Synthesis of Hydrophobically and Electrostatically Modified Polyacrylamides and Their Catalytic Effects on the Unimolecular Decarboxylation of 6-Nitrobenzisoxazole-3-carboxylate Anion

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A series of hydrophobically and electrostatically modified polyacrylamides (Copol(AM-C12)) has been synthesized by radical-initiated copolymerization of acrylamide with *n*-dodecylmethyldiallylammonium bromide as the hydrophobe in aqueous solution using ammonium persulfate as the initiator. The formation of hydrophobic microdomains of the copolymers was revealed by large hypsochromic shifts of the long-wavelength absorption band of the solvatochromic probe Methyl Orange, noncovalently bound to the macromolecule. It was found that the microdomains formed by these copolymers in aqueous solution are more hydrophobic than those of the cationic polysoaps poly(alkylmethyldiallylammonium halides) containing the same *n*-dodecyl groups as the side chains as a result of the reduced electrostatic repulsions at the periphery of the microdomains. The reduced cationic character of the copolymers Copol(AM-C12) most likely also accounts for the observation that the anionic dye Methyl Orange does not induce microdomain formation in aqueous solution. The effect of the hydrophobically and electrostatically modified polyacrylamides on the unimolecular decarboxylation of 6-nitrobenzisoxazole-3-carboxylate anion (6-NBIC) has been investigated in aqueous solutions at pH 11.3 and 30 °C. It is suggested that the relatively modest catalytic effects induced by Copol(AM-C12) should be ascribed to hydrogen-bond stabilization of the initial state by NH groups in the macromolecules. The decarboxylation rates of 6-NBIC at binding sites in hydrophobic microdomains increase with increasing *n*-dodecyl group content in the copolymers.

Introduction

Hydrophobically modified polyacrylamides have recently attracted considerable interest.[1-15] Particular emphasis has been placed on their rheological behavior in aqueous solution, as well as on the interactions of these macromolecules with conventional surfactants.[7-15] Copolymers of polyacrylamide with various hydrophobic functionalities are of immediate interest for many industrial applications such as teriary oil recovery and latex paint technology.[5-7] This interest originates mainly from their unique rheological properties in aqueous solution which allow control of their solution viscosity under a variety of shear conditions. When these copolymers are dissolved in water or brine solutions, intermolecular association brought about by attractions between their hydrophobic groups results in a dramatic increase in solution viscosity above a critical polymer concentration and at low shear rates.[8-10] Increased shear rates disrupt the intermolecular interactions between the hydrophobic side chains leading to solutions of low viscosity. As the shear rates are reduced, the intermolecular aggregation of hydrophobic groups belonging to different macromolecules is regenerated and the solution viscosity returns to its original value. Furthermore, polyacrylamides modified with relatively low amounts of hydrophobic comonomers exhibit interesting rheological behavior in aqueous solution in the presence of conventional surfactants.[13-15] An associative phase separation, in which both phases contain copolymers and surfactants, has been found in a mixture of hydrophobically modified polyacrylamide and sodium dodecyl sulfate (SDS) in aqueous solution.[15]

Radical-initiated polymerization of (substituted) acrylamides in aqueous solution has been the most widely employed method for preparing polyacrylamides, and the mechanism has been studied extensively.[16-18] Since hydrophobic monomers such as long-chain *N*-alkylacrylamides are insoluble in water, the copolymers of acrylamide and *N*-alkylacrylamide are usually synthesized by specialized copolymerization techniques such as the use

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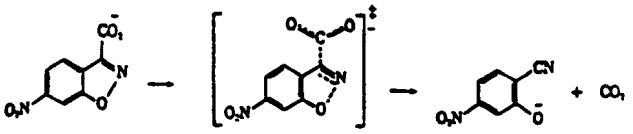
Scheme 1



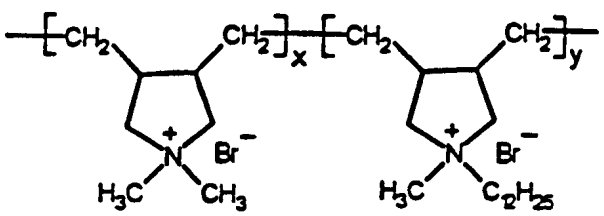
of a solvent mixture[15,19] and microemulsion or micellar polymerization.[11,12,20,21]

In this paper we describe the synthesis of a series of novel copolymers of acrylamide with water-soluble *n*-dodecylmethyldiallylammonium bromide in which the content of the *n*-dodecyl group was varied between 2.0 and 10% (mol/mol) in aqueous solution. Solvatochromic probe Methyl Orange was used to probe the formation of hydrophobic microdomains from the copolymers in aqueous solution.

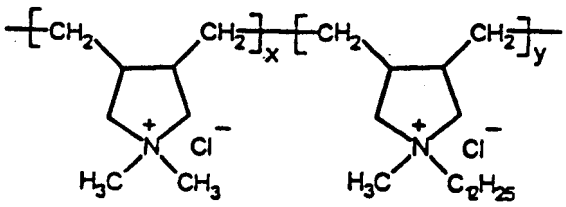
The unimolecular decarboxylation of 6-nitrobenzisoxazole-3-carboxylate anion (6-NBIC, Scheme 1) is notable for its remarkable sensitivity to the reaction medium.[22-31] Kemp et al.[22-25] observed that the decarboxylation rate is retarded by solvents that can form hydrogen bonds to the reactant carboxylate. The presence of an intramolecular hydrogen bond in 4-hydroxybenzisoxazole-3-carboxylate anion leads to slow decarboxylation rates in all solvents.[24] Recent multiple linear regression analysis of solvent effects on the reaction of 6-NBIC clearly revealed the importance of the hydrogen bonding effect as a major factor in determining the decarboxylation rates.[32-34]

Our previous studies[35-39] have provided strong evidence that hydrophobically modified poly(alkylmethyldiallylammonium bromides) and poly(alkylmethyldiallylammonium chlorides) which contain n-dodecyl side chains (CopolC1-12 and CopolC1-12-Cl, respectively, Chart 1) possess similar aggregate properties in aqueous solution as a result of intra- and intermolecular hydrophobic interactions between the alkyl side chains. Both CopolC1-12 and CopolC1-12-Cl induce large rate accelerations for the unimolecular decarboxylation of 6-NBIC in aqueous solution.[35,36] Polysoaps with chloride counterions are more efficient catalysts than the corresponding polysoaps with bromide counterions owing to the smaller chloride counterions binding to the cationic groups at the periphery of the hydrophobic microdomains leading to increased initial state destabilization.[35,36] Herein we report a detailed characterization of hydrophobically and electrostatically modified polyacrylamides that display significant catalytic effects on the unimolecular decarboxylation of 6-NBIC in aqueous solution. It is suggested that the decarboxylation rate is significantly retarded by intermolecular hydrogen bonding of the macromolecules to the carboxylate functionality of 6-NBIC at binding sites in the hydrophobic microdomains.

Chart 1



CopolC1-12



CopolC1-12-Cl

Experimental Section

Materials and Reagents. The syntheses of *n*-dodecylmethyldiallylammonium bromide monomer, poly(dimethyldiallylammonium-*co*-*n*-dodecylmethyldiallylammmonium bromides) (CopolC1-12(88/12) (*x*/*y*: 88/12)) and poly(dimethyldiallylammonium-*co*-*n*-dodecylmethyldiallylammmonium chlorides) (CopolC1-12-Cl (89/11) (*x*/*y*: 89/11)) have been described previously.[35,36] Acrylamide (AM) monomer (Janssen) was recrystallized from acetone and vacuum dried at room temperature before use. Ammonium persulfate was purchased from Janssen. Methyl Orange (Aldrich) was used as received. 6-Nitrobenzisoxazole-3-carboxylate (6-NBIC) was prepared according to a standard procedure.[29]

Copolymerizations. The hydrophobically and electrostatically modified polyacrylamides were synthesized by radical copolymerization of acrylamide dissolved in deionized water (6%, w/w) with *n*-dodecylmethyldiallylammonium bromide in a flask equipped with a magnetic stirrer using commercial grade ammonium persulfate as the initiator under a nitrogen atmosphere at 50 °C. In these copolymerization reactions the monomer ratio was varied (Table 1). The homopolymer polyacrylamide was also synthesized under similar polymerization conditions but in the absence of hydrophobic monomer. After a reaction time of 18 h, the reaction solution was cooled and dialyzed against deionized water using dialysis tubes (Servapore dialysis tubing 29 mm) for at least 5 days at room temperature to remove unreacted monomers and oligomers. The polymerization solutions of the copolymers were gel-like, had very high viscosities, and were difficult to handle when removing from three-necked flask and dialysis tube. The viscosity of the copolymer solutions increases strongly upon increasing *n*-dodecyl group content in the copolymers. The final solution was subsequently freeze-dried for at least 3 days. The structures of the obtained copolymers were characterized by their ^{1}H-NMR spectra. No

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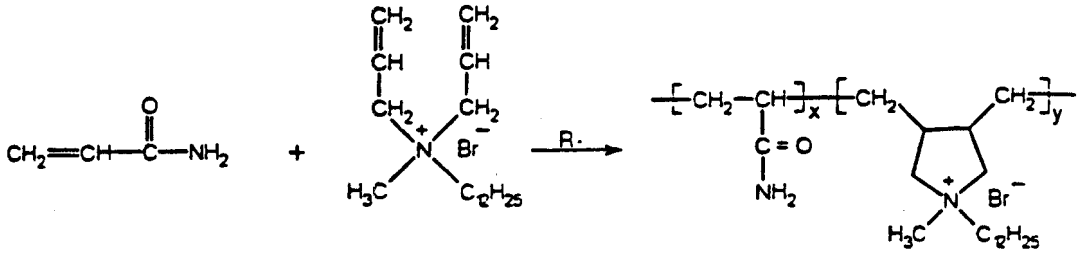
Table 1. Copolymerization of Acrylamide with *n*-Dodecylmethyldiallylammonium Bromide in Aqueous Solution

(co)polymer (*x/y*)	AM[a] (mol)	DMDAABr[b] (mol)	(AM)/(DMDAABr) (mol/mol)	APS[c] (mg)	yield[d] (%)	water solubility
Pol(AM)	0.038	0.0000	100/0	1.0	95	soluble
Copol(AM-C12)(98/2)	0.036	0.0007	98/2	1.0	91	soluble
Copol(AM-C12)(95/5)	0.036	0.0019	95/5	1.0	85	soluble
Copol(AM-C12)(90/10)	0.036	0.0040	90/10	1.2	81	soluble

[a] Acrylamide. [b] *n*-Dodecylmethyldiallylammonium bromide. [c] Ammonium persulfate. [d] Polymerization time 18 h.

Scheme 2



Copol(AM-C12)

olefinic proton resonances are present in the spectra of the copolymers. All ^{1}H-NMR resonances of the copolymers could be easily assigned upon comparison with spectroscopic data for structurally related polymers.[35,36,40,41] The copolymers reported in Table 1 showed the same ^{1}H-NMR resonances but exhibit small differences in signal integrations. As the copolymers are made at relatively high conversion, they probably have broad molecular weight distributions and copolymer compositions due to the fact that the acrylamide is much more reactive than *n*-dodecylmethyldiallylammonium bromide[1,3a] in polymerization processes.

Poly(acrylamide-*co*-*n*-dodecylmethyldiallylammonium bromides) (Copol(AM-C12)). White amorphous solids; ^{1}H-NMR *d* 0.75 (CH_3), 1.15 (CH_2), 1.35-1.75 (CH_2), 2.05-2.55 (CH(C=O), CH(ring, trans), CH(ring, cis)), 3.00-3.25 (CH_3(N), CH_2(N), CH_2(ring, cis/trans)), 3.65 (CH_2(ring, cis/trans)) ppm. No other resonances were observed.

The polymer solutions for UV-vis spectral and kinetic measurements were prepared using double-distilled water. The copolymers had a slower dissolution rate than that of polyacrylamide. Often considerable time (ca. 48 h) was needed for complete dissolution of the macromolecules.

^{1}H-NMR Measurements. ^{1}H-NMR spectra were recorded on a VXR 300 MHz instrument using TMS as an external reference. AlI NMR spectra for the monomers and (co)polymers were taken in D_2O.

UV-Vis Spectral Measurements. A solution of Methyl Orange (2.5×10^{-5} M) was made up in double-distilled water. UV-vis absorption spectra of Methyl Orange in the presence of (co)polymers were determined using a Philips PU 8740 UV-vis scanning spectrophotometer in aqueous solutions adjusted to pH 9.4 with a 0.02 M sodium borate buffer at 30 °C.

Kinetic Experiments. A 2.5-mL portion of a solution of the (co)polymers in a 2.0×10^{-3} M aqueous NaOH solution (pH 11.3) was added to the cell and the solution was equilibrated for 10 min in the thermostated cell compartment (30 ± 0.1 °C) of a Perkin-Elmer *l*2 spectrophotometer equipped with a data station. A fresh stock solution (5 *m*L) of 6-nitrobenzisoxazole-3-carboxylate anion (6-NBIC) 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 by monitoring the reaction for at least 5-6 half-lives.

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Results and Discussion

Synthesis. In previous studies we have used *n*-dodecylmethyldiallylammonium bromide as a water-soluble hydrophobic co-monomer in the synthesis of cationic polysoaps which formed hydrophobic microdomains in aqueous solution.[35,37,38] The co-monomer possesses both the electrolytic and hydrophobic character of a polymerizable surfactant which can form micelles at concentrations above the critical micelle concentration (cmc) in aqueous solution.[28b] We have now employed the same hydrophobic monomer for the preparation of a series of hydrophobically and electrostatically modified polyacrylamides. The radical-induced copolymerization of acrylamide with *n*-dodecylmethyldiallylammonium bromide using ammonium persulfate as initiator is depicted in Scheme 2. The kinetics of similar radical-initiated polymerizations of acrylamide in aqueous solution have been extensively studied.[18,42] In our experiments, the content of the hydrophobic monomer was varied between 2.0 and 10% (mol/mol). Synthetic details and the nomenclature used in the text are shown in Table 1. The Copol(AM-C12) macromolecules are all water-soluble. The structures and compositions of the copolymers were analyzed by ^{1}H-NMR spectroscopy. The ^{1}H-NMR resonances of the copolymers were completely reconcilable with the structures proposed for the hydrophobically and electrostatically modified polyacrylamides (Scheme 2). The copolymers of the hydrophobic monomer and acrylamide by radical-initiated copolymerization in aqueous solution are presumed to be random. However, it may be possible that blocky microstructures are formed during the copolymerization with acrylamide due to the formation of the micelles by the polymerizable surfactant, providing a high concentration of the reactive allyl groups in the micelles.[3a] The copolymer compositions (*x/y*) were obtained from integration of relevant peaks and were consistent with the feed ratio of monomers in the polymerization processes.

Hydrophobic Microdomains of the Hydrophobically and Electrostatically Modified Polyacrylamides Copol(AM-C12). The solvatochromic dye Methyl Orange is a sensitive probe to explore the formation of hydrophobic microdomains in a compact coil conformation of a macromolecule in aqueous solution.[35,37] The nonco-

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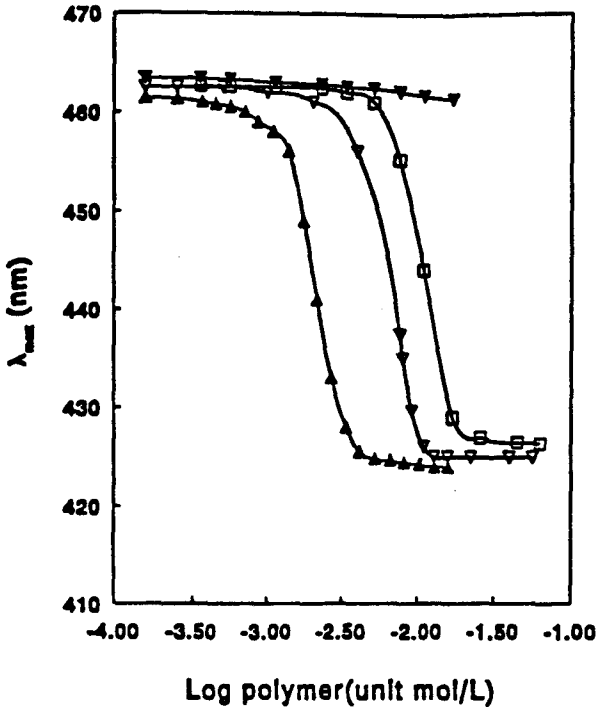

Figure 1. Position of the long-wavelength absorption maximum of Methyl Orange in aqueous solutions in the presence of (co)polymers at pH 9.4 and 30 °C: ▼, Pol(AM); ❑, Copol(AM-C12)(98/2); ∇, Copol(AM-C12)(95/5); ▲, Copol(AM-C12)(90/10).

valent binding of Methyl Orange to the hydrophobic aggregates is reflected by a hypsochromic shift of the long-wavelength absorption band. Figure 1 shows the position of the long-wavelength absorption maximum (l_{max}) of Methyl Orange (2.5×10^{-5} M) in the presence of the (co)-polymers in aqueous solution as a function of polymer concentration at pH 9.4 and 30 °C. As anticipated, no spectral changes of Methyl Orange were found in the presence of homopolymer Pol(AM) in the concentration range investigated. At low copolymer concentration no significant spectral shifts were observed, indicating that Methyl Orange resides in an aqueous environment. Upon increasing copolymer concentration, substantial spectral shifts are observed and the magnitude of the spectral shifts increases with an increase in the *n*-dodecyl group content of Copol(AM-C12). This indicates that Methyl Orange is bound at hydrophobic binding sites located in hydrophobic aggregates in aqueous solution. It is noted that the copolymers containing even small quantities of the hydrophobic groups (i.e. 2.0% (mol/mol)) exhibit considerable spectral shifts with increasing copolymer concentration. For comparison, the cationic polysoaps (Chart 1) containing the same *n*-dodecyl groups as the hydrophobic side chains (CopolC1-12(88/12) and CopolC1-12-Cl(89/11)) are also included in this study. The hypsochromic shifts are presented in Table 2, where the l_{max} of Methyl Orange at high copolymer concentration is given for the different (co)polymers. The data reveal that microdomains formed by Copol(AM-C12) in aqueous solution are more hydrophobic than the corresponding domains formed by CopolC1-12(88/12) and CopolC1-12-Cl(89/11). This result may be rationalized in terms of the smaller electrostatic repulsions in the macromolecular chains of the copolymers Copol(AM-C12) which leads to the formation of more compact polymer coils. Relevant plots of l_{max} of Methyl Orange vs polymer concentration as a function of the structure of different polysoaps bearing the same hydrophobic side chains are shown in Figure 2. Both CopolC1-12(88/12) and CopolC1-12-Cl(89/11) display striking spec-

Table 2. Position of the Long-Wavelength Absorption Maximum of Methyl Orange in Aqueous Solution of the (Co)polymers at pH 9.4 and 30 °C

(co)polymer	concentration (unit mol/L)	l_{max}[a] (±1) (nm)
CopolCl-12(88/12)	1.0×10^{-2}	432
CopolCl-12-Cl(89/11)	1.0×10^{-2}	432
Pol(AM)	1.0×10^{-2}	462
Copol(AM-C12)(98/2)	2.5×10^{-2}	427
Copol(AM-C12)(95/5)	1.25×10^{-2}	425
Copol(AM-C12)(90/10)	1.25×10^{-2}	424

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

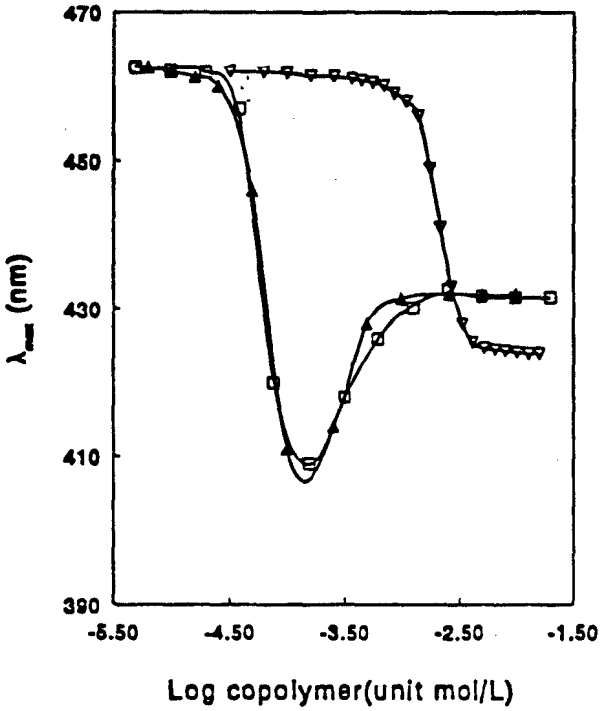

Figure 2. Position of the l_{max} of Methyl Orange in aqueous solutions in the presence of different copolymers containing the same hydrophobic side chains at pH 9.4 and 30 °C: ∇, Copol(AM-C12)(90/10); ▲, CopolC1-12(88/12); ❑, CopolC1-12-Cl(89/11).

tral shifts in the low concentration range between ca. 10^{-5} to 10^{-3} unit mol/L due to the formation of the hydrophobic microdomains induced by the presence of Methyl Orange. A similar dye-induced aggregation process was not observed for Copol(AM-C12)(90/10). Apparently there is much less electrostatic interaction between Copol(AM-C12) and dye molecule, consistent with the notion that the induction of hydrophobic aggregation at low concentrations is governed by both electrostatic and hydrophobic interactions.[37]

The Unimolecular Decarboxylation of 6-NBIC Catalyzed by the Hydrophobically and Electrostatically Modified Polyacrylamides Copol(AM-C12). As reported previously,[35,36] both CopolC1-12 and CopolC1-12-Cl induce large rate enhancements for the unimolecular decarboxylation of 6-nitrobenzisoxazole-3-carboxylate anion (6-NBIC) in aqueous solution. In the present study we have examined the effect of the Copol(AM-C12) copolymers on the unimolecular decarboxylation of 6-NBIC, in order to probe how the rate of the model reaction responds to the nature of the hydrophobic microdomains. Figure 3 shows the first-order rate constants (k_d) for the unimolecular decarboxylation of 6-NBIC catalyzed by Copol(AM-C12) in aqueous solution as a function of copolymer concentration at pH 11.3 and 30 °C. Copol-

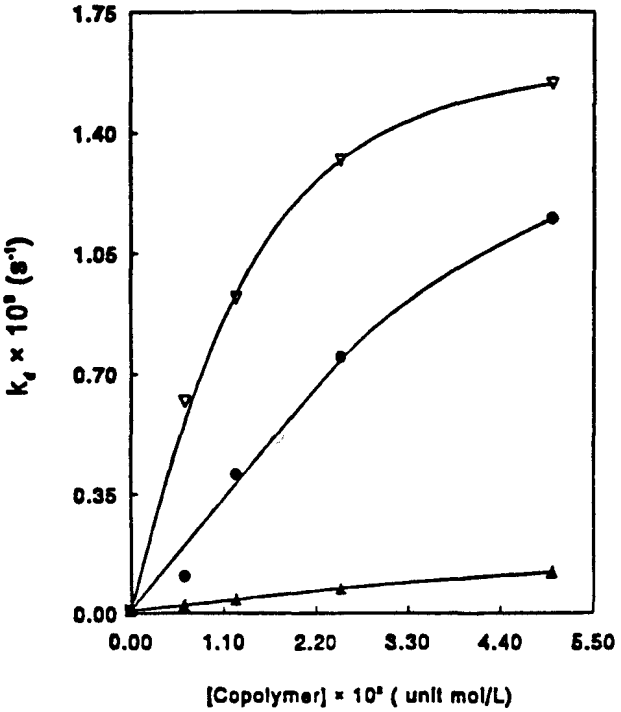

Figure 3. Rate constants (k_d) for the unimolecular decarboxylation of 6-NBIC in aqueous solutions of copolymers at pH 11.3 and 30 °C: ∇, Copol(AM-C12)(90/10); ●, Copol(AM-C12)(95/5); ▲, Copol(AM-C12)(98/2).

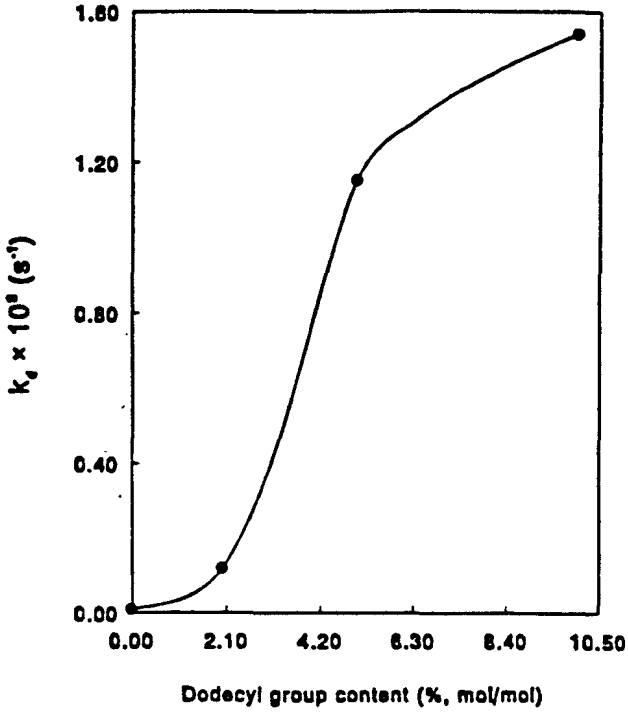

Figure 4. Effect of the *n*-dodecyl group content on the rate constant for the unimolecular decarboxylation of 6-NBIC catalyzed by copolymers Copol(AM-C12) (5.0×10^{-2} unit mol/L) in aqueous solution at pH 11.3 and 30 °C.

(AM-C12)(90/10) was found to exhibit only a modest catalytic efficiency for the unimolecular decarboxylation of 6-NBIC. The rate constants for the decarboxylation of 6-NBIC catalyzed by Copol(AM-C12)(90/10) and Copol-(AM-C12)(95/5) increased with increasing copolymer concentration. However, no plateau values in rate constants were observed in plots of rate costants vs copolymer concentration in the concentration range studied. This is indicative for relatively weak binding of 6-NBIC to the compact coils. It is noted that Copol(AM-C12)(98/2), which is undoubtedly able to form hydrophobic microdomains in aqueous solution as indicated by the substantial spectral shifts of Methyl Orange (vide supra), only induced small rate enhancements for decarboxylation of 6-NBIC. Consistent with the observations based on UV-vis spectroscopy, Pol(AM) has no significant effect on the unimolecular decarboxylation of 6-NBIC in aqueous solution due to the absence of compact coil conformations. A plot of the rate constants for the unimolecular decarboxylation of 6-NBIC against the *n*-dodecyl group content for Copol(AM-C12) is presented in Figure 4.

The data reveal that the copolymers Copol(AM-C12) exhibit a rapid increase in rate constants for decarboxylation of 6-NBIC when the *n*-dodecyl group content is increased from 2.0 to 5.0% (mol/mol). Figure 5 shows the rate constants for the unimolecular decarboxylation of 6-NBIC catalyzed by different types of copolymers containing the same hydrophobic side chains in aqueous solution as a function of the detailed structures of the macromolecules. Clearly the rate acceleration for decarboxylation of 6-NBIC is markedly dependent on the detailed structures of the macromolecules. As a result of the smaller chloride counterion binding to the cationic groups at the periphery of the hydrophobic microdomains, CopolC1-12-Cl is the most efficient catalyst for the 6-NBIC decarboxylation.[36] We suggest that the relatively small rate acceleration for decarboxylation of 6-NBIC catalyzed by Copol(AM-C12) may be the result of hydrogen bonding by NH moieties of the macromolecules to the carboxylate functionality at binding sites in hydrophobic micro-

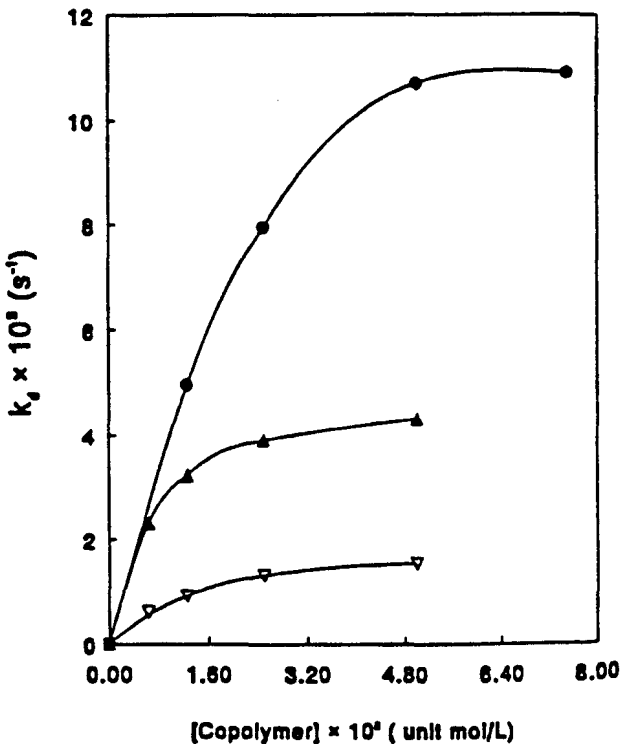

Figure 5. Rate constants for the unimolecular decarboxylation of 6-NBIC in aqueous solutions of different copolymers containing the same hydrophobic side chains at pH 11.3 and 30 °C: ●, CopolC1-12-Cl(89/11); ▲, CopolC1-12(88/12); ∇, Copol(AM-C12)(90/10).

domains. These hydrogen-bonding interactions stabilize the initial state of the reaction and reduce the efficiency of the catalytic effects on the decarboxylation. The hydrogen-bond donors provided by the macromolecules are apparently less effictive than water in retarding the decarboxylation process since Pol(AM) induces no appreciable effect on decarboxylation of 6-NBIC. The copolymers CopolC1-12 and CopolC1-12-Cl do not carry

hydrogen-bonding donor groups. In addition, there is a much higher positive charge at the periphery of the microdomains, leading to much stronger binding of 6-NBIC.

Conclusions

Hydrophobically and electrostatically modified polyacrylamides Copol(AM-C12) were found to form more strongly hydrophobic microdomains in a compact coil conformation in aqueous solution as compared with the corresponding poly(alkylmethyldiallylammonium halides) containing the same hydrophobic side chains as a result of the smaller electrostatic repulsions at the periphery of the domains. The unimolecular decarboxylation of 6-nitrobenzisoxazole-3-carboxylate anion (6-NBIC) is markedly dependent on the detailed structures of the macromolecules. It is suggested that the catalytic efficiency of the copolymers Copol(AM-C12) for the unimolecular decarboxylation of 6-NBIC in aqueous solution is reduced by hydrogen bonding of NH groups of the macromolecules to the carboxylate functionality of 6-NBIC at binding sites in hydrophobic microdomains.

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