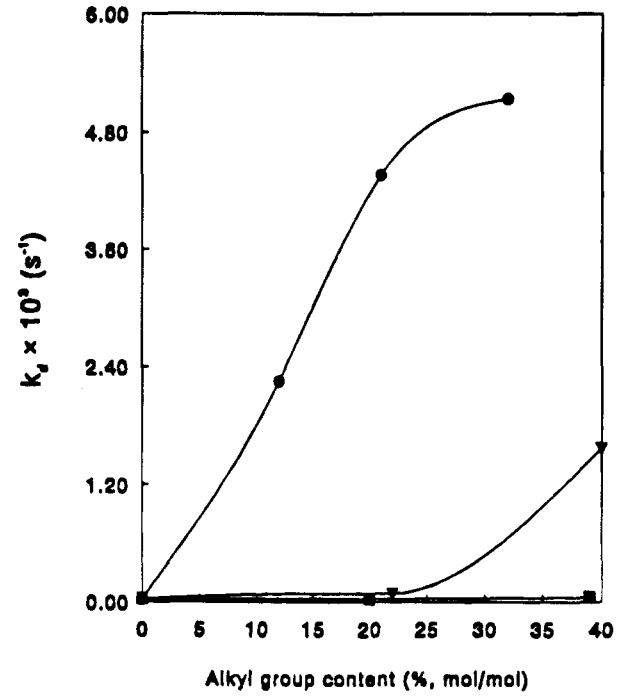


Figure 13. Effect of the alkyl group content on the rate constant for the decarboxylation of 6-NBIC in aqueous solutions of cross-linked copolymers containing 0.40% (w/w) of cross-linking agent (5.0×10^{-2} unit mol/L) at pH 11.3 and 30 °C: ●, CL-CopolC1-10; ▼, CL-CopolC1-8; ■, CL-CopolC1-6.

enhancement of a factor of 1000 or more for the decarboxylation of 6-NBIC.[8a] The results presented in Figure 10 reveal that (CL)-CopolC1-10 also exhibits remarkable catalytic efficiency. The unimolecular decarboxylation is only accelerated by those copolymers which are able to form hydrophobic microdomains as indicated by the spectral shifts of Methyl Orange. The rate constant for

the decarboxylation of 6-NBIC in the presence of CL-CopolC1-10 with a high *n*-decyl group content rapidly increases with increasing polysoap concentration and finally reaches plateau values. (CL)-CopolC1-8 induces only modest rate enhancements for the decarboxylation of 6-NBIC with enhancing *n*-octyl group content, in accord with the notion that they do not form extensive hydrophobic microdomains in aqueous solution. (CL)-CopolC1-6 only induces small rate enhancements in the concentration range studied, indicative for the absence of significant intramolecular micelle formation. Therefore, in this case the kinetic data cannot be analyzed according to the Menger–Portnoy kinetic model.[3] We conclude that in the series of the non-cross-linked and cross-linked copolymers, the rate acceleration for the decarboxylation of 6-NBIC increases with increasing local hydrophobicies in the series (CL)-CpolC1-10 > (CL)-CopolC1-8 > (CL)-CopolC1-6. The kinetic parameters for the unimolecular decarboxylation of 6-NBIC in aqueous solution in the presence of (CL)-CopolC1-10 have been obtained from a kinetic analysis in terms of the Menger–Portnoy model for micellar catalysis[3] (Table 7). Thus, k_m is the unimolecular decarboxylation rate constant for the substrate fully bound to the polysoap, and K (M^{-1}) is the equilibrium constant for the binding of 6-NBIC to the polysoap. We note that the K values strikingly increase with increasing *n*-decyl group content for CL-CopolC1-10, suggesting that hydrophobic interaction of 6-NBIC with the polysoap prior to the catalytic reaction plays an important role in determining the catalytic efficiency. Figure 12 shows the rate constants for decarboxylation of 6-NBIC plotted against the content of the cross-linking agent for CL-CopolC1-10 and CL-CopolC1-8. Clearly, the rate constant for decarboxylation of 6-NBIC is markedly sensitive to changes of the cross-linking agent content in the cross-linked copolymers.

For CL-CopolC1-10, a maximum rate constant is observed at about 0.20% (w/w) cross-linking agent content. CL-CopolC1-8 exhibits a slight rate maximum at about 0.4% (w/w). The results indicate that formation of hydrophobic microdomains for the polysoaps is quite dependent on the detailed structure of macromolecular chains. The presence of a small amount of cross-linking in CL-CopolC1-10 leads to more efficient intramolecular micelle formation as compared with that the corresponding non-cross-linked copolymers.[8] The results given in Figure 13 reveal that decarboxylation rates of 6-NBIC in the presence of CL-CopolC1-10 are drastically enhanced with an increase in the *n*-decyl group content and that CL-CoplC1-10(6) is the most efficient catalyst among the copolymers studied. A modest rate enhancement for the decarboxylation of 6-NBIC is only obtained for CL-CopolC1-8 when the content of the *n*-octyl group is increased to 40% (mol/mol). The decarboxylation rate is not changed for CL-CopolC1-6 when the *n*-hexyl group content is varied from 0 to 38% (mol/mol). Obviously, the catalytic activity of the copolymers is strongly influenced by the total hydrophobicities of the side chains in the macromolecules.

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

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