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Microstructure, Neighboring Group Inhibition, and Electrostatic Effects in the Base-Catalyzed Degradation of Polyacrylamide[1]

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ABSTRACT: The degradation of polyacrylamide in basic solution has an extremely fast component characterized by the buildup and disappearance of an imide absorption band at 235 nm. Comparison with the behavior of low molecular weight model compounds shows that such imides are formed from monomer residues added head-to-head. Results suggest that 4.5% of amide groups belong to such pairs of residues and that about two-thirds of these have the racemic configuration. Initial amide hydrolysis rates of polyacrylamide and acrylamide–acrylic acid copolymers in 0.2 N NaOH at 53 °C showed that the reactivities of amide groups with one and two nearest-neighbor carboxyls are reduced by factors of 0.108 and 0.013, respectively, relative to amides flanked by two amide groups. Using these data to predict the course of polyacrylamide hydrolysis, we find that Keller's theory of polymer reactions with neighboring group effects is able to match experimental results in the early stages of the process but leads to low estimates for the conversion at high reaction times. The assumption that the electrical free energy of activation for the hydroxyl ion attack on chains with acrylamide and acrylic acid residues is equal to the electrical free energy of ionization for partially ionized poly(acrylic acid) with the same charge density leads to satisfactory predictions for the reactivity of random copolymers of acrylamide and acrylic acid but underestimates grossly the decrease in the rate constant with an increasing hydrolysis of polyacrylamide. The inadequacy of Keller's model to account fully for the course of polyacrylamide hydrolysis is due to long-range electrostatic effects and possibly to the effect of stereoisomerism.

The reaction kinetics of polymers carrying closely spaced reactive chain substituents are frequently complicated by the effect exerted by a reacted group on the reactivity of its unreacted neighbor.[2,3] The reaction kinetics of vinyl polymers in which each monomer residue carries a reactive substituent subject to such "neighboring group effects" exhibits then a complex pattern requiring the specification of at least three rate constants, k_0, k_1, and k_2, characterizing the reactivity of residues with 0, 1, and 2 reacted neighbors, respectively, and Keller[4] derived an expression for the course of such a reaction.

Unfortunately, relatively few polymer reactions lend themselves to a complete comparison with the predictions based on Keller's analysis, since for such transformations solvents for the initial polymer will usually not dissolve the reaction product. Yet, such a comparison is no idle exercise since Keller's model lacks some features which further complicate the reactivity of macromolecules. In many cases[5–9] neighboring group effects on the reactivity of a polymer substituent have been shown to depend on the stereoisomerism of the chain molecules. In addition, when the reaction leads to the generation of ionic charges on the polymer chain, charge effects on the reactivity of a chain substituent need not be limited to charges carried by the nearest-neighbor monomer residues.

The base-catalyzed hydrolysis of polyacrylamide has been previously interpreted by Higuchi and Senju[10] in terms of the three characteristic rate constants with $k_1/k_0 = 0.25$ and $k_2/k_0 = 0.005$. Like other workers[11] studying such complex polymer reaction kinetics, Higuchi and Senju obtained their k_0, k_1, and k_2 values as the best fit to their kinetic curve. It seemed to us that a more stringent test of the theory should involve the derivation of these rate constants from the initial amide hydrolysis rates of polyacrylamide and acrylamide–acrylic acid copolymers. The course of the polyacrylamide hydrolysis could then be compared with that predicted on the basis of these rate constants.

Another possible approach to the interpretation of the kinetics of the basic hydrolysis of polyacrylamide would interpret the decrease in the rate constant with increasing conversion as a consequence of the increasing negative polymer charge opposing the approach of the catalyzing hydroxyl ion. Such an effect was first described by Deuel et al.[12] in their study of the basic hydrolysis of pectin, a partially esterified acidic polysaccharide. They proved qualitatively the electrostatic origin of the decreasing polymer reactivity by showing that the shielding of the charge of the polyion by added NaCl leads to a large acceleration of the reaction. Later, Katchalsky and Feitelson[13] showed that the data of Deuel et al. can be interpreted quantitatively on the basis of the reasonable assumption that the electrostatic work required to remove a hydrogen ion from a carboxyl of a partially hydrolyzed pectin molecule is equal to the electrostatic work required to bring a catalyzing hydroxyl ion into the vicinity of an ester group against the polyion repulsion. Thus, if k is the effective rate constant for the reaction of a charged polymer molecule and k^0 is the corresponding rate constant of an uncharged analogue, K_a is the acid dissociation constant of the polymer and K_a^0 that of its uncharged analogue

$$k = k^0 \exp(-\Delta G^{*}_{\mathrm{el}}/RT)$$
$$K_a = K_a^0 \exp(-\Delta G^{i}_{\mathrm{el}}/RT) \qquad (1)$$

the equality of the electrostatic free energy of activation, $\Delta G^{*}_{\mathrm{el}}$, and of ionization, $\Delta G^{i}_{\mathrm{el}}$, implies that $k/k^0 = K_a/K_a^0$. If such a treatment were applicable to the basic hydrolysis of polyacrylamide, the course of the reaction should be predictable from the dependence of the ionization content of poly(acrylic acid) on its charge density.

Early studies of the reaction in this laboratory revealed an unexpected complication: When polyacrylamide was exposed to a basic medium, ammonia was released very rapidly from a small fraction of the amide groups with the appearance and decay of an absorption due to imide.[14] By comparing the polymer behavior with that of succinamide and glutaramide, we found that this imide formation results from amide groups attached to neighboring carbons of the polyacrylamide chain backbone; i.e., it furnishes an analytical method for the estimation of polymer residues added head-to-head.[15]

This report has then two objectives. First, it aims at a detailed interpretation for the imide formation observed when polyacrylamide is placed in a basic medium. Second, it assesses the limitation of existing theories in predicting

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Table I
Acrylamide–Acrylic Acid Copolymers

copolymers	mole ratio acrylamide/acrylic acid		monomer conversion, %
	in monomer	in copolymer	
1	19.4	11.3	5.1
2	9.1	6.6	11.5
3	4.05	2.90	5.0
4	2.37	1.87	14.9
5	1.01	0.79	9.7
6	0.67	0.49	14.9
7	0.253	0.203	5.0
8	0.053	0.047	7.6

the kinetics of amide hydrolysis once the imidization reaction has run its course.

Experimental Section

Polymers. Acrylamide and its mixtures with acrylic acid were polymerized in 10% aqueous solution at 25 °C using 25 mg/100 mL of potassium persulfate and 25 mg/100 mL of sodium metabisulfite as redox initiators. For the copolymerizations sodium hydroxide was added to the monomer solution to bring it to pH 4.0. The intrinsic viscosity of the polyacrylamide in water at 30 °C was 1.71 g/dL, corresponding[16] to $\bar{M}_\eta = 3.48 \times 10^5$. The copolymer compositions were obtained from Kjeldahl analyses for nitrogen and carboxyl determination by potentiometric titration in the presence of 0.3 M KCl. Table I lists conversions and compositions of the various copolymers.

Model Compounds. Succinamide (Aldrich) was recrystallized from water (mp 260 °C dec). Succinimide was prepared by thermal decomposition of ammonium succinate and recrystallized from anhydrous ether (mp 124–125 °C). Succinamic acid (mp 156–157 °C) was prepared by Vogel's[17] procedure. Glutaric acid was dehydrated by acetic anhydride and the glutaric anhydride was treated with ammonia to obtain glutaramide (mp 175–176 °C). Glutaramic acid (mp 91–92 °C) was obtained by a procedure analogous to that used for succinamic acid. Glutarimide (mp 152 °C) was obtained by the dehydration of glutaramic acid. *meso*-α,α'-Dimethylsuccinic acid (Aldrich) was esterified and the ester aminolyzed to the amide (mp 299–301 °C). To obtain *dl*-α,α'-dimethylsuccinamide, a mixture of the *meso*- and *dl*-dimethylsuccinic acid (Aldrich) was treated with ammonia, distilling off *dl*-α,α'-dimethylsuccinimide at 240–260 °C. This was recrystallized to a product with melting point 107–108 °C and converted to the amide (mp 236–238 °C) by treatment with aqueous ammonia at room temperature. Prof. L. Eberson of Lund University kindly supplied us with samples of *meso*- and *rac*-2,4-dimethylglutaric acid.

Kinetics. Imide formation and decomposition at 25 °C were followed in 0.2 N NaOH solution by the absorption at 235 nm. Alternatively, it was followed by the release of ammonia using the Nessler reagent for the determination. Amide hydrolysis could be neglected under the conditions of these experiments. To follow ammonia evolution during the hydrolysis of polyacrylamide and acrylamide–acrylic acid copolymers in 0.2 N NaOH at 53 °C, aliquots were cooled to quench the reaction, and the optical density at 410 nm was read at 25 °C, 60 s after addition of the Nessler reagent.[18] The method was calibrated against ammonium chloride solutions. This procedure was not applicable to the hydrolysis of the two copolymers with the highest acrylic acid content since they were precipitated by Nessler's reagent. In these cases the pyridine–pyrazolone reagent[19] was employed.

Results and Discussion

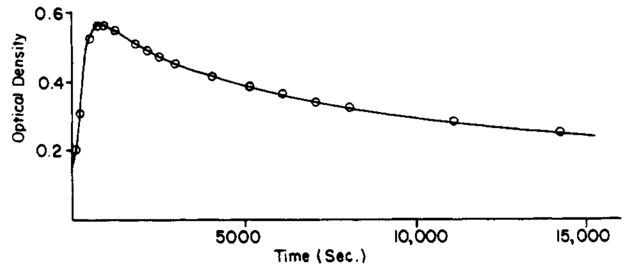


Figure 1. Imide formation and hydrolysis in polyacrylamide (2.2 mg/mL) in 0.2 M NaOH at 25 °C as monitored by UV absorption at 235 nm.

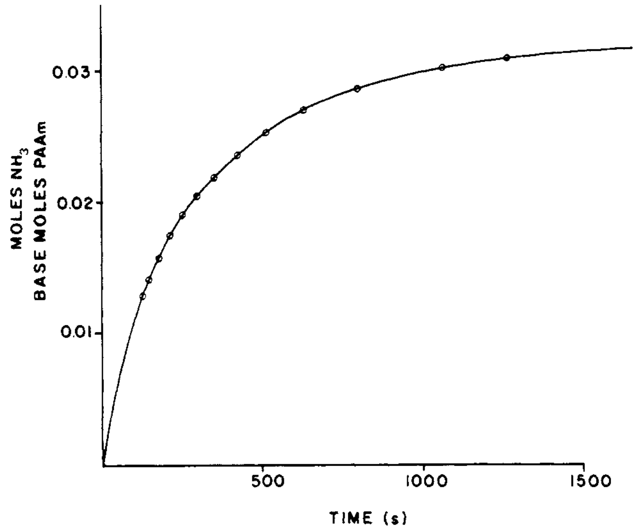
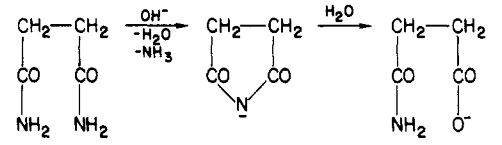


Figure 2. Ammonia evolution from polyacrylamide in 0.2 M NaOH at 25 °C.

Imide Formation. Initial ammonia evolutions from polyacrylamide in 0.2 N NaOH at 53 °C yielded invariably a significant intercept, indicating that several percent of the amide groups were destroyed by a side reaction much faster than amide hydrolysis. The nature of this process was clarified by following the UV spectrum of the solution at 25 °C as a function of time. As seen in Figure 1, the absorption at 235 nm increased rapidly and then gradually decayed. This behavior is analogous to that described by Vigneron et al.[20] for succinamide which was shown to react in basic solution by the sequence



(2)

where the imide intermediate is responsible for the UV absorption.

Succinamide seemed a poor analogue of polyacrylamide in which neighboring amide groups are separated by three carbon atoms and we investigated, therefore, the behavior of glutaramide. To our surprise, we observed no imide absorption when this compound was exposed to a basic medium. This was explained when we compared the rate at which glutarimide was hydrolyzed with the rate at which ammonia was evolved from glutaramide; this showed that the imide is destroyed, in this case, almost 300 times as fast as it is formed. A comparison of the behavior of the polymer with that of succinamide and glutaramide suggests then that imide forms in the polymer from amide residues attached to neighboring carbons of the chain backbone, i.e., from monomer residues added head-to-head.

The decomposition of the imide groups of the polymer followed first-order kinetics with a rate constant similar to that observed for succinimide. The corresponding rate constant for imide formation in polyacrylamide exposed to 0.2 N NaOH at 25 °C was obtained both from the rate of appearance of the imide absorption band and from data on ammonia evolution since amide hydrolysis can be neglected under these conditions. (Extrapolation of rate constants for amide hydrolysis between 53 and 85 °C to 25 °C shows that this reaction is 1000 times slower than

Table II
Rate Constants for Imide Formation and Hydrolysis in 0.2 N NaOH at 25 °C

	rate constant, $s^{-1} \times 10^4$	
amide	amide formation	imide hydrolysis
succinamide	2.7	1.03
dl-α,α'-dimethylsuccinamide	25	0.80
meso-α,α'-dimethylsuccinamide	1.61	1.26
glutaramide	0.62	178
polyacrylamide	40	1.06

imide formation.) The imide formation deduced from the data plotted in Figure 2 conformed to first-order kinetics with 2.9% of the amides characterized by a rate constant 16 times as high as the rate constant for succinimide formation. We thought that this discrepancy might be due to the fact that in the polymer the amide groups are attached to tertiary carbon atoms and that the two stereoisomers of α,α'-dimethylsuccinamide would be better analogues of the acrylamide residues added head-to-head than those of the unsubstituted succinamide. Table II compares the rate constants for imide formation and hydrolysis for polyacrylamide and the various model compounds, and it may be seen that these constants are quite similar for the polymer and for the *rac*-α,α'-dimethylsuccinamide. It is not surprising that steric hindrance renders imide formation from *meso*-α,α'-dimethylsuccinamide much more difficult.

When ammonia evolution for polyacrylamide was followed in 0.2 N NaOH solution at 53 °C, a linear plot was obtained with an intercept corresponding to 4.5% of the amide groups, suggesting that these had reacted at a much higher rate. We believe that all of this is due to imide formation and that the excess over that observed at 25 °C is due to head-to-head monomer pairs with the meso configuration which would form imides much more slowly than similar racemic residue pairs. We conclude that polymerization of acrylamide under our conditions led to 4.5% of amides to be placed in head-to-head pairs of monomer residues with about two-thirds of them in the racemic configuration.

The large difference in the rate of succinimide and glutarimide hydrolysis is undoubtedly a consequence of the resonance stabilization of the planar succinimide anion which renders it much less reactive than the anion of the puckered six-membered glutarimide. The same consideration makes succinimide, $pK_a = 9.65$, a much stronger acid than glutarimide, $pK_a = 11.43$.[21] The rate of imide hydrolysis is the sum of the spontaneous and the hydroxyl ion catalyzed processes involving the imidate anion, so that the rate constant is given by

$$k_{obsd} = [k + k'(OH^-)]K_a/[K_a + (H^+)] \qquad (3)$$

where K_a is the imide ionization constant. Our data on the pH dependence of the hydrolysis rates of the two imides fit this expression with $pK_a = 9.85$ for succinimide and $pK_a = 11.43$ for glutarimide, in good agreement with the literature data based on potentiometric titration.

In spite of the close correspondence between the reactivity of the racemic α,α'-dimethylsuccinamide and the imide-forming residues of polyacrylamide, there is a puzzling difference in the spectroscopic characteristics of the imide formed from the polymer and that formed from the model compound. The polymer imide exhibits a maximum at 235 nm in 0.2 N NaOH, while in neutral water solution the absorption increases continuously with decreasing wavelength; the model imide has an absorption maximum at 242 nm in neutral solution but no absorption maximum in a basic medium.

Table III
Amide Hydrolysis in Polyacrylamide and Acrylamide–Acrylic Acid Copolymers

mol % acrylic acid in polymer	$10^3 k_{in}$, min^{-1}	intercept, %
0	2.90	4.54
14	2.46	3.18
26	1.68	2.79
35	0.71	0.24
57	0.53	0.08
68	0.19	0.01
84	0.15	
96	0.05	

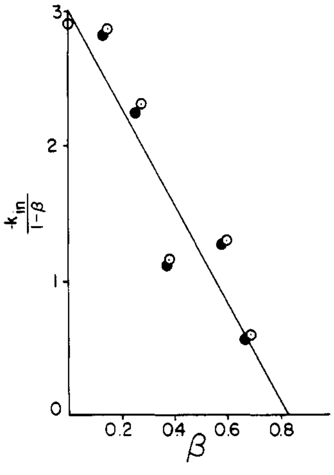


Figure 3. Estimate of k_1 from a plot of $k_{in}/(1-\beta)$ against β. The β values are based on $r_{AAm} = 0.68$ (⊙) and $r_{AAm} = 0.72$ (●).

Amide Hydrolysis. The initial first-order rate constants for ammonia evolution from polyacrylamide and acrylamide–acrylic acid copolymers in 0.2 N NaOH at 53 °C are given in Table III which also lists the ammonia release obtained when the linear kinetic data are extrapolated to zero time. This initial fast ammonia release was undoubtedly due to imide formation as discussed in the preceding section and will not be considered in what follows.

The initial rate constant, k_{in}, for the hydrolysis of an acrylamide–acrylic acid copolymer may be represented by

$$k_{in} = (1-\beta)^2 k_0 + 2\beta(1-\beta)k_1 + \beta^2 k_2 \qquad (4)$$

where k_0, k_1, and k_2 are rate constants for acrylamide residues with 0, 1, and 2 acrylic acid neighbors, β being the probability that the site next to an acrylamide is occupied by an acrylic acid residue. It can easily be shown that β is related to the ratio, Q, of acrylamide and acrylic acid in the polymerizing system and the reactivity ratio r_{AAm} of the acrylamide radical with acrylamide and acrylic acid, respectively, by

$$\beta = [1 + r_{AAm}Q]^{-1} \qquad (5)$$

so that k_0, k_1, k_2 can be evaluated, in principle, from k_{in} values for polyacrylamide and at least two copolymers.

Our data for the composition of copolymers derived from various monomer mixtures, as listed in Table I, yield a r_{AAm} value of 0.70 ± 0.02. Since we know that acrylamide residues flanked by two acrylate residues have very small reactivity, we can neglect the last term in eq 4 for copolymers with all but the highest acrylic acid contents, so that

$$k_{in}/(1-\beta) = k_0 + \beta(2k_1 - k_0) \qquad (6)$$

and k_1 can be estimated from a plot of $k_{in}/(1-\beta)$ against β. Such a plot (Figure 3) leads to an estimate of $k_0 = 3.0$

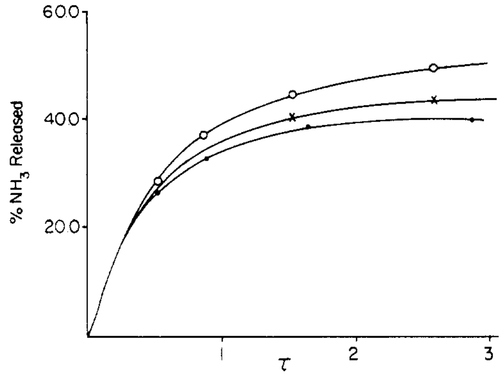


Figure 4. Comparison of data on polyacrylamide hydrolysis (●) with the prediction of Keller's theory for $p = 0.11$ and $q = 0.013$ (○) and for $p = q = 0$ (x).

$\times 10^{-3}$ min^{-1} and $k_1 = 0.31 \pm 0.11 \times 10^{-3}$ min^{-1}. Using these values in conjunction with the k_{in} obtained with copolymer 8 (containing only 4.7 mol % acrylamide residues), we obtained $k_2 = 0.036 \pm 0.008$ min^{-1}. Thus, $k_1/k_0 \equiv p = 0.11$ and $k_2/k_0 \equiv q = 0.013$.

According to Keller's analysis[4] the formation of reactive groups with two unreacted neighbors, N_0, with one reacted neighbor, N_1, and with two reacted neighbors, N_2, should be given as a function of $\tau \equiv k_0 t$ by

$$N_0(\tau) = \exp[-(2p + 1)\tau - 2(p - 1)(e^{-\tau} - 1)]$$

$$N_1(\tau) = 2[\exp(\tau) - 1] \exp[-(2p + 1)\tau - 2(p - 1)(e^{-\tau} - 1)]$$

$$N_2(\tau) = 2 \exp(-q\tau) \int_0^\tau \exp(q\tau) \times [1 - 2p + (p - 1) \exp(-\tau) + p \exp(\tau)] \times N_0(\tau)\, d\tau \quad (7)$$

Figure 4 compares the experimental results obtained in the hydrolysis of polyacrylamide in 0.2 N NaOH at 53 °C with the prediction based on the neighboring group effect using the parameters p an q derived from the reactivity of acrylamide–acrylic acid copolymers. It may be seen that the experimental data fit the prediction in the initial stages of the process, but that the conversion for long reaction times is distinctly lower than predicted. In fact, it is even lower than the conversion predicted for the case where even a single reacted neighbor inhibits fully the reaction of a polymer substituent.

Polyelectrolyte Effect. An alternative treatment of the decay of the rate constant for the basic hydrolysis of polyacrylamide with increasing conversion would assign the effect to the repulsion of the catalyzing hydroxide ion from the polymer carrying an increasing negative charge. We may then use the assumption of Katchalsky and Feitelson[13] that $\Delta G^{\ddagger}_{\text{el}} = \Delta G^{\text{i}}_{\text{el}}$, assuming that $\Delta G^{\text{i}}_{\text{el}}$ of acrylamide–acrylic acid copolymers in a basic medium in which the carboxyls may be considered to be fully ionized is the same as in poly(acrylic acid) with the same charge density.

To assess the relative contribution of charges on neighboring and more distant monomer residues to $\Delta G^{\text{i}}_{\text{el}}$, we compared the titration behavior of poly(acrylic acid) to that of its dicarboxylic acid analogues, all in 0.2 N NaCl at 25 °C. For *meso*-2,4-dimethylglutaric acid, we found $pK_1 = 4.20$, $pK_2 = 5.16$, and $\Delta pK = 0.96$ and for the racemic isomer $pK_1 = 4.15$, $pK_2 = 5.20$, and $\Delta pK = 1.05$. Since $K_2/K_1 = (1/4) \exp(-\Delta G^{\text{i}}_{\text{el}}/RT)$ and $\Delta pK = \log 4 + 0.43\Delta G^{\text{i}}_{\text{el}}/RT$, we have $0.43\Delta G^{\text{i}}_{\text{el}}/RT = 0.40 \pm 0.05$. For the titration of poly(acrylic acid) in 0.2 N NaCl, Mandel[22] obtained $\Delta pK = 0.9\alpha_{\text{i}} + 0.6\alpha_{\text{i}}^2$, where α_{i} is the degree of ionization. Thus, poly(acrylic acid) is characterized, as full ionization is approached, by $\Delta pK = 0.43\Delta G^{\text{i}}_{\text{el}}/RT = 1.5$. Since any carboxyls of the polymer have two ionized neighbors, the contribution of nearest-neighbor interactions to $\Delta G^{\text{i}}_{\text{el}}$ should be twice as large as in dimethylglutaric acid. We conclude, therefore, that only 50–60% of $\Delta G^{\text{i}}_{\text{el}}$ in highly ionized poly(acrylic acid) is due to charges carried by neighboring monomer residues.

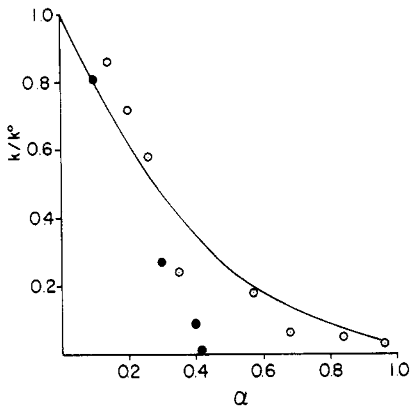


Figure 5. Dependence of amide hydrolysis rate on the fraction α of monomer residues carrying an anionic charge. The solid line corresponding to $\Delta G^{\ddagger}_{\text{el}} = \Delta G^{\text{i}}_{\text{el}}$ is compared with the results (○) for random acrylamide–acrylic acid copolymers and (●) results for partially hydrolyzed polyacrylamide.

According to the treatment of Katchalsky and Feitelson, and using Mandel's titration data, the rate constant, k, for the hydrolysis of an acrylamide–acrylic acid copolymer in a basic medium should be related to k^0, the initial rate constant for the hydrolysis of the uncharged polyacrylamide, by $k/k^0 = \exp[-2.3(0.9\alpha + 0.6\alpha^2)]$, where α is the fraction of acrylic acid residues in the copolymer. This prediction is compared in Figure 5 with results obtained for random acrylamide–acrylic acid copolymers and the decay of the rate constant for the hydrolysis of polyacrylamide. In spite of the scatter of the data, it appears that the Katchalsky–Feitelson approach is reasonable in describing the behavior of the random copolymer. On the other hand, it completely failed to predict the rapid decrease of the rate of polyacrylamide hydrolysis to a negligible rate at a conversion of only 41%. The reason for this difference is obvious: Because of the strong inhibition of the reaction by a reacted neighboring group, the partially hydrolyzed polyacrylamide will be much more likely to have amide groups flanked by acrylic acid residues.

Concluding Remarks

Head-to-head addition during the polymerization of acrylamide is probably characterized by a higher activation energy than head-to-tail addition. It would then be expected that polyacrylamide as usually prepared at a substantially higher temperature than used in our study would contain a higher proportion of head-to-head units leading to imide formation. Also, we should like to draw attention to a puzzling factor of our results: Table III shows that the contribution of the fast reaction, presumably due to imide formation, decreases rapidly with an increasing content of acrylic acid. For instance, copolymer 4, containing 35 mol % acrylic acid, yielded on a plot of ammonia evolution in 0.2 N NaOH at 53 °C an intercept only 5% as large as that for the acrylamide homopolymer, although there was a 64% probability that an acrylamide residue is followed by another one during the polymerization.

The deviation of the course of polyacrylamide hydrolysis from predictions based on the nearest-neighbor effect could be due to two causes. In view of the demonstration that the electrostatic free energy of ionization of poly(acrylic acid) contains a significant contribution from interactions with charges which are not carried by neighboring monomer residues, it is reasonable to assume that the three parameters k_0, k_1, and k_2 are also functions of the overall polymer charge. If this is so in 0.2 N NaOH, it would of course be even more pronounced at lower ionic strength. Beyond this, it is also possible that k_0, k_1, and k_2 are dependent on the stereoisomerism of the chain. If this effect is important, it might be revealed by comparing the course of amide hydrolysis of polyacrylamides prepared at different temperatures, since a lowering of the polymerization temperature generally favors syndiotacticity.

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Interactions of Sodium Ions with Polyelectrolytes of Varying Charge Density

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ABSTRACT: Sodium ion interactions with polyelectrolytes of varying charge densities have been determined from tracer diffusion measurements. Sodium acrylate/acrylic acid, sodium acrylate/acrylamide, and sodium acrylate/*N*,*N*-dimethylacrylamide copolymers, each of varying linear charge density parameter ξ between 0.2 and 2.7, were used. The first copolymer was studied in aqueous salt-free and NaCl-containing solutions and the latter two copolymers only in salt-free solutions. It was found that the sodium ion diffusion coefficients were linear with ξ^{-1} above $\xi = 1$ for both salt-free and NaCl-containing solutions, as predicted from the Manning theory. Evidence for a critical ξ value is discussed. Also, constant values for the sodium ion diffusion coefficients were observed below the critical ξ value. An empirical additivity rule is discussed. The charge fractions for the sodium acrylate/acrylic acid copolymers were evaluated.

The theories that describe the dilute solution properties of polyelectrolytes have not been widely accepted. The failure of the establishment of accepted limiting laws for polyelectrolyte solutions is in part due to the lack of systematic experimental investigations, making it difficult to judge the dominant theories adequately to note where their modifications would be appropriate. The line charge model of Manning[1-7] has, of course, received the most attention because of its simplicity, because it represents high charge density polyelectrolytes fairly well, and because limiting laws are derived for thermodynamic, mass, and electric transport properties of polyelectrolyte solutions.

Briefly, when the stoichiometric charge density parameter ξ, where $\xi = e^2/kTb$, with e, k, and T the standard constants and b the average axial distance between stoichiometric charges along the polyelectrolyte chain, is greater than ξ_c, where $\xi_c = |Z_1|^{-1}$, with Z_1 the counterion valence, counterions condense onto the polyion until ξ_c is reached and the remaining counterions are in the Debye–Hückel atmosphere. Recently, Zimm and LeBret gave further theoretical justification of the Manning "two state" condensation theory.[8] Experimental evidence exists for this type of counterion binding, and the operational definition of counterion condensation, where the charge fraction of the polyelectrolyte equals a constant value of $(\xi|Z_1|)^{-1}$ over a broad concentration range, was found to hold for several polyelectrolytes.[9-12] The nature of the counterion condensed state may vary from a localized, dehydrated counterion which is site bound to a delocalized, hydrated counterion which can translate along the polyion. When $\xi < \xi_c$, the polyelectrolyte is thought by Manning to be completely dissociated with all counterions interacting with the polyion by Debye–Hückel forces. Co-ion–polyion interactions have been discussed elsewhere.[13-15]

Here we report the results of investigations of the interactions of Na^+ ions with polyelectrolytes determined by Na^+ ion tracer diffusion coefficients, which, of course, monitor the long-range counterion–polyion interactions. Recently, it was reported by Kowblansky and Zema[16,17] that the sodium ion activity coefficients in salt-free aqueous solutions of sodium acrylate/acrylamide copolymers and of sodium methacrylate/methacrylic acid copolymers are linearly dependent on $\xi^{1/2}$ over the range $0.2 < \xi < 2.7$. This is not in accord with the Manning