The Reaction of the Hydroxamic Acid Group in Polymer with *p*-Nitrophenyl Acetate[1]

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Water-soluble copolymers containing protected hydroxamate groups were prepared by radical copolymerization of acetyl *N*-phenylacrylohydroxamate and acrylamide, and the hydroxamic acid group (PHA) was unmasked by treating it with hydroxylamine. In acetylation with *p*-nitrophenyl acetate (1.4 v/v% CH_3CN-H_2O, 30 °C) the PHA unit was less reactive than the corresponding monomeric compound. When the PHA content was low (3 mol%), the reactivity of a given PHA anion (true reacting species) was invariant (9.1 $M^{-1}\,s^{-1}$) over a wide range of the dissociation of the PHA unit. However, in the case of the copolymer of a higher PHA content (11 mol %) the reactivity decreased as the neutralization of the PHA anion progressed. This phenomenon was attributed to the intramolecular aggregation of the undissociated PHA side chain. The deacylation rate of the acetylated PHA unit was comparable to those of the monomeric counterparts, in contrast with the acylation process. Finally, the probable role of the PHA unit as catalyst for the ester hydrolysis was discussed.

In the past several years, we have studied the catalytic hydrolysis of phenyl esters by imidazole-containing polymers.[2] Apart from a few exceptional cases,[3] the efficiency of the imidazole catalysis is limited by the rate-determining acylation step.

The hydroxamate anion is known to be highly nucleophilic toward phenyl esters,[4-9] and attempts to use it as catalyst for the hydrolysis of phenyl esters have been carried out by Bender and coworkers in small-molecule systems.[10,11] However, in polymeric systems, introduction of hydroxamic acid groups has not been necessarily straight-forward, and their nucleophilic reactivity was not examined. Thus, in the present study the hydroxamic acid group was introduced into water-soluble polymers and characterized unambiguously, and the reaction with *p*-nitrophenyl acetate(PNPA) was investigated in order to evaluate the usefulness of the hydroxamic acid group in polymer as a catalyst for the ester hydrolysis.

Experimental

All melting points are uncorrected. The UV-visible spectroscopic measurements were made with a Hitachi 124 spectrophotometer. NMR spectra were obtained with a Varian A60 instrument.

Materials. *p*-Nitrophenyl acetate was prepared by acylation of *p*-nitrophenol with acetic anhydride and recrystallized from cyclohexane, mp 78 °C (lit,[12] 81—82 °C). Acrylamide was purified by repeated recrystallizations from benzene, mp 83.5—84.5 °C.

N-Phenylacrylohydroxamic acid (**1**) was prepared according to Barda and Manole from *N*-phenylhydroxylamine and acryloyl chloride.[13] Repeated recrystallizations from cyclohexane gave pale yellow plates; yield 46—58%, mp 90—91 °C (lit,[13] 88—89 °C).

Similar procedures were employed in ether or chloroform solvent for the preparation of the following hydroxamic acids.

N-Phenylisobutyrohydroxamic acid (**2**); yield 60%, colorless plates from a cyclohexane-*n*-hexane mixture, mp 49—50 °C. Found: C, 67.01; H, 7.26; N, 7.86%. Calcd for $C_{10}H_{13}NO_2$: C, 67.02; H, 7.31; N, 7.82%.

N-Methylisobutyrohydroxamic acid (**3**); yield 45%, bp 91—95 °C/5 mmHg. Found: C, 51.18; H, 9.57; N, 11.81 %. Calcd for $C_5H_{11}NO_2$: C, 51.25; H, 9.46; N, 11.95%.

N-Methyl-α-naphthohydroxamic acid (**4**); yield 52%, colorless plates from acetone, mp 133—134 °C. Found: C, 71.52; H, 5.43; N, 6.86%. Calcd for $C_{12}H_{11}NO_2$: C, 71.53; H, 5.53; N, 6.96%.

Acetyl *N*-phenylacrylohydroxamate (**1a**); *N*-phenylacrylohydroxamic acid (38 g, 0.23 mol) and 24 g (0.24 mol) of triethylamine were dissolved in a mixture of 700 ml of ether and 100 ml of chloroform. To this solution was added dropwise 17.7 g (0.23 mol) of freshly-distilled acetyl chloride in 100 ml of ether with stirring at −10 °C over 30 min, and stirring was continued for an additional hour at room temperature. The reaction mixture was washed with 100 ml of saturated aqueous NaCl and with three 50-m*l* portions of a dilute Na_2CO_3 solution, and dried over Na_2SO_4. The solvent was evaporated and the tan-brown residue was distilled *in vccuo*. The distillate (dark yellow oil, bp 100—110 °C/0.08 mmHg) was recrystallized from petroleum ether in a dry ice-methanol bath; pale yellow oil, yield 52—65%. Found: C, 64.19; H, 5.53; N, 6.60%. Calcd for $C_{11}H_{11}NO_3$: C, 64.38; H, 5.40; N, 6.83%.

Similar procedures were applied to the preparation of the following acetyl hydroxamates.

Acetyl *N*-phenylisobutyrohydroxamate (**2a**); yield 80%. colorless plates from *n*-hexane. mp 77—78 °C. Found: C, 65.14; H, 6.31; N, 6.31%. Calcd for $C_{12}H_{15}NO_3$: C, 65.03; H, 6.83; N, 6.33%.

Acetyl *N*-methylisobutyrohydroxamate (**3a**); yield 53%. bp 95—98 °C/20 mmHg. Found: C, 52.78; H, 8.26; N, 8.81%. Calcd for $C_7H_{13}NO_3$: C, 52.82; H, 8.23; N, 8.80%.

Copolymerization. The radical copolymerization of acetyl *N*-phenylacrylohydroxamate and acrylamide was performed with azobisisobutyronitrile as an initiator in acetonitrile. The polymerization mixture was placed in an ampoule, which was sealed under nitrogen. After given polymerization periods, water was added to the reaction mixture, and the polymer was recovered by precipitation in excess methanol and dried *in vacuo*. The polymerization results are summarized in Table 1.

Deacetylation. A copolymer sample was dissolved in a small amount of water which contained a large excess of hydroxylamine, and was allowed to stand for 24 hr. The product polymer was recovered by precipitation in excess methanol, washed with methanol and dried *in vacuo*. Completion of deacylation was confirmed by disappearance of an IR peak at 1800 cm^{-1} due to the acetyl hydroxamate group ($\nu_{C=O}$). IR spectra of the copolymer before and after deacetylation are compared in Fig. 1. The corresponding spectra of the model compound are shown for comparison.

Determination of Copolymer Composition. The composition of the deacetylated copolymer was determined by NMR

TABLE 1. COPOLYMERIZATION[a]

Run No	Monomer feed		Time min	Conversion wt %	Copolymer Composition PHA unit, mol%
	PHA, M	AAm, M			
1 (PHA-AAm-1)	0.60	3.40	7	18	11.0[b] (11.1)[c]
2 (PHA-AAm-2)	0.20	3.80	10	8	3.9 (4.6)
3	0.40	3.60	7	22	(8)
4[d]	—	4.00	60	40	100

a) 70 °C, AIBN 0.02 M, CH_3CN solvent. b) Determined by the UV method. c) Data given in parentheses are obtained by the NMR method. d) 80 °C, AIBN 0.02 M, benzene solvent.

TABLE 2. TITRATION OF HYDROXAMIC ACID GROUP[a]

Hydroxamic acid	Polymer composition PHA, mol%	pK_a		n' [b]	pK_{int}[c]	k_a $M^{-1}s^{-1}$
		UV,	potentiometric			
PHA-AAm-1	11	8.69	8.64	1.35	8.58	5.31
PHA-AAm-2	3.9	8.60	—	1.04	8.56	9.12
2	—	8.81	—	—	—	25.1
3	—	9.08	9.03	—	—	32.6
4	—	8.23	8.20	—	—	10.5

a) Titration condition: 30 °C, 0.1 M KCl, 1.4 vol% CH_3CN-H_2O. b) Obtained from UV titration data. c) $pK_{int} = \lim_{\alpha \to 0} pK_{apparent}$.

TABLE 3. ELECTRONIC SPECTRA

Species	Medium	λ_{max}, nm (ε)	
PHA-AAm-1	0.01 M HCl	240 (4200)	205 (1.17×10^4)
	0.01 M NaOH	218 (9280)	275 (2200)
o-Acetyl-PHA-AAm-1	H_2O	240 (7200)	195 (2.15×10^4)
2	0.01 M HCl	240 (4200)	205 (1.10×10^4)
	0.01 M NaOH	218 (9200)	275 (2280)
2a	CH_3CN	240 (7180)	200 (2.10×10^4)

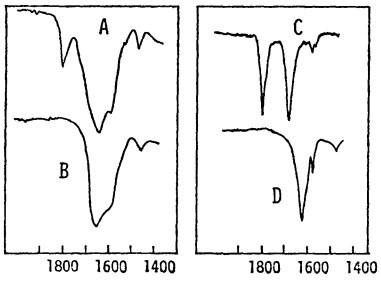


Fig. 1. Partial IR spectra (KBr disk)
A: *o*-acetyl PHA-AAm-1; before deacylation
B: PHA-AAm-1; after deacylation
C: **2a** (acetylated), D: **2** (not acetylated)

spectroscopy and by the UV titration of the hydroxamate group. In the first method, the copolymer composition was determined from the relative peak area of the phenyl protons and the methine and methylene protons. In the second method, the UV absorption characteristics of the hydroxamic acid unit (PHA) in the polymer was assumed to be the same as that of *N*-phenylisobutyrohydroxamic acid, and the copolymer composition was calculated by using the absorption of the hydroxamate anion at 300 nm (ε 1230). The PHA homopolymer prepared by radical polymerization was not utilized for this purpose because of its insolubility in water. The copolymer compositions thus determined are included in Table 1. The UV method appears to be more reliable particularly for samples of the low PHA content.

Determination of pK_a *Value.* The pK_a value of the hydroxamic acids (including the PHA unit in polymer) was determined by the UV spectroscopic and potentiometric titrations. The UV titration was conducted by using the absorbance of the hydroxamate anion at 300 nm in 1.4 vol% CH_3CN-H_2O at 30 °C (0.1 M KCl, 0.05 M Tris buffer), and the potentiometric titration was carried out in 1.4 vol% CH_3CN-H_2O at 30 °C, 0.1 M KCl. The UV titration data for the polymer hydroxamic acids were plotted according to the modified Henderson-Hasselbach equation[14]

$$pK_a = pH + n' \log \frac{1-\alpha}{\alpha} \quad (1)$$

where α is the fraction of the dissociated hydroxamic acid group. The pK_a value corresponds to pH at the half neutralization, and the deviation of the n' value from unity is a qualitative measure of the electrostatic repulsion between the negatively-charged groups.

These titration data are summarized in Table 2. The agreement between the two methods is satisfactory.

Rate Measurements. The rate of acetylation of hydroxamic acids with *p*-nitrophenyl acetate was determined by following the increase in the absorption of the *p*-nitrophenolate anion at 401 nm. The hydrolysis of acetyl hydroxamates was followed in 1.4 vol% CH_3CN-H_2O (0.1 M KCl) at 30 °C by observing the increase in the absorption of the hydroxamate anion at 300 nm. Tris and phosphate buffers

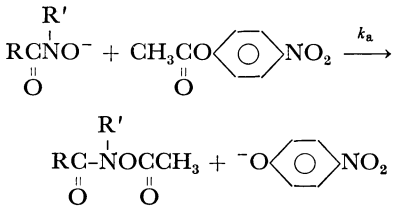
were used. The pH of the reaction mixture was confirmed not to vary from pH measurements (Toa Digital pH Meter Model HM-15A) before and after the reaction.

Results

Electronic Spectra. Electronic spectra of the copolymer are shown in Fig. 2. The absorption of the hydroxamate anion is shifted to the longer wavelength compared with those of the acid and the acetate. The spectral characteristics are summarized in Table 3 together with those of the model compound. It is apparent that the PHA unit gives almost identical spectra with those of the model compound. These results are not inconsistent with those of other hydroxamic acids.[15]

The extinction coefficient of the PHA anion at 300 nm (ε 1250) is much greater than those of the corresponding acid or ester ($\varepsilon<100$). Therefore, the alkaline hydrolysis of acetyl hydroxamates can be followed by the use of the absorption difference at 300 nm, as mentioned above.

Reaction of Hydroxamic Acids with PNPA. The reaction of hydroxamic acids with PNPA leads to the release of *p*-nitrophenol as follows.



(2)

This was confirmed for the polymer hydroxamic acid employed. A solution of PHA-AAm-1 (1×10^{-3} baseM of the PHA unit) in 20 vol% EtOH–H_2O was made alkaline and treated with 0.01 M of 3-nitro-4-acetoxybenzoic acid at room temperature. After 4 hrs, the mixture was poured into excess methanol. The polymer recovered possessed an IR peak at 1800 cm^{-1} which indicated the presence of the acetyl hydroxamate group and the validity of Eq. (2) for the polymeric system.

The nitrophenol release due to spontaneous hydrolysis, v_{H_2O}, was corrected: $v_a=v_{total}-v_{H_2O}$. Figures 3 and 4 show the dependence of the rate of nitrophenol release on the concentrations of hydroxamic acid (HA) and PNPA.

$$v_a = k_{a,obs}[HA][PNPA] \quad (3)$$

When the concentrations of hydroxamic acid and PNPA are comparable as in these experiments, the reaction rate, v_a, follows the overall second-order kinetics. On the other hand, the spontaneous hydrolysis

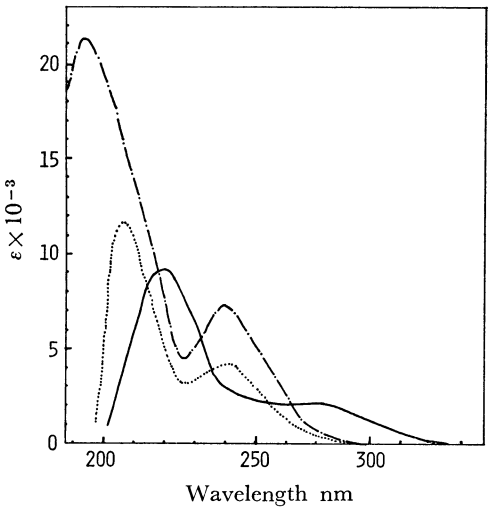


Fig. 2. Electronic spectra of the polymer.
·—· *o*-acetyl PHA-AAm-1 in CH_3CN
---- PHA-AAm-1 in 0.01 M HCl
—— PHA-AAm-1 in 0.01 M NaOH

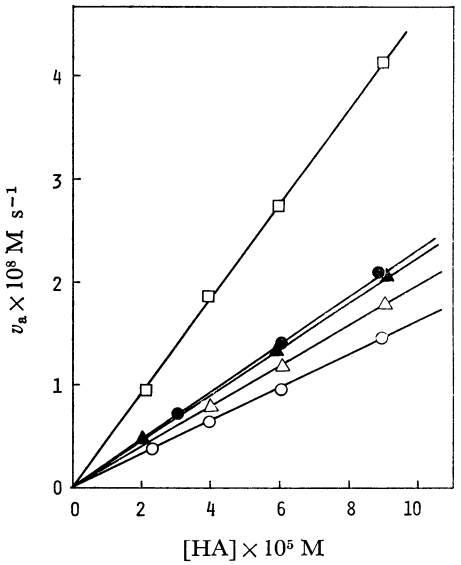


Fig. 3. Reaction of PNPA with a series of hydroxamic acids.
○: PHA-AAm-1, ● PHA-AAm-2; □ **2**, ▲ **3**, △ **4**
pH=8.57, 30 °C, 1.4 vol% CH_3CN–H_2O, 0.1 M KCl, 0.05 M Tris., [PNPA]$=5.01\times10^{-5}$ M

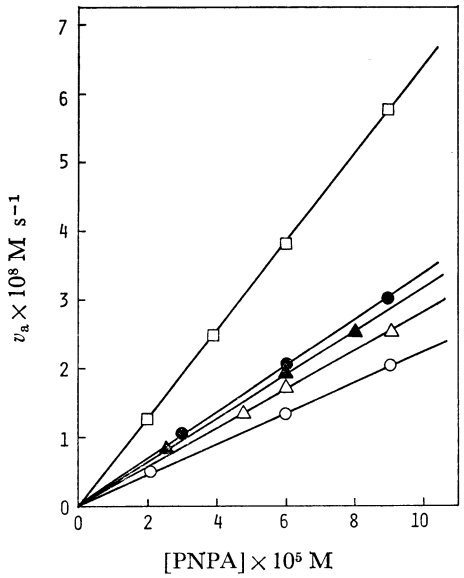


Fig. 4. Reaction of PNPA with a series of hydroxamic acids.
○ PHA-AAm-1, ● PHA-AAm-2, □ **2**, ▲ **3**, △ **4**
pH=8.57, 30 °C, 1.4vol%CH_3CN–H_2O, 0.1 M KCl, 0.05 M Tris., [HA]$=7.01\times10^{-5}$ M

Table 4. Reaction of hydroxamic acid with PNPA[a]

Hydroxamic acid	pH of the reaction medium	$k_{a,obs}$ $M^{-1}s^{-1}$	
		A[b]	B[c]
2	8.57	9.18	9.30
	8.99	14.9	15.2
3	8.57	7.35	7.40
	9.00	14.1	13.9

a) Reaction condition: 30 °C; 0.05 M Tris buffer; 0.1 M KCl; 1.4 vol% CH_3CN-H_2O. b) Obtained from the initial rate. [PNPA] = 3.15×10^{-5} M. [HA] = 5.28×10^{-5} M. c) Obtained from the first-order plot. [PNPA] = 3.15×10^{-5} M. [HA] = 6.28×10^{-3} M.

is a pseudo-first-order process. Therefore, the initial rate of the phenol release was employed for calculating $k_{a,obs}$ values from these data.

The total phenol release adheres strictly to the pseudo-first-order kinetics up to more than 90% reaction, when a large excess of the hydroxamic acid was used. In this case, the rate constant ($k_{a,obs}=k_{total}-k_{H_2O}$) was determined by the Guggenheim method.[16] In Table 4 are compared the rate constants obtained with and without large excesses of hydroxamic acids. The agreements are satisfactory. The use of excess hydroxamic acid concentrations was difficult in the polymeric system, because of the limitation in solubility.

Subsequently, the reaction of hydroxamic acids with PNPA was carried out at the pH range of 7 to 9. The apparent rate constants $k_{a,obs}$ at different pH's are plotted against α(degree of dissociation of hydroxamic acids). Linear relationships were obtained except for PHA-AAm-1, as shown in Fig. 5. An upward curvature was obtained for PHA-AAm-1. This result will be discussed later. It is clear that the hydroxamate anion is the true reacting species and that the reaction rate can be expressed as follows for the first three cases.

$$v_a = k_a\cdot\alpha\cdot[HA][PNPA] \quad (4)$$

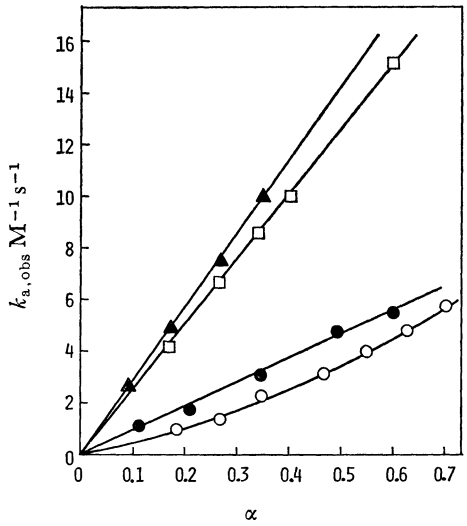


Fig. 5. Reaction of PNPA with a series of hydroxamic acids.
○ PHA-AAm-1, ● PHA-AAm-2, □ **2**, ▲ **3**
30 °C, 1.4vol%CH_3CN-H_2O, 0.1 M KCl, 0.05 M Tris.

where [HA] is the total concentration of the hydroxamic acid employed, and k_a is the true second-order rate constant of acylation.

It is to be noted that the rate of acylation of the polymeric hydroxamate anion was much smaller than that of the model compounds. The k_a value was also calculated for the PHA-AAm-1 case, from the slope at $\alpha=0$. The k_a values are summarized in Table 2.

Hydrolysis of Acetyl Hydroxamates. The hydrolyses of polymeric and monomeric acetyl hydroxamates were performed at three buffer concentrations (0.05, 0.10, 0.15 M) over the pH range between 8.8 and 9.6. The ionic strength was maintained at 0.1 by adding necessary amounts of a KCl solution. The apparent first-order rate constants were calculated by the method of Guggenheim and they were extrapolated to the zero buffer concentration, giving the observed first-order rate constant of deacetylation, $k_{d,obs}$.

$$k_{d,obs} = k_{OH}[OH^-] + k_w \quad (5)$$

The rate constants for the hydroxide and water hydrolyses were determined from the slope and intercept of the linear relationships shown in Fig. 6, and summarized in Table 5.

The k_{OH} values of acetyl *N*-methylhydroxamates were greater than those of the *N*-phenyl counterparts. It is interesting that there is not much difference in k_{OH} values between the corresponding polymeric and small-

Table 5. Hydrolysis of acetyl hydroxamates[a]

hydroxamate	pK_a of hydroxamic acid	k_{OH} $M^{-1}s^{-1}$	$10^4\cdot k_w$ s^{-1}	$10^4\cdot k_{d,obs}$ at pH 7 s^{-1}
o-acetyl-PHA-AAm-1	8.58[b]	11.1	0.15	0.16
o-acetyl-PHA-AAm-2	8.56[b]	13.8	0.31	0.32
2a	8.81	9.10	0.23	0.24
3a	9.08	24.2	0.03	0.27

a) Reaction condition: 30 °C, 0.1 M KCl. b) pK_{int}.

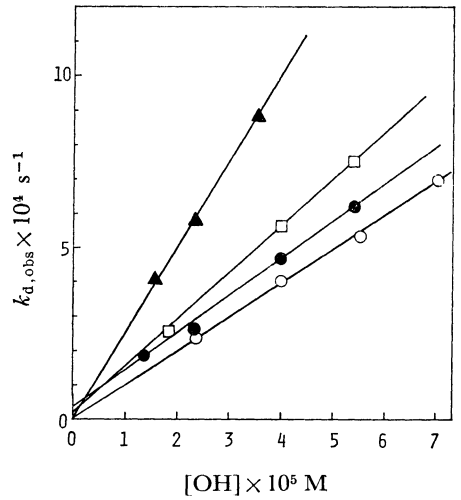
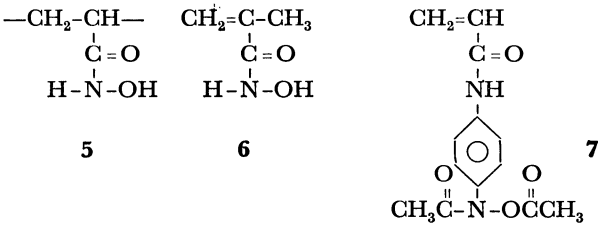


Fig. 6. Deacylation of acetyl hydroxamates.
○ *o*-acetyl PHA-AAm-1, ● *o*-acetyl PHA-AAm-2, □ **2a**, ▲ **3a**
30 °C, 1.4vol%CH_3CN-H_2O, 0.1 M KCl

molecule acetyl hydroxamates. This result is in sharp contrast with that observed in the acylation process.

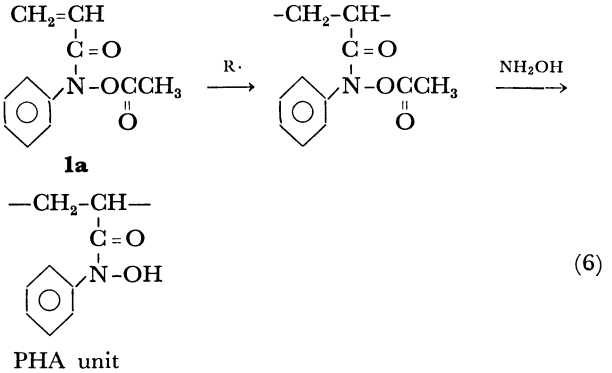
Discussion

Preparation of Polymers Containing the Hydroxamic Acid Group. The introduction of the hydroxamic acid group into polymer has been investigated by several groups. For example, Reiz[17] and Hatano *et al.*[18] prepared polymers containing the hydroxamic acid group (**5**) by reaction of poly(methyl acrylate) with NH_2OH. The conversion was, however, not quantitative. Okawara and coworkers reported a quantitative conversion of the *p*-nitrophenyl ester unit to the hydroxamic acid group in a crossed-linked copolymer. However, the radical polymerization of methacrylohydroxamic acid (**6**) was not successful.[19] Previously we copolymerized a new monomer (**7**) with acrylamide. The hydroxamic acid unit was generated by hydrolysis.[20]



5 **6** **7**

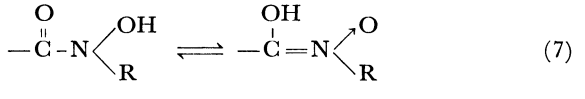
Incorporation of the functional group by polymer reactions often leads to ambiguous results. This is particularly true for rather labile functional groups like hydroxamic acid. Therefore, we synthesized a new monomer (**1a**) which possessed the acetyl hydroxamate group. The hydroxamic acid group was regenerated by NH_2OH treatment of the original polymer.



1a

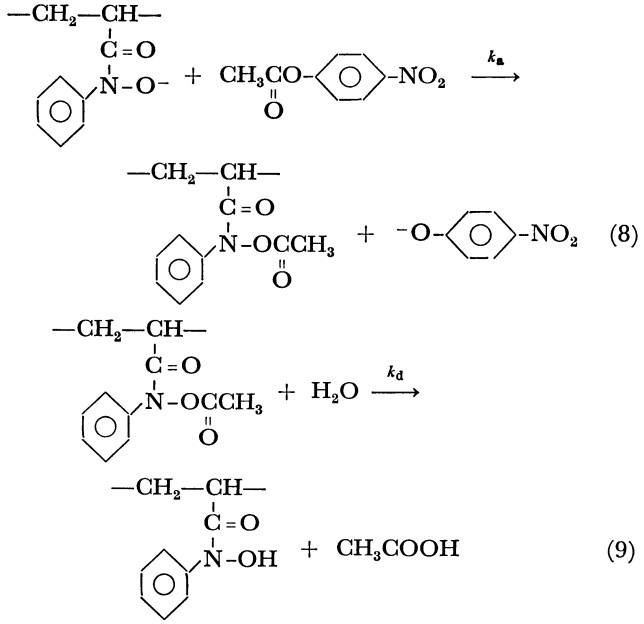
PHA unit (6)

The polymerization of monomers with unprotected hydroxamic acid groups seems difficult, probably because the hydroxamic acid group is tautomeric with the nitrone structure. Nitrones are known to be very efficient trapping agents of the propagating free radical.[21]



a nitrone (7)

Reactions of Hydroxamic Acids with Phenyl Esters. It has been confirmed by several research groups that the reaction of simple hydroxamate anions with phenyl esters yields acyl hydroxamates and phenols.[6,22] The acyl hydroxamate formed can undergo the Lossen rearrangement to isocyanates under strongly basic conditions if the nitrogen of the hydroxamate group is not substituted.[23,24] On the other hand, the Lossen rearrangement can be suppressed by alkyl substitution on the hydroxamic acid nitrogen, and the hydrolysis of acyl hydroxamate to regenerate hydroxamic acid occurs exclusively under basic conditions.[10,25] Thus, Bender and coworkers[10,11] employed *N*-alkylhydroxamic acids as catalysts for the hydrolysis of some phenyl esters. That the same sequence of reactions occurs for polymeric hydroxamic acids (Eqs. (8) and (9)) was established by the present study.



(8)

(9)

Acylation Step. As is clear from Fig. 5, the reaction of the PHA unit in polymer was much slower than that of the monomeric counterpart **2**. Furthermore, two polymer hydroxamic acids show different dependence of the acylation rate on α. This different acylation behavior is interesting. The $k_{a,obs}$ value increases linearly with the increase in α in the case of PHA-AAm-2, whereas the same relation for PHA-AAm-1 is not linear; instead a concave curve is observed. The $k_{a,obs}$ values for PHA-AAm-1 are somewhat lower than those for PHA-AAm-2 at small α values, but they become closer at higher α values.

The n' value determined by the UV titration was 1.35 for PHA-AAm-1 (PHA unit content: 11%) and 1.04 for PHA-AAm-2 (PHA unit content: 3.9%). Therefore, there must be considerable electrostatic repulsion among the hydroxamate anion when the PHA unit content is high. The electrostatic repulsion is conceivably intensified by intramolecular aggregation of the hydrophobic PHA unit. When the content of the PHA unit is small as in PHA-AAm-2, there is not observed noticeable electrostatic repulsion ($n'=1.04$): the dissociation behavior of a given PHA unit is almost the same throughout titration.

The acylation behavior of the polymer hydroxamic

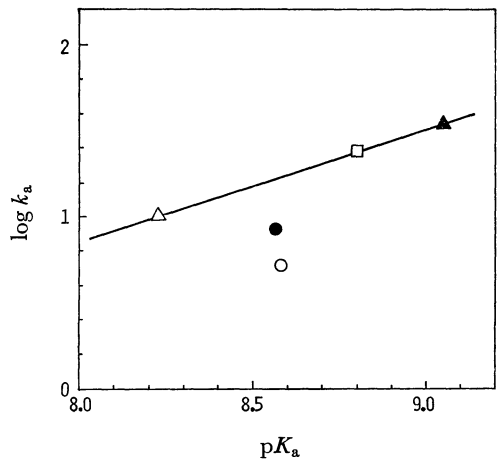


Fig. 7. Brønsted plots.
○ PHA-AAm-1, ● PHA-AAm-2, □ **2**, ▲ **3**, △ **4**
The pK_{int} value was used instead of pK_a for the polymers

acid can be explained by referring to the titration data. The reactivity of the hydroxamate anion in PHA-AAm-2 is invariant since the electrostatic interaction promoted by the side-chain aggregation is negligible. In the case of PHA-AAm-1, the reactivity of a given hydroxamate anion is lessened because of intramolecular aggregation probably with the undissociated PHA unit. As the degree of dissociation increases, the side-chain aggregation is destroyed by expansion of the polymer coil due to increasing electrostatic repulsion among the negatively-charged groups. Therefore, the reactivity of the individual hydroxamate anion increases with α, approaching that of PHA-AAm-2 at higher α values. In the latter polymer, the electrostatic interaction among the PHA unit is considered to be negligible.

The difference in the nucleophilic reactivity between the polymeric and small-molecule systems is also apparent in the Brønsted plot shown in Fig. 7. The three plots for the monomeric hydroxamic acid fall on a straight line, which is expressed by the following equation.

$$\log k_a = 0.62\, pK_a - 4.0 \qquad (10)$$

The slope of the line, the so-called β value in the Brønsted correlation, is 0.62, in fair agreement with those obtained by other workers. Dessolin, *et al.* found β=0.72 for the reaction of PNPA with series of benzohydroxamic acids and cinnamohydroxamic acids.[6] Hershfield and Bender obtained a β value of 0.68 for the reaction of PNPA with three *N*-methylhydroxamic acids.[11] Therefore, it is concluded that the structure variation in the acyl portion and in the *N*-substituent exerts simply the ordinary electronic influence on the nucleophilic reactivity of the hydroxamate group in these systems. The deviation of Brønsted plots for the PHA unit in polymer is, thus, reasonably ascribed to the steric hindrance of the polymer chain on the acylation, rather than to its electronic influence.

Deacylation. The deacylation results are contrasting with the acylation data, in that there is no polymer effect. Thus, the rate constants of deacylation k_{OH} are very similar for three acetyl hydroxamates studied. It might be expected that the hydrolysis rate would decrease with the increase in the basicity of the corresponding hydroxamic acid. However this is not the case, as is clear from the data given in Table 5. It is to be noted that the acetyl hydroxamate unit in polymer possesses a little higher k_{OH} values than the model compound, **2a**. Apparently, the polymer chain does not interfere with the hydroxide attack contrary to the acylation by PNPA. The probable electrostatic repulsion between the partially hydrolyzed O-acetyl-PHA-AAm copolymers and OH^- seemingly does not affect deacylation of the remaining acetyl hydroxamate unit, since the pseudo-first order plot holds well in the deacylation process up to at least 90% completion.

Concluding Remark. As described above, the hydroxamic acid group in polymer undergoes clean acylation and deacylation reactions, as are the monomeric counterparts.* Therefore, polymer hydroxamic acids are potential catalysts for the hydrolysis of phenyl esters. However, the deacylation process is not efficient and the acetyl intermediate is accumulated under the ordinary reaction condition. In fact, the k_{OH} value of PNPA (9.5 $M^{-1}\,s^{-1}$, 25 °C, 1.0 M KCl)[25] is in the same range as those of acetyl hydroxamates. This behavior of the hydroxamic acid is quite contrasting with that of imidazole. In the catalytic hydrolysis of PNPA with imidazole, the acylation process is rate-limiting[26] and the deacylation process is much more efficient than that of acetyl hydroxamates. Therefore, it appears that the catalytic efficiency of the hydroxamic acid can be enhanced by introduction of the intramolecular imidazole unit which assists deacylation of acetyl hydroxamates. This has been accomplished to some extent in a polymeric system.[27]

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