The Esterolytic Activity of Poly(*N*-alkylimidazoles) in Ethanol–Water. The Poly(1-methyl-5-vinylimidazole)-Catalyzed Hydrolysis of *p*-Nitrophenyl Acetate and 3-Nitro-4-acetoxybenzoic Acid

C. G. Overberger* and Thomas W. Smith

Department of Chemistry and the Macromolecular Research Center, The University of Michigan, Ann Arbor, Michigan 48104. *Received February 18, 1975*

ABSTRACT: 1-Methyl-4-vinylimidazole (1-Me-4-VIm) and 1-methyl-5-vinylimidazole (1-Me-5-VIm) have been synthesized and polymerized. The esterolytic activity of these polymers in 28.5% ethanol–water toward *p*-nitrophenyl acetate (PNPA) and 3-nitro-4-acetoxybenzoic acid (S_2^-) has been evaluated as compared to that of the model compounds 1,4-dimethylimidazole (1,4-DMIm) and 1,5-dimethylimidazole (1,5-DMIm). Poly(1-methyl-4-vinylimidazole) [poly(1-Me-4-VIm)] and 1,4-DMIm are not catalytically active, as compared to buffer solution, toward PNPA and S_2^- in 28.5% ethanol–water. The rate of hydrolysis of PNPA by 1,5-DMIm and poly(1-methyl-5-vinylimidazole) [poly(1-Me-5-VIm)] was proportional to the concentration of neutral imidazole residues for both catalysts; however, 1,5-DMIm was five times more active than poly(1-Me-5-VIm). Poly(1-Me-5-VIm) displayed a bell-shaped pH-rate profile toward the negatively charged ester S_2^- while the rate of hydrolysis by 1,5-DMIm was again proportional to the concentration of neutral imidazole. At their respective optimum pH's, poly(1-Me-5-VIm) was 20% more active than 1,5-DMIm.

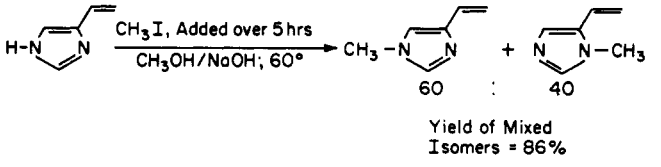
In recent years, we have extensively studied the esterolytic activity of poly[4(5)-vinylimidazole] (poly[4(5)-VIm]).[1-7] In these studies, it was shown that at high pH, ca. >8, poly[4(5)-VIm] was a more efficient catalyst than monomeric imidazole toward the hydrolysis of the neutral ester *p*-nitrophenyl acetate (PNPA). This rate enhancement was attributed to cooperative interactions between pendant imidazole residues.[7] Morimoto and Overberger[5] demonstrated that cooperativity in poly[4(5)-VIm] was most pronounced when the conformation of the polymer was most compact, i.e., in aqueous solutions of either high or low ethanol content. This cooperativity was felt to entail general base catalysis by one pendant imidazole of attack by a second imidazole residue.[8-10]

Poly(1-methyl-5-vinylimidazole) [poly(1-Me-5-VIm)] and poly(1-methyl-4-vinylimidazole) [poly(1-Me-4-VIm)] are similar to poly[4(5)-VIm] in many respects; however, there are some notable differences. With respect to cooperativity, the absence of the amine hydrogen precludes general-base catalysis of attack by an *N*-alkylated residue. In addition, nucleophilic attack by an *N*-alkylated residue must occur with the intermediate formation of a positively charged acyl intermediate.[11] This fact has important kinetic ramifications, particularly with respect to the hydrolysis of long-chain nitrophenyl esters. (See following papers.)

Results and Discussion

Synthesis. 1-Methyl-4-vinylimidazole (1-Me-4-VIm) and 1-methyl-5-vinylimidazole (1-Me-5-VIm) were synthesized simply by alkylation of 4(5)-vinylimidazole [4(5)VIm], which was prepared by the method of Overberger and Vorchheimer[12] (see Scheme I). The procedure employed was a modification of that used by Häring[13] for the alkylation of imidazole. The mixed isomers of 1-Me-4-VIm and 1-Me-5-VIm were thus obtained in 86% yield, the isomer ratio being 60:40 as determined by NMR.

Scheme I
Synthesis of 1-Methyl-4-vinylimidazole and 1-Methyl-5-vinylimidazole



Separation of the isomers was initially achieved by GLC on a 25% QF-1 on Chromosb W column.[14] The method was not attractive as a preparative tool because no more than 10 μl of a 30% solution of the mixed isomers could be injected with adequate separation. Further, the 25% QF-1 column bled excessively.

The isomeric *N*-methyl-4- and -5-vinylimidazoles can best be separated by preparative thin-layer chromatography (TLC) on alumina [Brinkmann, Alox-100 UV_{254}, 1.0 mm plates or Brinkmann, $Al_2O_3F_{254}$ (type T) 1.5 mm plates] eluting with acrylonitrile and developing each plate two to three times. As much as 10 g of the mixed isomers was separated in this manner.

The individual isomers were characterized by NMR, uv, and ir. The NMR exhibited marked differences in the vinyl regions and in the chemical shifts of the imidazole ring protons (see Figure 1). Although the pattern in the vinyl re-

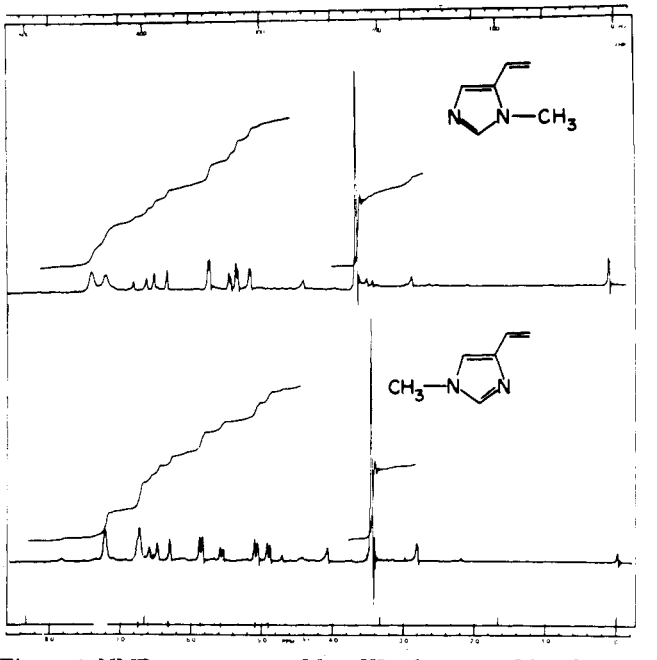


Figure 1. NMR spectra: top, 1-Me-5-VIm; bottom, 1-Me-4-VIm.

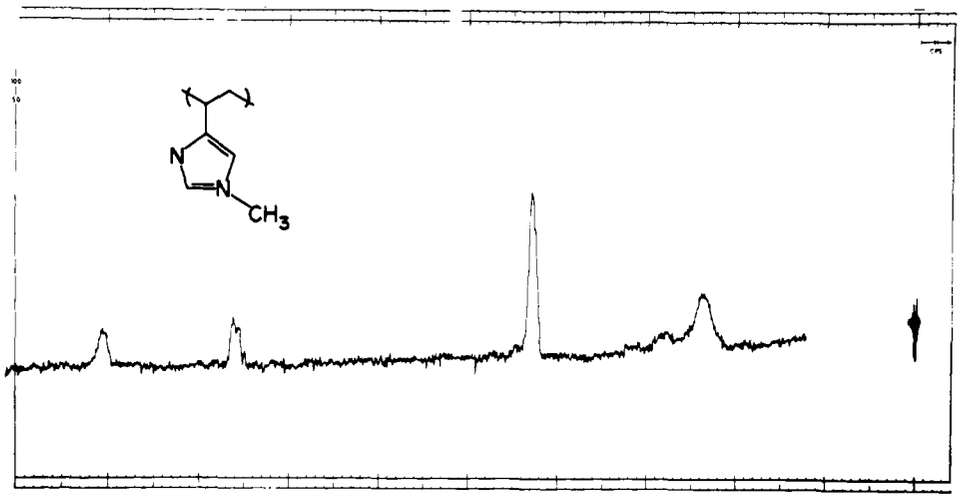


Figure 2. NMR spectrum of poly(1-Me-4-VIm).

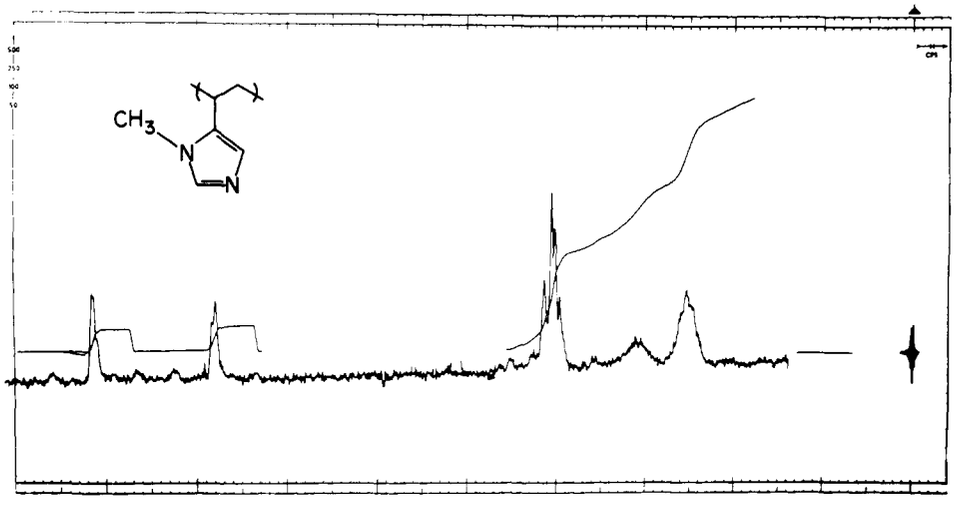


Figure 3. NMR spectrum of poly(1-Me-5-VIm).

gion appeared to be characteristic, the isomers could not be assigned unequivocally as 1,4 and 1,5 without further evidence. However, the compound having the highest extinction coefficient (λ_{max} 244 nm, ϵ = 7860 vs. λ_{max} 259 ϵ = 6930) comprised 60% of the mixture and thus was termed 1-Me-4-VIm.

Poly(1-Me-4-VIm) and poly(1-Me-5-VIm) were prepared in bulk. The polymerizations were carried out at 65° initiating with 2,2′-azobis(2-methylpropionitrile), AIBN. The polymers were purified first by reprecipitating concentrated methanol solutions in benzene. The reprecipitated polymers were then dissolved in methanol and passed over a gel permeation column (Sephadex LH-20). After reprecipitation and before elution over the Sephadex column, the uv spectra of the polymers exhibited two peaks, one at about 220 nm and a shoulder at about 250 nm due to residual monomer. After gel filtration the polymers exhibited only a single peak at about 220 nm.

The NMR spectra of poly(1-Me-4-VIm) and poly(1-Me-5-VIm) were quite informative (see Figures 2 and 3). The multiplicity of the N-CH_3 peak allows one to unequivocally assign the 1,4 and 1,5 isomers. In poly(1-Me-5-VIm), the *N*-methyl group extends into the polymethylene chain. As the conformation of the chain changes, the environment of the methyl group changes. Thus, the methyl signal in a homopolymer of poly(1-Me-5-VIm) should appear as a multiplet. In poly(1-Me-4-VIm), the *N*-methyl group will be directed away from the methylene chain, therefore it should appear as a singlet (see Figures 4 and 5).

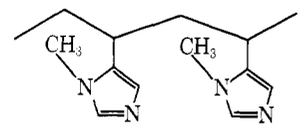


Figure 4. Poly(1-Me-5-VIm).

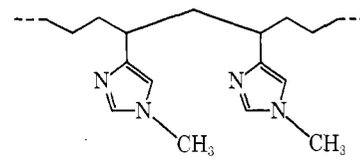


Figure 5. Poly(1-Me-4-VIm).

Kinetics. The kinetics in ethanol–water were typically carried out in excess catalyst, ca. 5×10^{-4} *M* polymer, 5×10^{-5} *M* substrate. Under these conditions, the linearity of the plots of ln $(A_\infty - A_t)$ vs. time demonstrated the first-order nature of the kinetics. The slope of this line was taken as the pseudo-first-order rate constant (k_{meas}). The first-order rate constant (k_{obsd}) and the second-order rate constant k_{cat} were calculated from the following relationships.

$$k_{obsd} = k_{meas} - k_{blank} \quad (1)$$

$$k_{cat} = k_{obsd}/(\text{catalyst}) \quad (2)$$

Determination of pK_a's. The degree of ionization as a function of pH for all catalysts was determined by poten-

Table I
Solvolysis of PNPA in 28.5% Ethanol-Water[a] (k_{cat}, M^{-1} min^{-1})

Catalyst	pK_a[g]	pH 3.90	4.95	6.00	6.85	7.75	8.15	8.75
1,4-DMIm	7.0			0.05				−0.56
Poly(1-Me-4-VIm)	5.20	−0.008		0.028	0.00	0.00		0.00
1,5-DMIm	7.35			2.08	10.0	22.0		29.4
Poly(1-Me-5-VIm)	4.70	0.16	1.15	3.26	4.00	4.20	5.48	5.86
Imidazole[b]	7.00[h]			3.12[b,c]	11.48[b,d]			16.92[b,f]
Poly[4(5)-VIm]	6.00[h]			4.68[b,c]	11.04[b,d]	18.24[b,e]		22.64[b,f]

[a] [Catalyst] = 5×10^{-4} M, [PNPA] = 5×10^{-5} M, μ = 0.02, 26°. [b] From ref 16, [catalyst] = 2.5×10^{-4} M. [c] pH 6.02. [d] pH 7.14. [e] pH 8.04. [f] pH 9.14. [g] Determined in 28.5% ethanol-water, μ = 0.02, 26°. [h] From ref 5, determined in 25% ethanol-water, μ = 0.02, 26°.

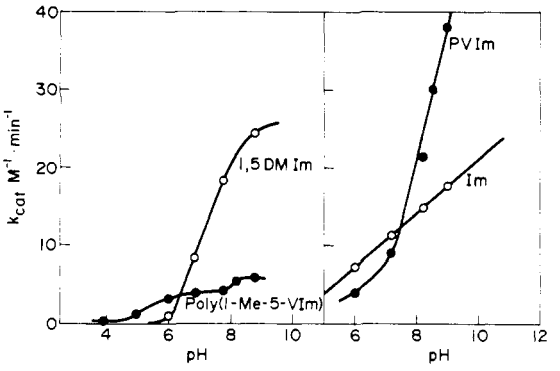


Figure 6. Solvolysis of PNPA in 28.5% EtOH. Second-order rate constants for the hydrolysis of PNPA in 28.5 vol % EtOH/H_2O, [PNPA] = 5×10^{-5} M, μ = 0.02, 26°.

tiometric titration in 28.5% ethanol–water, μ = 0.02 M (KCl) at 26°.

Plots of ln $(1 - \alpha_1/\alpha_1)$ vs. pH for all polymers were essentially linear, following the modified Henderson–Hasselbach equation[15]

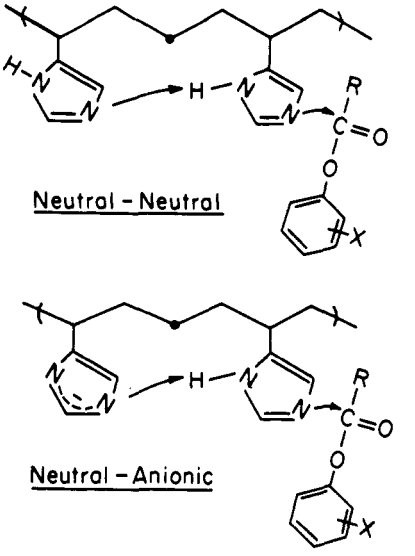
$$pK_a = pH + n' \log ((1 - \alpha_1)/\alpha_1) \quad (3)$$

where α_1 is equal to the fraction of neutral imidazole residues.

Kinetic Studies in Ethanol–Water. The esterolytic activity of poly(1-Me-4-VIm) and poly(1-Me-5-VIm) has been evaluated. It was desirable to carry out these studies in such a way as to allow comparison with the previous work done on 4(5)-vinylimidazole polymer systems. The expectation was that poly(1-methyl-5-vinylimidazole) would exhibit esterolytic activity similar to that shown by poly[4(5)-VIm], except that the *N*-methylated polymer would not be capable of cooperative interactions and would not suffer from rate-determining decylation.[2] A rather common solvent system for the hydrolysis of nitrophenyl esters by poly[4(5)-VIm] has been 28.5% ethanol–water (v), μ = 0.02. This, therefore, was the system in which this study of the esterolytic activity of poly(*N*-alkyl-4- and -5-vinylimidazoles) was initiated. As model compound to which to compare the activity of poly[4(5)-VIm], imidazole itself was chosen. The model compounds chosen for this study of the catalytic activity of poly(1-alkyl-4-vinylimidazoles) and poly(1-alkyl-5-vinylimidazoles) are 1,4-dimethylimidazole (1,4-DMIm) and 1,5-dimethylimidazole (1,5-DMIm), respectively.

The Effect of pH on the Rate of Solvolysis. (a) The Hydrolysis of the Neutral Ester, PNPA. The existence of cooperative interactions in catalysis by poly[4(5)-VIm] was first observed by monitoring the effect of pH on the rate of hydrolysis of *p*-nitrophenyl acetate (PNPA).[8] While the pH-rate profile for the imidazole-catalyzed hydrolysis

Scheme II
Cooperative Interactions in Poly-4(5)VIm



shows a linear dependence on the fraction of neutral imidazole, that for poly[4(5)-vinylimidazole] is nonlinear, the polymer being a less efficient catalyst than imidazole at less than 80% neutral imidazole residues and more efficient at greater than 80% neutral imidazole residues. This behavior was explained in terms of neutral–neutral and neutral–anionic cooperative interactions between pendant imidazole groups.[8] Overberger and Shen[10] have shown that these interactions are most likely between imidazole residues positioned 1–3 along the chain. The mechanism of this reaction probably involves general base catalysis of the attack of one pendant imidazole by another neutral or anionic imidazole residue not favorably disposed to carry out the catalysis (see Scheme II). Such a general base mechanism results in attack by a species which is essentially an anionic imidazole residue.

Over the pH range 4–9, the poly(1-Me-5-VIm)-catalyzed hydrolysis of PNPA shows no rate enhancement over the rate exhibited by 1,5-DMIm. As a matter of fact, at pH 8.75, where their respective imidazole residues are in their catalytically active neutral form, 1,5-DMIm is almost five times more active than poly(1-Me-5-VIm).

Poly(1-Me-4-VIm) displays essentially no catalytic activity toward PNPA in the pH range 4–9. Surprisingly, 1,4-DMIm also lacks any measurable catalytic activity toward PNPA. Table I and Figure 6 display the data for the hydrolysis of PNPA, at varying pH, by 1,4-DMIm, 1,5-DMIm, poly(1-Me-4-VIm), and poly(1-Me-5-VIm). These data are compared to Salamone's data[16] for the poly[4(5)-VIm]-catalyzed hydrolysis of PNPA.

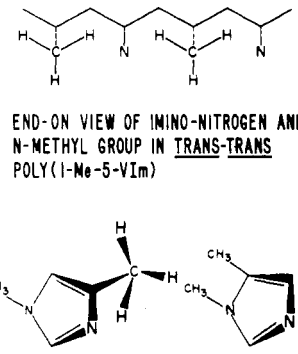


Figure 7. Perspective drawings of model compounds.

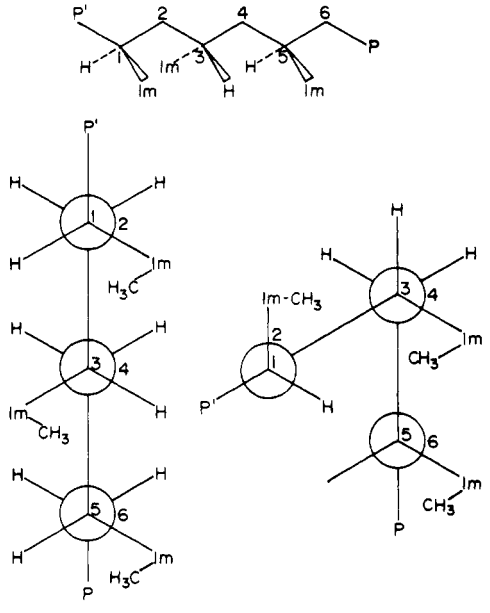


Figure 8. Newman projections: left, trans; right, skew.

The first fact that one should glean from this data is that steric considerations are of overriding importance in nucleophilic catalysis. One has only to note that 1,4-DMIm is not catalytically active, while 1,5-DMIm exhibits a k_{cat} value of about 30 M^{-1} min^{-1}, to come to such a realization. With respect to the factor of 5 difference in the rate of hydrolysis by 1,5-DMIm and poly(1-Me-5-VIm), it should be pointed out that the steric accessibility of the imino nitrogen in poly(1-Me-5-VIm) may be more closely approximated by 1,4-DMIm. This becomes evident if one makes models of 1,4-DMIm, 1,5-DMIm, and poly(1-Me-5-VIm). Figure 7 shows an end-on view of the pendant imidazole groups sandwiched beside each other in a trans, syndiotactic polymer of 1-methyl-5-vinylimidazole. Also shown are perspective drawings of the model compounds.

Actually, the trans conformation is probably not the preferred conformation of the 1,5 polymer. Models indicate that some type of skew conformation would be most stable (see Figure 8). The Newman projections shown in Figure 8 are designed to show how one gets fewer steric interactions between the *N*-methyl group and the polymethylene chain when the chain assumes a skew conformation. Notice how the 5-methyl group of the imidazole residue on C-3 does not extend into the chain when the chain takes on a skew conformation.

Along another vein, one must consider the effect on the rate due to changing pK_a of the nucleophile. In 28.5% ethanol–water, poly(1-Me-4-VIm) exhibits a pK_a of 5.20, while poly(1-Me-5-VIm) has a pK_a of only 4.70. 1,4-DMIm and

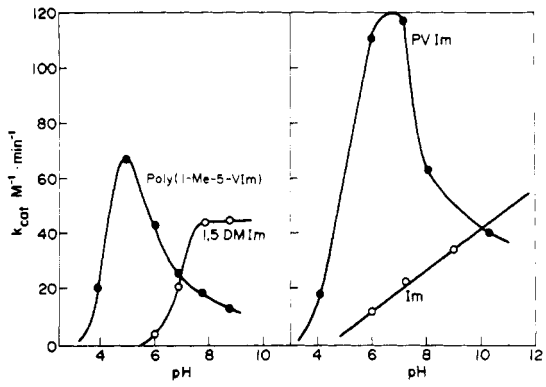


Figure 9. Solvolysis of S_2^- in 28.5% EtOH. Second-order rate constants for the hydrolysis of S_2^- in 28.5 vol % EtOH/H_2O, $[S_2^-] = 5 \times 10^{-5}$ *M*, $\mu = 0.02$, 26°.

1,5-DMIm display pK_a's of 7.00 and 7.35, respectively. The relationship between the pK_a of the nucleophile and the catalytic activity of monomeric five-membered ring heterocycles is described by the Brønsted catalysis law,[17] $\log k = B(pK_a) + \log C$, where $B = 0.612$ and $\log C = -2.97$.[18] Taking into account the pK_a of 1,5-DMIm and poly(1-Me-5-VIm), if no rate enhancement occurs due to the polymeric nature of the catalyst, a second-order rate constant, k_{cat}, of −1.87 would be predicted for poly(1-Me-5-VIm), while a value of 33.9 is predicted for 1,5-DMIm. The experimentally determined value for 1,5-DMIm is 29.4 while that for the polymer is 5.86. Based on such an interpretation it can be stated that poly(1-Me-5-VIm) exhibits a significant rate enhancement over its monomeric species (a 1,5-substituted imidazole with a pK_a of 4.70).

Lastly, it should be recognized that there is indeed no possibility for general-base cooperative interactions of the type postulated in catalysis by poly[4(5)-VIm].[9,10] That no real enhancement is observed in catalysis by poly(1-Me-5-VIm) can, in fact, be taken as support for the general-base mechanism of cooperativity in catalysis by poly[4(5)-VIm].

(b) The Hydrolysis of the Negatively Charged Ester 3-Nitro-4-acetoxybenzoic Acid, S_2^-. The role of electrostatic interactions in the catalytic activity of synthetic polymers has been extensively investigated. As early as 1959, Ladenheim and Morawetz had studied the reaction of the α-bromoacetate ion with poly(4-vinylpyridine).[19] The rate of the displacement of the bromide ion increased with increasing ionization of the pyridine groups, while the monomeric analog, 4-methylpyridine, had no effect on the rate of bromide displacement. The high reactivity of the polymer was attributed to the electrostatic attraction of the bromoacetate anion by the protonated residues of the polymer, thus accumulating the substrate in the vicinity of a high local concentration of catalytically active neutral pyridine groups.

Letsinger and Savereide[20] studied the hydrolysis of potassium 3-nitro-4-acetoxybenzene sulfonate (NABS) catalyzed by partially protonated poly(4-vinylpyridine) in a pH range in which the substrate existed extensively as anion. A bell-shaped pH-rate profile was obtained, with a maximum at pH 4 where approximately 70–80% of the pyridine groups were in the neutral form. At pH values where similar concentrations of neutral pyridine groups were present, NABS was hydrolyzed 9.3 times faster by poly(4-vinylpyridine) than by the model system, picoline.

Overberger and coworkers[21] have obtained rate enhancements of up to 50 times the rate exhibited by monomeric imidazole in the poly[4(5)-VIm]-catalyzed hydrolysis of the netatively charged substrates, S_2^- and NABS. Bell-shaped

Table II
Solvolysis of S_2^- in 28.5% Ethanol-Water[a] (k_{cat}, M^{-1} min^{-1})

Catalyst	pK_a[h]	pH 3.90	4.95	6.00	6.85	7.75	8.75	10.30
1,5-DMIm	7.35			3.99	21.1	44.2	44.4	
Poly(1-Me-5-VIm)	4.20	20.2	67.0	42.7	25.4	18.7	13.1	
Imidazole[b]	7.00[i]			6.0	20.4		0.77[b,g]	
Poly[4(5)-VIm][b]	6.00[i]	17.2[b,c]		110.4[b,d]	117.2[b,e]	62.8[b,f]		40.0

[a] [Catalyst] = 5×10^{-4} M, [PNPA] = 5×10^{-5} M, μ = 0.02, 26°. [b] From ref 16, [catalyst] = 2.5×10^{-4} M. [c] pH 4.08. [d] pH 6.02. [e] pH 7.14. [f] pH 8.04. [g] pH 9.14. [h] Determined in 28.5% ethanol-water, μ = 0.02, 26°. [i] From ref 5, determined in 25% ethanol-water, μ = 0.02, 26°.

pH-rate profiles were observed for the hydrolysis of either of these esters. The maximum in the bell occurred around pH 7, where about 75% of the imidazole residues were in their neutral form. For the reaction of monomeric imidazole with these negatively charged substrates, the catalytic rate constants were found to be linearly dependent on the fraction of neutral imidazole present.

Poly(1-Me-5-VIm) also displays a bell-shaped pH-rate profile for its hydrolysis of S_2^- (see Figure 9). As with imidazole itself, the rate of the 1,5-DMIm-catalyzed hydrolysis of S_2^- is linearly dependent upon the fraction of neutral imidazole residues.

These bell-shaped pH-rate profiles, exhibited by the polymers, result from a proper concentration of charged groups in the polyion to facilitate an electrostatic interaction with substrate and a proper concentration of neutral residues acting as nucleophiles.[22]

At its optimum pH, poly(1-Me-5-VIm) was 20% more catalytically active toward S_2^- than the model compound, 1,5-DMIm, at its optimum pH. The peak of the bell occurs about pH 5 where 60% of the methylimidazole residues are neutral. This peak occurs at a higher degree of protonation than that in catalysis by poly[4(5)-VIm]. It is felt that the poly[4(5)-VIm] peak is shifted to a higher percentage of neutral residues because of rate enhancement from neutral–neutral cooperativity. Table II and Figure 9 present the data for the 1,5-DMIm-, poly(1-Me-5-VIm)-, imidazole, and poly[4(5)-VIm]-catalyzed hydrolysis of S_2^- in 28.5% ethanol–water at varying pH.

Experimental Section

A. Synthesis. 1. 4(5)-Vinylimidazole [4(5)-VIm]. 4(5)-VIm was prepared by the procedure of Overberger, Glowaky, Pacansky, and Sannes.[23]

2. 1-Methyl-4-vinylimidazole (1-Me-4-VIm) and 1-Methyl-5-vinylimidazole (1-Me-5-VIm). Crude 4(5)-VIm, 9.40 g (0.10 mol), was charged to a 200 ml pressure bottle along with 10 ml of methanol and 10 ml of 10 N sodium hydroxide. The bottle was capped with a crown cap and neoprene gasket and immersed in a constant temperature bath at 60°. Methyl iodide was injected via syringe in 250-μl increments every 10 min for 4 hr and 20 min.

After an additional 3 hr at 60°, the reaction mixture was quenched by dilution with chloroform and water. The aqueous layer was saturated with potassium carbonate and extracted several times with chloroform. The chloroform extract was subsequently dried over anhydrous potassium carbonate. A drop of saturated picric acid solution in ethanol was added to the chloroform extract and the solvent was removed in vacuo. The crude mixed isomers of 1-Me-4-VIm and 1-Me-5-VIm remained as an oily residue.

The crude mixture was passed over a Florisil column, eluting with chloroform. The N-methylimidazole isomers eluted gradually, while the unreacted 4(5)-vinylimidazole remains on the column. A drop of saturated picric acid solution was added to the chloroform eluent and the solvent was removed, yielding 9.32 g (86%) of the mixed N-methyl-4- and -5-vinylimidazoles.

The 1,4 and 1,5 isomers were separated by preparative thin-layer chromatography (TLC) on alumina [Brinkman, Alox-100 UV_{254}, 1.0 mm plates or Brinkman, Al_2O_3 F_{254} (type T) 1.5 mm plates]. Approximately 250 mg of the mixed isomers was applied per 1.0 mm plate and 300 mg was applied to each 1.5 mm plate. The sample was applied to the plates by the method of Weaver and Teegarden.[24] Each plate was developed twice eluting with acrylonitrile. The 1.0 mm plates were dried at ambient temperature for at least 0.5 hr between developments; the 1.5 mm plates were dried for 1 hr [R_{f2} (1-Me-5-VIm) 0.266, band width 8 cm; R_{f2} (1-Me-4-VIm) 0.713, band width 2.7 cm; band separation 1 cm]. Thirty-one plates were required to separate 9.3 g of the mixed isomers.

The isomers can be separated by gas–liquid chromatography (GLC) on a fresh 0.25 in., 25% QF-1 on 60–40 Chromosorb W column.[14] Typical separation conditions are: oven temperature, 150° isothermal; injector temperature, 250°; detector temperature, 270°; helium flow rate, 8 ml/sec.

The separated isomers were extracted off the alumina into methanol–chloroform; a drop of picric acid was added to each extract and the respective isomer solutions were evaporated, in vacuo, to oily residues, yielding 2.61 g of 1-Me-5-VIm and 3.59 g of 1-Me-4-VIm. The total overall yield was 6.20 g (57%).

Portions of each of these isomers were distilled. 1-Me-4-VIm: bp 62–63° (0.025 mm); n^{26}D 1.5397, uv λ_{max} 243, ϵ = 7860; ir (neat film) cm^{-1} 1641 s (C=C); NMR (neat) δ_{TMS} 3.46 (3 H, s, N-CH_3), 5.0 (1 H, q, *cis*-vinyl H), 5.73 (1 H, q, *trans*-vinyl H), 6.59 (1 H, q, vinyl H–C) 6.74 (1 H, s, C-5H), 7.22 (1 H, s, C-2H); mass spectrum m/e 108. 1-Me-4-VIm·picrate: mp 181.5–182.5°. Anal. Calcd for $C_6H_8N_2$: C, 66.67; H, 7.41; N, 25.92. Found: C, 65.43; H, 7.47; N, 25.86. 1-Me-5-VIm: bp 60–61° (0.025 mm); n^{26}D 1.5435; uv λ_{max} 258 nm, ϵ = 6930; ir (neat film) cm^{-1} 1630 s (C=C); NMR (neat) δ_{TMS} 3.57 (3 H, s, N-CH_3), 5.25 (1 H, q, *cis*-vinyl H), 5.60 (1 H, q, *trans*-vinyl H), 6.59 (1 H, q, H–C), 7.13 (1 H, s, C-4H), 7.31 (1 H, s, C-2H); mass spectrum m/e 108. Anal. Calcd for $C_6H_8N_2$: C, 66.70; H, 7.41; N, 25.92. Found: C, 66.75; H, 7.47; N, 25.91. 1-Me-5-VIm·picrate: mp 177–178°.

3. Poly(1-methyl-4-vinylimidazole). 1-Methyl-4-vinylimidazole, freshly distilled, 1.0 g, and AIBN, 0.0152 g, were charged to a 5 ml ampoule. The materials were degassed by the standard freeze–thaw technique prior to sealing the evacuated ampoule. The ampoule (properly sheathed) was immersed in an oil bath at 60°. After 16 hr the ampoule was removed. The ampoule was crushed and the polymer was dissolved in chloroform before precipitating in acetone. The colloidal precipitate was agglomerated by heat digestion and the polymer was isolated by filtration through a medium porosity sintered glass funnel. The material was then dried, yielding 1.0 g of poly(1-Me-4-VIm).

Half of this polymer, 0.5 g, was dissolved in 5 ml of methanol and eluted over the Sephadex LH-20 column and the eluent was monitored by uv. Most of the methanol was removed in vacuo before dilution with benzene. Lyophilization of this solution yielded the poly(1-Me-4-VIm) employed in these studies: [η] methanol (26°) = 0.405; NMR (methanol-d_4) δ_{TMS} 1.69 (broad -CH_2-), 2.15 (broad -CH-), 3.71 (s, N-CH_3), 6.45 (m, C-5H), 7.45 (broad s, C-2H). Anal. Calcd for $C_6H_8N_2$: C, 66.67; H, 7.91; N, 25.9. Found: C, 61.62; H, 7.63; N, 23.09; C, 61.79; H, 7.54; N, 23.19.

4. Poly(1-methyl-5-vinylimidazole). Poly(1-Me-5-VIm) was prepared in bulk by a procedure identical with that employed for poly(1-Me-4-VIm). Thus, 1.0 g of freshly distilled 1-methyl-5-vinylimidazole and 0.0152 g of AIBN gave a quantitative yield of poly(1-Me-5-VIm). Elution over the Sephadex LH-20 column and lyophilization of the benzene–methanol solution yielded the poly(1-Me-5-VIm) utilized in these studies: [η] methanol (26°) = 0.275; NMR (methanol-d_4) δ_{HMS} 1.93 (broad -CH_2-), 2.41 (broad -CH-), 3.13 (m, N-CH_3), 6.75 (s, C-4H), 7.61 (s, C-2H). Anal. Calcd for $C_6H_9N_2$: C, 66.67; H, 7.91; N, 25.92. Found: C, 65.76; H, 7.43; N, 24.07; C, 65.64; H, 7.39; N, 24.17.

5. 1,4-Dimethylimidazole (1,4-DMIm) and 1,5-Dimethylimidazole (1,5-DMIm).[25-27] 4-Methylimidazole (Aldrich, Reagent), 10 g (0.122 mol), was charged to a 200 ml pressure bottle along with 15 ml of methanol and 10.4 ml (0.130 mol) of 50% aqueous sodium hydroxide. The contents were stirred with a magnetic stirrer and the bottle was capped with a crown cap and neoprene gasket. The bottle was immersed in a constant temperature bath at 55° and allowed to equilibrate over 0.5 hr. At this time 2 ml of methyl iodide was added via syringe. Thereafter, methyl iodide was injected every 15 min in 0.5 ml increments until a total of 8.3 ml of methyl iodide was added. The reaction mixture was subsequently held at 55° for 2 hr before quenching by dilution with chloroform and water.

The aqueous layer was saturated with potassium carbonate and extracted with chloroform. The chloroform extract was dried over anhydrous potassium carbonate before removal of solvent in vacuo. The residue was eluted over a Florisil column with chloroform to remove any unreacted 4-methylimidazole and the solvent was again removed in vacuo, yielding 7.5 g (64%) of the mixed isomers in a ratio estimated by NMR to be 60:40 1,4 to 1,5.

An attempt was made to fractionally distill the respective isomers at atmospheric pressure on a spinning band column. The only fraction which came over was 1,4-DMIm, distilling at 200° (lit.[26] 198–200°): NMR (neat) δ_{TMS} 2.2 (3 H, s, CH_3), 3.54 (3 H, s, N-CH_3), 6.67 (1 H, s, C-5H), 7.03 (1 H, s, C-2H).

The residue was vacuum distilled in a short path distillation apparatus, bp 40° (0.010 mm). By NMR this fraction was estimated to be 83% 1,5-DMIm and 17% 1,4-DMIm: NMR (neat) δ_{TMS} 2.0 (3 H, s, CH_3), 3.34 (3 H, s, N-CH_3), 6.67 (1 H, s, C-4H), 7.38 (1 H, s, C-2H).

B. Characterization of Monomers and Polymers. All melting points were determined in open capillary tubes on a Thomas Hoover capillary melting point apparatus and are uncorrected. Analyses were determined by Spang Laboratories, Ann Arbr, Mich., or by Galbraith Laboratories, Inc., Knoxville, Tenn. Ir spectra were recorded on a Perkin-Elmer Model 237 spectrophotometer. NMR spectra on monomeric compounds were recorded on a Varian T-60 spectrophotometer. NMR of polymers were recorded at +100° on a Varian HA-100 spectrophotometer.

C. Potentiometric Titrations. About 75×10^{-3} mmol of sample and 0.3 ml of 1 *N* HCl was diluted in a thermostated cell to 15 ml with either 28.5% ethanol–water or water. The respective solutions were subsequently titrated with 1 *N* NaOH or 0.25 *N* NaOH. The concentration of acid was such that at the end point of the titration, the ionic strength (μ) = 0.02. The NaOH was added incrementally from a micropipet (Manostat Digi-Pet). The change of pH was monitored at every addition of NaOH by a Radiometer Type TTT1-titrator. Blank titration curves were obtained in water at 16, 26, 36, and 46° and in 28.5% ethanol–water at 26° by titrating 15 ml of 10^{-2} *N* HCl. The differences between the amounts of 1 *N* NaOH added to the blank solution at the same pH (Δ ml) were plotted as a function of pH to give the differential titration curves.[15] The pK_a of the respective samples was determined at half-neutralization via a plot of pH vs. log $\alpha_1/(1 - \alpha_1)$ from the modified Henderson–Hasselbach equation

$$pH = pK_a + n \log \alpha_1/(1 - \alpha_1)$$

D. Kinetic Measurements. 1. Preparation of the Solution for Kinetics. To 2.9 ml of a buffered catalyst solution in a 1 cm quartz cell, at 26°, was added 0.10 ml of an acetonitrile solution of substrate. The final concentration of species in the cell was the following: [catalyst] = 5×10^{-4} *M* and variable, [substrate] = 5×10^{-5} *M*; μ = 0.02, [buffer] = 0.02 *M*, and 26.7% ethanol, 3.3% acetonitrile, 70% water by volume. The buffer employed above pH 6 was tris(hydroxymethyl)aminomethane–HCl. For pH 6 and below the systems were buffered with sodium acetate–acetic acid. In determining the pH-rate profiles the substrate was added as an ethanol–water solution, thus the final solvent composition was simply 28.5% ethanol–water by volume.

2. Treatment of Data. All data obtained under conditions of [catalyst] ≫ [substrate] were, unless otherwise noted, treated as first-order kinetics by plotting ln $(A_\infty - A_t)$ vs. time. The slope of this line was taken as the pseudo-first-order rate constant (k_{meas}). Whenever the blank rate was significant, k_{obsd} was calculated, $k_{obsd} = k_{meas} - k_{blank}$. The second-order rate constant k_{cat} was calculated either from k_{meas} or from k_{obsd}: $k_{cat} = k_{obsd}/[\text{catalyst}]$.

Acknowledgment. This work has been supported by the National Institutes of Health under Grant No. 2 RO1 GM 15256.

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