Cross-Linking of Hydroxamic Acid Copolymers through Iron Chelation

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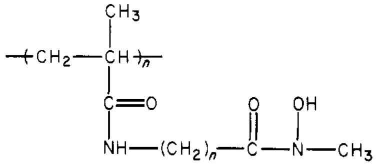
Received December 2, 1980

ABSTRACT: Polymers bearing widely spaced hydroxamic acid (HA) groups were synthesized by copolymerization of the *N*-hydroxysuccinimide ester of *N*-methacryloyl-β-alanine with acrylamide, followed by treatment with methylhydroxylamine. The HA content of the three copolymers was measured spectrophotometrically, using the λ_{max} 504 nm absorption of the 1:1 HA–Fe^{III} complex. The copolymers contained 0.749, 0.259, and 1.80 mol % HA units, and their intrinsic viscosities in water at 30 °C were 0.58, 1.86, and 0.52 dL/g, respectively. The effect of the HA:Fe ratio and the overall polymer concentration on the intrinsic viscosity was studied. At high concentrations of polymer, addition of iron(III) caused $[\eta]$ to increase up to a maximum at an HA:Fe ratio of 3:1. Below the 3:1 ratio, $[\eta]$ decreased rapidly back to the value of the original solution. At low concentrations of polymer, addition of iron caused a decrease in $[\eta]$ to a minimum at an HA:Fe ratio of 3:1. Below 3:1, $[\eta]$ increased back to the values of the original solution. At higher concentrations, the probability of intermolecular complexation is high, resulting in cross-linking and increasing $[\eta]$. At lower concentrations the probability of intermolecular bonding is low compared to that for the intramolecular process. Hence, ring formation predominates and the decreased polymer dimensions result in decreased $[\eta]$. When the HA:Fe ratio is reduced to 1:1, both the inter- and intramolecular complexes are broken because each HA group is bonded only to a single iron. Hence, $[\eta]$ changes back toward the value of the original polymer. The viscosity of a cross-linked polymer decreased with time, showing a spontaneous interconversion of cross-linked form to ring form. A kinetic analysis showed that the interconversion is first order with an activation energy of 15.1 kcal/mol. At sufficiently high concentrations of copolymer, gel formed at HA:Fe ratios of approximately 3:1. The critical concentration for the formation of gel was measured for the three copolymers. The average distance between HA groups of different chains at the critical concentration was determined assuming close-packed spheres. This distance was compared with the root-mean-square distance between neighboring HA groups on the same polymer chain. A generally good agreement of these two distances confirms that the HA groups of the copolymers react randomly and form infinite networks only when the probability of intermolecular complexation exceeds 50%.

In earlier work[2,3] we reported upon the synthesis and characterization of vinyl polymers bearing the hydroxamic acid group, a powerful iron chelator. The polymers, structure 1, were constructed with varying spacings between hydroxamic acids, achieved by simply changing the length of the side chain. We found that the formation constant of the polymer–iron complex was governed, in part, by this spacing and that an 11-atom spacing appeared to be optimum for high complex stability. These results, together with some spectral studies, indicated that the complexes were formed through intramolecular reactions of three neighboring hydroxamic acids with a single iron, giving a 3:1 hydroxamic acid–iron complex. Further evidence that the proximity of hydroxamic acid groups to one another contributes to the high stability of the iron complex was that, whereas excess iron causes the conversion of the 3:1 complex to the 2:1 complex, further additions of iron fail to convert the 2:1 complex to the 1:1 complex. Normally, when there is no cooperation between hydroxamic acids, as in the case of monohydroxamic acids, the purple 1:1 complex is easily formed in the presence of excess iron.[4]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In the present work, we investigate the other end of the scale, polymers bearing hydroxamic acids far removed from one another. Instead of intramolecularly bonded complexes, which result when the hydroxamic acid groups are close together, polymers with widely separated hydroxamic acids would tend to form intermolecular cross-links, and this phenomenon would be observable through increases in viscosity and the onset of gelation.

Table I
Characteristics of Hydroxamic Acid Copolymers

MAS in feed, mol %	HA units in copolym, mol %	$[\eta]$,[a] dL/g	$\overline{M}_w$[b]	$\overline{M}_n$[c]
2.00	0.749	0.58	91 000	28 000
2.44	0.259	1.86	397 000	162 000
3.92	1.80	0.52	79 500	23 700

[a] Solvent, water; temperature, 30 °C. [b] Using Mark–Houwink constants for acrylamide:[9] $K = 6.31 \times 10^{-5}$ dL/g, $a = 0.80$. [c] Using Mark–Houwink constants for acrylamide:[10] $K = 6.8 \times 10^{-4}$ dL/g, $a = 0.66$.

Cross-linking through metal ion chelation has long been of interest in polymer science[5-8] and we felt that because the hydroxamic acid–iron system has extremely high formation constants (10^{30}), it would be a particularly interesting one to study on a theoretical basis.

One of the easiest ways to synthesize a polymer with widely separated functional groups is through copolymerization. Polyacrylamide was selected as the base polymer because of its high solubility in water and its ease of formation from the monomer. The hydroxamic acid copolymers were prepared according to the procedure shown in Scheme I. Acrylamide (AA) and the *N*-hydroxysuccinimide ester (MAS) of *N*-methacryloyl-β-alanine were copolymerized at low mole percent MAS:AA ratios. The ester groups of the copolymer were converted to hydroxamic acids through treatment with methylhydroxylamine. The copolymers were dialyzed against distilled water and dried to give clear filmy solids. The hydroxamic acid (HA) content of the copolymers was measured spectrophotometrically, using the absorbance of the 1:1 HA–Fe complex at λ_{max} 504 nm together with the molar absorptivity of the 1:1 complex of aceto-

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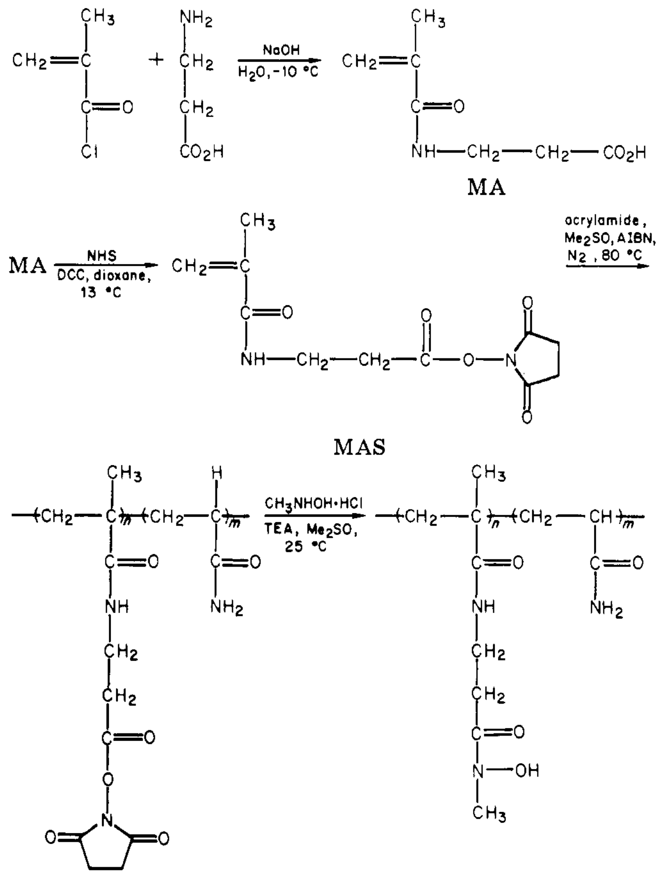
Scheme I[a]
Synthesis of Copolymers



[a] NHS, *N*-hydroxysuccinimide; DCC, dicyclohexylcarbodiimide; AIBN, α,α'-azobis(isobutyronitrile); Me_2SO, dimethyl sulfoxide; TEA, triethylamine.

hydroxamic acid used as the model. The results are given in Table I. The molecular weights of the polymers were also determined by viscometry, using the Mark–Houwink constants for pure polyacrylamide, with the assumption that the small amount of comonomer residue present would have no significant affect on these constants.

Experimental Section

General Procedures. Melting points were determined by using a Uni-Melt (Arthur H. Thomas Co.). Spectropor membrane tubing, molecular weight cutoff 6000–8000, was used for dialysis. The pH measurements were made on a Beckman Model 96 pH meter. Infrared spectra were recorded on a Beckman IR-8 spectrophotometer. UV–vis spectra were recorded on a Beckman DB-G. Proton magnetic resonance spectra were recorded on a Varian T-60 spectrometer and are referenced to Me_4Si as internal standard. Viscosities were run in Ubbelohde viscometers (Cannon-Fenske Co.). Aliquots of copolymer and iron solutions were measured with Finnpipettes. *N*-Methylhydroxylamine hydrochloride and acetohydroxamic acid were obtained from Aldrich Chemical Co., *N*-hydroxysuccinimide from Sigma Chemical Co., acrylamide from Eastman Chemical Co., and azobis(isobutyronitrile) (AIBN) from E. I. du Pont de Nemours and Co. *N*-Methacryloyl-β-alanine (MA) and its *N*-hydroxysuccinimide ester (MAS) were prepared according to previously published procedures.[2,3] All complexes were made with iron(III) perchlorate (Alfa Products).

Preparation of Copolymers. Typical Procedure. Into a a 500-mL three-neck flask were placed 2.04 g (0.008 mol) of MAS, 27.88 g (0.392 mol) of acrylamide, and 400 mL of dimethyl sulfoxide. The clear solution was purged with nitrogen, heated to 80 °C, and stirred. AIBN (40 mg) was added and the solution was stirred and heated for 2.5 h. The copoly(AA–MAS) was not isolated and the solution was used directly in the next step.

A solution of *N*-methylhydroxylamine was prepared by stirring 2.00 g (0.024 mol) of $CH_3NHOH{\cdot}HCl$ and 2.42 g (0.024 mol) of triethylamine in 30 mL of dimethyl sulfoxide for 15 min at room temperature. The triethylamine hydrochloride was removed by filtration and discarded. This solution was then added to the MAS copolymer solution and stirred at room temperature for 18 h. The resulting polymer solution was dialyzed against distilled water for 2 days. After removal of water on a rotary evaporator, the polymer was dried over Drierite in a vacuum oven for 18 h at 55 °C to constant weight. A flaky, clear, water-soluble solid (15.0 g) was collected, 51% yield based on 0.400 mol of starting monomers. In some cases the copolymers were not isolated as solids but were used as obtained from dialysis after appropriate dilution or concentration. The concentration of polymer in these solutions was determined by transferring aliquots of the solutions to tared weigh pans, allowing the water to evaporate, drying thoroughly, and reweighing.

Determination of the Hydroxamic Acid Content of the Copolymers. A. Molar Absorptivity of the Standard Acetohydroxamic Acid. Acetohydroxamic acid was dried under vacuum for 3 days over P_2O_5 at 80 °C, mp 89–91 °C (lit.[11] mp 87–88 °C). A 1.000 M aqueous solution was prepared in a 10-mL volumetric flask from 0.7507 g (0.010 mol). A 0.010 M solution was prepared by diluting a 0.100-mL aliquot to 10 mL.

An aqueous solution of ferric perchlorate (15.25 g in 990 mL of distilled water) was prepared. After the pH was adjusted to 1.3 by the addition of 10 mL of concentrated nitric acid, the solution was standardized by the EDTA–bismuth method[12] and found to be 2.765×10^{-2} M in iron(III).

Solutions of the 1:1 acetohydroxamic acid–iron(III) complex were prepared in 10-mL volumetric flasks by diluting aliquots of the 0.010 M solution with the standard iron(III) solution. The absorbance of each of the solutions was measured at λ_{max} 504 nm. The Beer's law plot was linear and passed through the origin. The molar absorptivity, as determined from the slope of the least-squares plot, was 882 $L{\cdot}M^{-1}{\cdot}cm^{-1}$.

B. Hydroxamic Acid Content of Copolymers. Aliquots of solutions of known concentrations of the HA copolymers were placed in 10-mL volumetric flasks and diluted with 2.765×10^{-2} M iron(III) solution to give the purple 1:1 complex. The absorbance at 504 nm of each of these solutions was measured and the mole percent hydroxamic acid was calculated from the molar absorptivity of the standard. The results are given in Table I.

Results and Discussion

Viscosity Effects. Preliminary tests were performed to see whether or not cross-linking of the copolymers could be readily observed. When a small amount of iron(III) was added to an aqueous solution of the copolymer, an immediate and dramatic increase in viscosity occurred and the characteristic red-brown color of the complex appeared. The viscosity became so great that filaments of the solution could be pulled out to a length of 2 or 3 in. Further additions of iron(III) caused the solution to gel. On the addition of still more iron(III), the color changed to purple, characteristic of the 1:1 HA–Fe complex, and the high viscosity formerly observed disappeared, thus indicating the break up of the cross-links. Addition of EDTA to the viscous solution also caused the viscosity to drop, and, in this case, the color disappeared as well, since the iron was now bound to the EDTA rather than the hydroxamic acids. From these tests, it was clear that the hydroxamic acids were sufficiently separated on the copolymer to cause them to behave independently in their reactions with iron(III) and to form cross-links. The large viscosity changes observed gave assurance that the cross-linking reactions could be readily monitored by normal viscometric techniques.

The initial investigation was to determine the HA:Fe ratio required to achieve maximum cross-linking, predicted to occur at an HA:Fe ratio of about 3:1. The experimental plan was to observe the change in the intrinsic viscosity of the polymer as a result of changing the HA:Fe ratio. However, it soon became apparent that the viscosity of the

Table II
Martin Constants for Hydroxamic Acid Copolymers

HA in copolym, mol %	k^a
0.749	0.150
1.80	0.110
0.259	0.075

[a] Aqueous, 30 °C.

polymer–iron complex was time dependent and decreased steadily within a few hours to a value not much different from that of the original polymer solution before the addition of iron. Also, the observation that the change in viscosity with respect to the HA:Fe ratio was quite different for different copolymer concentrations made it clear that the copolymer complexes formed at the different copolymer concentrations were discretely different in nature. This meant that the intrinsic viscosity could not be determined by the usual method of extrapolating the η_{sp}/c vs. c plot to zero concentration. Instead, an alternate method, introduced by Elliot et al.,[13] was used to predict the intrinsic viscosity of a polymer from a single viscosity measurement of a polymer solution. The method is based upon the empirical Martin equation,[14] which can be written

$$\log (\eta_{sp}/c) = \log [\eta] + k[\eta]c \qquad (1)$$

The Martin constant k was determined for each of the three copolymers (no iron added) from plots of $\log (\eta_{sp}/c)$ vs. c. The intrinsic viscosity was obtained from the intercept, and the Martin constant is the slope divided by the intrinsic viscosity. The results are given in Table II.

The Martin equation can also be written in the form

$$\log (k\eta_{sp}) = \log (k[\eta]c) + k[\eta]c \qquad (2)$$

This form of the Martin equation was used to extrapolate backward from various finite concentration conditions to zero concentration by insertion of a known Martin constant, Table II, and a specific viscosity measurement. This gave the intrinsic viscosity of the iron–copolymer complex existing at the particular concentration of copolymer under study. By this procedure it is assumed that the Martin constants of the iron complexes are the same as those of the copolymers. This may or may not be true, but since the only objective was to reduce the data for the various copolymers and complexes to a common base, it was felt that the overall results would not be appreciably distorted, at least by any reasonable deviation from such an assumption.

An aqueous solution of the copolymer was placed in an Ubbelohde viscometer and a small aliquot of a standard solution of iron(III) perchlorate was added. The solution was mixed and the efflux time was measured after a suitable time interval had elapsed. Additional aliquots of iron(III) were added and the efflux times were recorded as before. A range of HA:Fe ratios of about 12:1 to 1:1 was covered. This procedure was carried out for each of the three copolymers over a range of concentrations. The efflux times were converted to specific viscosities and these values were then converted to intrinsic viscosities by means of the Martin equation (eq 2) and the known Martin constants of the copolymers, Table II. Although Elliot has provided graphs based on the Martin equation that give direct readings of $k[\eta]c$ from $k\eta_{sp}$ data, it was found to be somewhat more convenient and accurate to calculate the intrinsic viscosity directly from eq 2 with a programmable desk calculator, using a successive approximation method. The change in intrinsic viscosity, $\Delta[\eta]$, observed on addition of iron(III) was plotted as a function of the HA:Fe ratio. The results for the three copolymers are shown in Figures 1–3. Horizontal lines have been drawn at $\Delta[\eta] = 0$ to provide a reference for comparison.

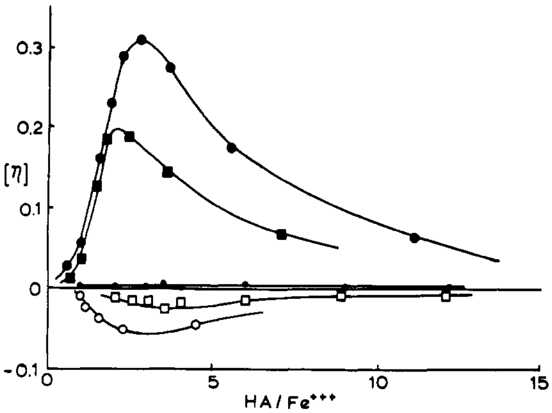


Figure 1. Change of intrinsic viscosity with HA:Fe ratio for acrylamide copolymer containing 0.749 mol % HA units. Concentrations of copolymer in g/dL: (●) 4.9; (■) 3.25; (•) 1.00; (□) 0.75; (○) 0.50.

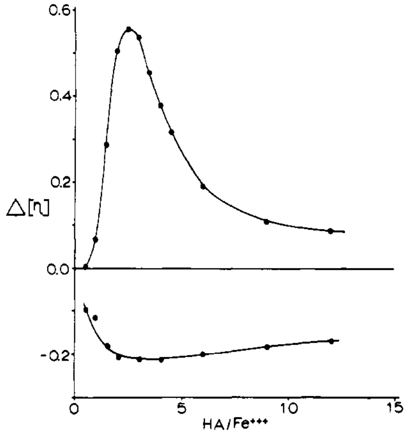


Figure 2. Change of intrinsic viscosity with HA:Fe ratio for acrylamide copolymer containing 1.80 mol % HA units. Concentrations of copolymer in g/dL: upper curve, 1.9; lower curve, 0.5.

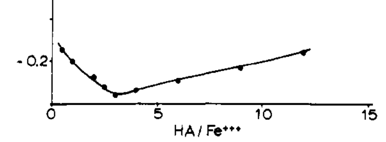
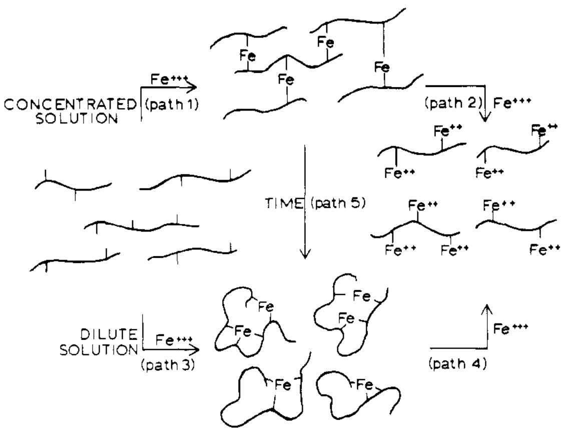


Figure 3. Change in intrinsic viscosity with HA:Fe ratio for acrylamide copolymer containing 0.259 mol % HA units (mol wt 387 000). Concentrations of copolymer in g/dL: upper curve, 4.8; lower curve, 0.5.

One sees from Figure 1 that for copolymer concentrations greater than 1 g/dL, addition of iron (decreasing HA:Fe ratio) causes an initial increase in viscosity of the solution. This increase reaches a peak at an HA:Fe ratio of (2.5–3.0):1, the value predicted to give maximum

Scheme II



cross-linking. On passing through the peak with continued additions of iron, the viscosity drops rapidly back to the base line at $\Delta[\eta] = 0$. If the copolymer concentration exceeds 8.4 g/dL, an infinite network forms and the solution gels. For copolymer concentrations less than 1 g/dL, addition of iron causes a decrease in viscosity, reaching a minimum at an HA:Fe ratio of 3. With continued additions of iron, the viscosity increases and again approaches the zero reference line.

The processes involved are illustrated by the pathways shown in Scheme II. The long wavy lines represent the polymer backbone; the short side branches, the hydroxamic acids. At high concentrations, the HA groups from different polymer chains are close enough together, in comparison to the nearest HA groups on the same chain, to improve the probability of intermolecular bond formation to an extent that cross-linking becomes a significant feature of the process; hence the increase in viscosity, path 1. On continued additions of iron, the cross-linked 3:1 complex is converted to the 1:1 complex, thus breaking up the cross-links because each iron is now bound to only one hydroxamic acid group, path 2. Similar viscosity increases due to intermolecular cross-linking through metal chelation were observed by Shah, Kopolow, and Smid[15] upon the addition of alkali metal salts to crown ether–styrene copolymers.

At low concentrations of copolymer, neighboring HA groups on the same chain are now much closer together than those from different chains and thus the probability for cross-linking is low. Under these conditions the iron complex forms intramolecularly to cause a reduction in the overall random coil dimension of the polymer and a consequent decrease in viscosity, path 3. Continued additions of iron causes the conversion of the 3:1 to the 1:1 HA–Fe complex, resulting in a break up of intramolecular bonds, an expansion of the polymer, and an increase in viscosity, path 4. Another example of a polymer system that undergoes a similar decrease in dimension and viscosity on intramolecular cross-linking is poly(vinyl alcohol) cross-linked with terephthaldehyde under conditions of high dilution.[16,17]

When the HA content of the copolymer is increased, the magnitude of the effect on viscosity is also increased, since cross-link density (at higher concentrations) or intermolecular complex formation (at lower concentration) would be increased, Figure 2. In the case of Figure 3, the HA content of the copolymer is lower, but the molecular weight is higher. Since the effect of iron on the viscosity is again enhanced over that of Figure 1, the higher molecular weight must be of greater significance than the lower HA content.

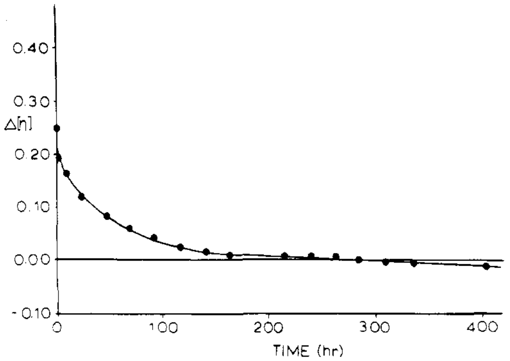


Figure 4. Effect of time on intrinsic viscosity. Aqueous solution, 3.5 g/dL of the 0.749 mol % HA copolymer with an HA:Fe ratio of 2.78:1.

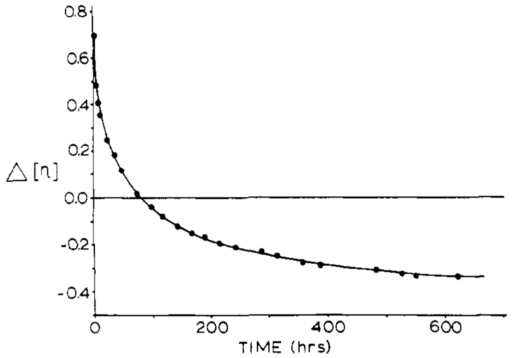


Figure 5. Effect of time on intrinsic viscosity. Aqueous solution, 1.9 g/dL of the 0.259 mol % HA copolymer with an HA:Fe ratio of 2.53:1.

The effect of time on the intrinsic viscosity of the cross-linked copolymer–iron complex was monitored for two of the prepared copolymers. A copolymer solution of known concentration was placed in an Ubbelohde viscometer together with enough iron(III) to give maximum viscosity; see Figures 1 and 3. The efflux time was measured periodically and the data were converted to intrinsic viscosity as before. The quantity $\Delta[\eta]$ was plotted as a function of time, Figures 4 and 5. A significant feature of this experiment is that the viscosity continues to fall until a value is reached below that of the original solution before any iron had been added. This result clearly demonstrates that the cross-linked polymer formed at high concentrations is the kinetic product of the reaction and that the intramolecularly complexed ring form is the thermodynamically stable state, path 5 of Scheme II. The equilibration is possible because of the reversible nature of the iron–hydroxamic acid reaction. Since the chemical bonding is the same in both states, ΔH should be zero and, therefore, the conversion must be entirely due to entropy.

The kinetic data were analyzed by the method of Guggenheim,[18] useful in cases when the final equilibrium value is approached very slowly. By this method, the quantity $\log ([\eta]_{t_x} - [\eta]_{t_{(x+\Delta)}})$ was plotted against time, t_x, where Δ is a period of time greater than the time taken for 75% of the total change in intrinsic viscosity. A straight line would indicate a first-order reaction.

Kinetic data were obtained for the 0.749 mol % HA copolymer at 30 and 60 °C. The data were plotted according to the Guggenheim method, using two different Δ values for each set. The results are shown in Figures 6 and 7.

The linearity of these plots indicates that the reaction proceeding from the cross-linked form to the ring form is indeed first order. The rate constants, as determined from

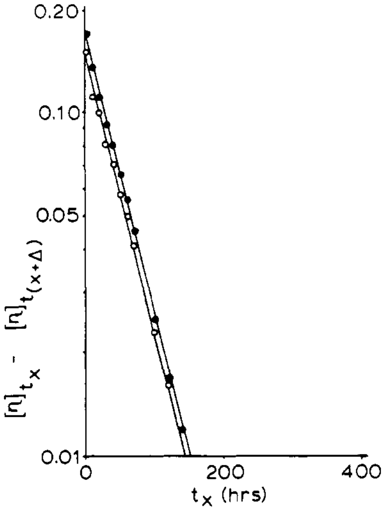


Figure 6. Guggenheim plot for conversion of intermolecular to intramolecular complexes. Aqueous solution, 3.5 g/dL of the 0.749 mol % HA copolymer with an HA:Fe ratio of 2.78:1, 30 °C.

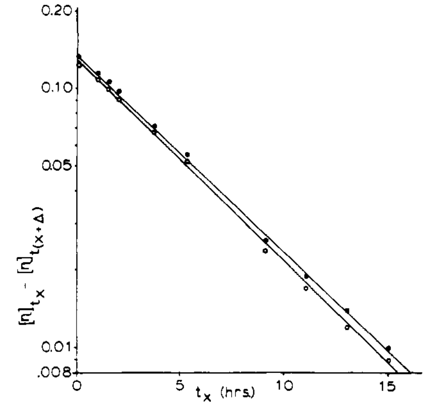


Figure 7. Guggenheim plot for conversion of intermolecular to intramolecular complexes. Aqueous solution, 3.5 g/dL of the 0.749 mol % HA copolymer with an HA:Fe ratio of 2.78:1, 60 °C.

Table III
Rate Constants for the Un-Cross-Linking Reaction[a]

T, K	10^6k, s^{-1}
303	5.21
333	49.7

[a] For the 0.749 mol % HA copolymer, 3.5 g/dL.

the slopes, are reported in Table III.

From the Arrhenius equation the activation energy was calculated to be 15.1 kcal/mol. The value for ΔS was found to be +1 eu.

Gelation. Concerning the gelation that occurs when a sufficiently concentrated solution of the copolymer is treated with iron(III), it would be interesting to see whether or not the critical copolymer concentration required for gelation could be predicted by statistical considerations. Since neighboring hydroxamic acid groups on a polymer chain are widely separated, the chelate effect observed when the groups are close together would be negligible. Thus, all HA groups will possess equal intrinsic reactivity toward iron, and the distribution of intermolecular bonds (cross-links) and intramolecular bonds (rings) would depend only upon the relative probabilities of these two processes. These probabilities would, in turn, depend upon the relative distance between HA groups of different chains and HA groups of the same chain, Scheme III, r(gel) and r(ring), respectively. The critical concentration for the formation of gel would be that concentration where $r(\text{gel}) = r(\text{ring})$. In order to verify this prediction, the critical concentrations required for gelation were determined experimentally. The average distance, r(gel), between all HA groups at this concentration was calculated and compared with the root-mean-square distance between HA groups on the same chain, r(ring). Gel should form only when $r(\text{gel}) \leq r(\text{ring})$.

Table IV
Calculation of r(gel)[a]

X_{HA}	C_p, g/dL	$\bar{M}_s$	$10^{-18}N_{\text{HA}}$	r(gel), nm
0.00749	8.40	71.9	5.27	6.45
0.0180	8.10	73.1	12.0	4.90
0.00259	4.58	71.4	1.00	11.2

[a] Calculated as close-packed spheres.

The critical concentrations for gel formation for the three copolymers of Table I were determined by the following procedure. Aliquots of known concentrations of polymer solutions were placed in a series of small test tubes and diluted with aliquots of water to give various polymer concentrations in the neighborhood of the expected critical concentration. A standard solution of iron(III) was then added to each tube in an amount to give an HA:Fe ratio corresponding to the maxima of Figures 1–3. The solution was stirred briefly and small bubbles of air were introduced at the bottom of the tubes. Solutions in which bubbles failed to rise were considered to be gels.[19] The critical concentration for the occurrence of gel could be determined within 0.1 g/dL.

The distance between HA groups at the gel point, r(gel), was calculated on the basis that the HA groups were spheres arranged close packed in a box. This distance is given by eq 3, where S is the length of the side of the box

$$r(\text{gel}) = S/(N_{\text{HA}}/2)^{1/3} \qquad (3)$$

(1 cm) and N_{HA} is the number of HA groups per cm^3. N_{HA} is given by eq 4, where C_p is the concentration of polymer

$$N_{\text{HA}} = (C_p/100\bar{M}_s)X_{\text{HA}}N \qquad (4)$$

at the gel point in g/dL, $\bar{M}_s$ is the average molecular weight of a structural unit, X_{HA} is the mole fraction of HA units in the polymer, and N is Avogadro's number. The results are shown in Table IV.

The distance between HA groups on the same chain, r(ring), is a function of the mole fraction of HA units in the copolymer and the dimensions of the copolymer as affected by the solvent. On the assumption that the polymer in solution is a random coil, the distance r(ring) can be calculated from eq 5 and 6, where r_0 is the root-

$$r_0^2 = C_\infty nl^2 \qquad (5)$$

$$r(\text{ring}) = r_0\alpha \qquad (6)$$

mean-square distance between neighboring HA groups, n is the average number of chemical bonds separating the HA groups, l is the bond distance (0.154 nm), nl^2 gives the dimension of the random walk model, C_∞ is the characteristic ratio and corrects for the increase in size of a polymer over the random walk model as a result of short-range effects, and α is the expansion factor to take into account the increase in size due to polymer–solvent interactions.

A problem was encountered in the selection of a value for C_∞. Use of the value 14.8 reported in the literature[20,21] did not give an r(ring) distance which was at all consistent with our theoretical analysis of the gelation problem. A

Table V
Calculation of *r*(ring)

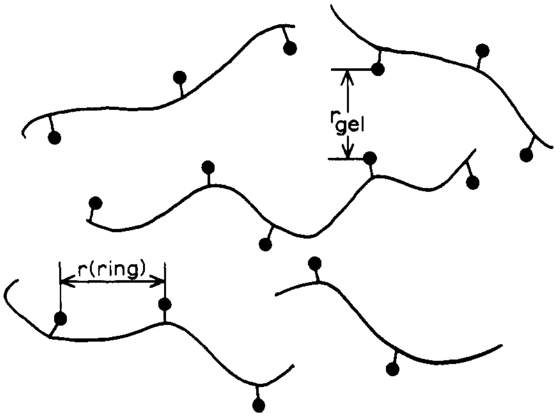
mol fraction HA in copolym	no. of AA units separating HA units[a]	no. bonds separating HA units[b] (*n*)	r_0 [c]	α	*r*(ring)[d]
0.00749	134	275	6.42	1.06	6.81
0.018	55.6	119	4.22	1.00	4.22
0.00259	386	780	10.8	1.19	12.85

[a] Reciprocal of mole fraction. [b] 2 × (no. of AA units) + 8. [c] $C_\infty n l^2$, $C_\infty = 6.32$,[21] $l = 0.154$ nm. [d] $r(\text{ring}) = r_0\alpha$.

Table VI
Comparison of *r*(ring) and *r*(gel)

mol % HA in copolym	*r*(ring), nm	*r*(gel), nm	% difference
0.749	6.8	6.4	6
1.80	4.2	4.9	15
0.259	12.8	11.2	13

Scheme III



search of the literature revealed that the C_∞ of 14.8 reported for polyacrylamide was unusually high when compared with the C_∞ for similar polymers having chain segments of similar or greater steric bulk.[20] This could mean that the literature value was incorrect. Since the calculation of *r*(gel) depended upon the use of a good value of C_∞, a new value was determined from different, and what appears to be more reliable, molecular weight–viscosity data[9] than were used in determining the 14.8 value as reported.[10] From this analysis,[22] C_∞ was calculated as 6.32, a much more reasonable value in view of other polymers of this class, and the results reported herein.

The expansion factor α of acrylamide in water was calculated for a molecular weight corresponding to a segment of copolymer separating two HA groups through use of eq 7 and 8. From the molecular weight–viscosity data

$$[\eta]_\Theta = K_0 M^{1/2} \tag{7}$$

$$[\eta] = [\eta]_\Theta \alpha^3 \tag{8}$$

of Scholtan[9] and the new value of K_0,[22] a plot of log $\bar{M}_w$ vs. log α was prepared from which the α value for the copolymer segment could be estimated. The values calculated for r_0, α, and *r*(ring) are reported in Table V.

The good agreement of the values obtained for *r*(ring) and *r*(gel) for the three copolymers, Table VI, supports the original contention that the hydroxamic acid groups of the copolymers react randomly and form infinite networks only when the probability of intermolecular HA–Fe reaction exceeds 50%. These results also support the need for the reevaluation of the unperturbed dimension parameters C_∞ and K_0 for polyacrylamide.[22]

Acknowledgment. This research was supported in part by the Water Research Institute, West Virginia University, under Grant PL 95-467 administered by the Office of Water Research and Technology, U.S. Department of the Interior.

References and Notes

(1) This work was carried out in partial fulfillment of the degree of Doctor of Philosophy, West Virginia University, 1979.
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