The Esterolytic Activity of Poly(*N*-alkylimidazoles). The Effect of Ester Chain Length in the Substrate and Alkyl Chain Length in the Catalyst on the Esterolytic Activity of Poly(*N*-alkylimidazoles)

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ABSTRACT: In an effort to exploit the enhancement in catalytic activity which might be derived through hydrophobic interactions between polymeric catalyst and substrate, 1-methyl-5-vinylimidazole (1-Me-5-VIm), 1-methyl-4-vinylimidazole (1-Me-4-VIm), 1-butyl-5-vinylimidazole (1-Bu-5-VIm), and 1-butyl-4-vinylimidazole (1-Bu-4-VIm) have been synthesized and polymerized. In 28.5% ethanol–water, poly(1-alkyl-5-vinylimidazoles) proved to be efficient catalysts for the hydrolysis of various 3-nitro-4-acyloxybenzoic acids (S_n^-, where n denotes the acyl chain length). Order of magnitude rate enhancements, as compared to the model compound, 1,5-dimethylimidazole (1,5-DMIm), were observed in the poly(1-alkyl-5-vinylimidazole)-catalyzed solvolysis of S_{12}^- and S_{18}^-. Poly(1-Me-5-VIm) catalyzes the hydrolysis of S_{18}^- 88 times faster than does 1,5-DMIm. The poly(1-Me-5-VIm)-catalyzed hydrolysis of S_{18}^- in ethanol–water was analyzed in terms of a simple Michaelis–Menten type mechanism. V_{max} and K_m were determined to be $40.2 \times 10^{-7}\ M\ \text{min}^{-1}$ and $2.20 \times 10^{-5}\ M$, respectively.

Poly(*N*-alkyl-4- and -5-vinylimidazoles) and especially poly(1-Me-5-VIm)[1] have proven to be effective catalysts for the hydrolysis of activated phenyl esters. While these polymers lack the ability to effect bifunctional catalysis[1] as can poly[4(5)-VIm] they have certain other advantages which allow them to be more effective catalysts than poly-[4(5)-VIm].

Most important among these is the fact that poly(*N*-alkyl-4- and -5-vinylimidazoles) do not suffer from the rate-determining deacylation in the hydrolysis of long-chain substrates which plagues poly[4(5)-VIm]. With poly[4(5)-VIm], the rate of release of phenolate ion can be a measure of the rate of acylation of catalytic sites, the rate of deacylation of catalytic sites, or a composite of both reactions. Poly(*N*-alkylimidazoles) catalyze the hydrolysis of activated esters via the formation of an intermediate 1-alkyl-3-acylimidazolium ion; such a species is much more reactive than a neutral acylimidazole and, as a result, the rate of release of phenolate ion is only a measure of the rate of acylation of catalytic sites. This fact leads to a simplification of the kinetics and allows for more efficient turnover of substrate.

The poly(1-Me-5-VIm)-catalyzed solvolysis of 3-nitro-4-dodecanoyloxybenzoic acid (S_{12}^-) in excess substrate and excess catalyst, and 3-nitro-4-octadecanoyloxybenzoic acid (S_{18}^-) in excess catalyst, was monitored as was the poly(1-Bu-5-VIm)-catalyzed solvolysis of S_{18}^- in excess catalyst. Order of magnitude rate enhancements, as compared to the model compound 1,5-dimethylimidazole (1,5-DMIm), were observed in the poly(1-Me-5-VIm)- and the poly(1-Bu-5-VIm)-catalyzed solvolyses of S_{12}^- and S_{18}^-. The poly(1-Me-5-VIm)-catalyzed hydrolysis of S_{18}^- proceeded 88 times faster than did the 1,5-DMIm-catalyzed reaction. Saturation kinetics were observed and the data were analyzed in terms of a simple Michaelis–Menten type mechanism. V_{max} and K_m values determined from a modified Lineweaver–Burke plot were $40.2 \times 10^{-7}\ M \cdot \text{min}^{-1}$ and $2.20 \times 10^{-5}\ M$, respectively.

The esterolytic activity of copolymers of 4(5)-vinylimidazole [4(5)-VIm] with 1-butyl-5-vinylimidazole (1-Bu-5-VIm) and 1-butyl-4-vinylimidazole (1-Bu-4-VIm) was investigated briefly. Toward 3-nitro-4-heptanoyloxybenzoic acid, S_7^-, only the 4(5)-VIm residues appeared to be catalytically active. On the basis of the concentration of unalkylated imidazole residues, the copolymers were much better catalysts than homopoly[4(5)-VIm]. Copolymers of *N*-alkylimidazoles with 4(5)-VIm offer the possibility of retaining bifunctional catalysis, while increasing the rate of steady-state turnover of substrate from the rate of deacylation of 4(5)-VIm residues to the rate of hydrolysis of substrate by the *N*-alkylated residues, plus the rate of deacylation of 4(5)-VIm residues.

Results and Discussion

Synthesis. 1-methyl-4-vinylimidazole (1-Me-4-VIm), 1-methyl-5-vinylimidazole (1-Me-5-VIm),[1] and 4(5)-vinylimidazole[3] were prepared as described previously. *N*-Vinylimidazole was purchased from BASF and was distilled just prior to polymerization.

1-Butyl-4- and -5-vinylimidazole were prepared via the intermediacy of 1-trimethylsily-4-vinylimidazole. Direct alkylation of 4(5)-VIm with butyl iodide, utilizing a modification of the procedure employed by Häring et al.,[4] yielded only 20% of the mixed isomers of 1-butyl-4-vinylimidazole and 1-butyl-5-vinylimidazole in an isomer ratio of 90:10 1,4 to 1,5, by NMR.

Alternatively, the reaction of 1-trimethylsilyl-4-vinylimidazole (prepared from 4(5)-vinylimidazole and 1,1,1,3,3,3,-hexamethyldisilazane) with butyl iodide in a sealed tube at 70° yielded 62.7% of the mixed *N*-butyl-4- and -5-vinylimidazoles, this time in an isomer ratio of 15:85 1,4 to 1,5.

The reaction is shown in Scheme I. The reaction presumably proceeds through the formation of 1-trimethylsilyl-3-

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

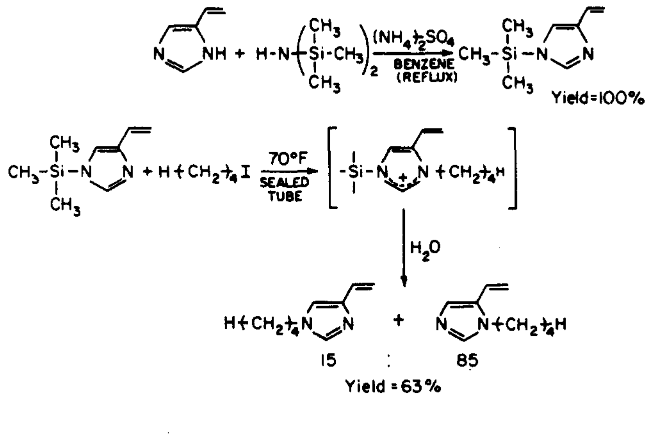

Table I
pK_a of Catalysts in 28.5% Ethanol–Water (26°, μ = 0.02)

Base	pK_a	n'
Poly(N-VIm)	4.62	1.910
Poly(1-Me-4-VIm)	5.20	1.15
1,4-DMIm	7.0	
Poly(1-Me-5-VIm)	4.70	1.77
1,5-DMIm	7.35	
Poly(1-Bu-5-VIm)	4.20	1.925
Copoly[1-Bu-4-VIm/4(5)-VIm] (1:1) M	5.12	1.39
Copoly[1-Bu-5-VIm/4(5)-VIm] (1:1) M	5.00	1.42
Poly[4(5)-VIm][a]	6.19	

[a] Taken from ref 16, 30% ethanol-water, μ = 0.02.

butylimidazolium iodide, which on hydrolysis would yield exclusively 1-butyl-5-vinylimidazole. The 1,4 compound apparently arises from some type of cleavage of the Si–N bond prior to alkylation. By analogy to the technique employed with the N-methyl-4- and -5-vinylimidazoles,[1] an attempt was made to separate the isomeric N-butyl-4- and -5-vinylimidazoles by preparative thin-layer chromatography on alumina, eluting with acrylonitrile. After developing each plate three times, a very slight separation of two bands was observed. The monomers were extracted into $CHCl_3$, the solvent was removed, and the respective fractions were distilled in vacuo. NMR revealed that one fraction was 16% 1-butyl-5-vinylimidazole and 84% 1-butyl-4-vinylimidazole while the other fraction was essentially pure 1-butyl-5-vinylimidazole.

Polymerization of N-Alkyl-4- and -5-vinylimidazoles. Poly[4(5)-VIm] has typically been polymerized free radically in benzene solution at 60–80°. Thus, it was surprising to find that the free-radical polymerization of 1-methyl-4-vinylimidazole and 1-methyl-5-vinylimidazole in benzene or methanol solution at 65° proceeded only to low conversion, ca. 5–20%. This observation was even more surprising in light of the fact that considerable difficulty had resulted from the tendency of the pure N-alkyl-4- and -5-vinylimidazoles to polymerize on standing at ambient temperature. It was subsequently determined that 4(5)-vinylimidazole polymerizes only sluggishly at 70° in aqueous solution, initiated by ammonium peroxydisulfate. In benzene solution, imidazole is known to aggregate through H bonding in clusters of about 20 imidazole molecules.[5] It may be that 4(5)-vinylimidazole polymerizes so readily in benzene solution because it aggregates in a similar manner. In the case of the alkylated 4- and 5-vinylimidazoles, there is no possibility for such H-bonded aggregates, thus accounting for the observed lack of polymerizability in benzene solution. The N-alkylated 4- and 5-vinylimidazoles were found to polymerize readily in bulk to high conversion.

The following polymers were prepared, in bulk, for utilization in kinetic studies: poly(1-methyl-4-vinylimidazole) (poly(1-Me-4-VIm)), poly(1-methyl-5-vinylimidazole) (poly(1-Me-5-VIm)), poly(1-butyl-5-vinylimidazole) (poly(1-Bu-5-VIm)), copoly(1-butyl-4-vinylimidazole/4(5)-vinylimidazole) (1:1) M (copoly(1-Bu-4-VIm/4(5)-VIm)), copoly(1-butyl-5-vinylimidazole/4(5)-vinylimidazole) (1:1) M (copoly(1-Bu-5-VIm/4(5)-VIm)), and poly[4(5)-VIm]. The polymerizations were typically carried out at 65°, initiating with 2,2′-azobis(2-methylpropionitrile) (AIBN). The poly(N-vinylimidazole) (poly(N-VIm)) used in these kinetic studies was prepared in benzene solution because N-vinylimidazole cross linked when polymerized in bulk.

The polymers were purified first by reprecipitating concentrated methanol solutions in acetone or 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 of 4- and 5-substituted vinylimidazoles exhibited two peaks, one at about 220 nm and a shoulder at about 250 nm. After gel filtration the polymers exhibited only a single peak in the ultraviolet at about 220 nm.

Table II
pK_a of Catalysts in Water (μ = 0.02)

Base	pK_a	n'	Temp, °C
1,4-DMIm	7.22		26
1,5-DMIm	7.35		26
Poly(1-Me-4-VIm)	5.45	0.94	26
Poly(1-Me-5-VIm)	5.28	1.48	16
	5.13	1.44	26
	4.90	1.12	36
	4.62	1.14	46

The actual composition of the copolymers was estimated by taking the ratio of the integral for the N-methylene protons to that over all other aliphatic hydrogens in the copolymers. Through such an analysis, it was determined that the copolymer composition was essentially as charged, (1:1) M.

The polymers were further characterized by their viscosity in methanol and/or water and ethanol–water, and by determination of their respective pK_a's in 28.5% ethanol–water and/or water.

Potentiometric Titrations. In comparing catalysis by various imidazole derivatives the relative basicity must be considered first. Thus, the degree of ionization, as a function of pH of all polymers utilized in these kinetic studies, as determined by the potentiometric titration of polymer solutions in 28.5% ethanol–water, μ = 0.02 at 26°. In addition, the pK_a's of poly(1-Me-4-VIm) in water at 26° (μ = 0.02) and poly(1-Me-5-VIm) in water (μ = 0.02) at 16, 26, 36, and 46° were determined.

Plots of ln [(1 − α_1)/α_1] vs. pH for all polymers were essentially linear, following the modified Henderson–Hasselbach equation[6]

$$pK_a = pH + n' \log\left[(1 - \alpha_1)/\alpha_1\right] \qquad (1)$$

where α_1 is equal to the fraction of neutral imidazole residues. The n' values for these polymers varied from about 1 to 2, depending on the solvent, the temperature, and the polymer. The amount by which n' deviates from unity is an indication of the influence of electrostatic effects in the titration.[7] Tables I and II summarize the results of all potentiometric titrations and Figure 1 shows the relationship between pK_a and temperature for poly(1-Me-5-VIm) in water, μ = 0.02.

Viscosity Studies. It has been demonstrated that the conformational state of a synthetic macromolecular catalyst can have a profound effect on the activity of the catalyst.[16] Thus, it was deemed advisable to investigate the solution viscosity of the polymeric catalysts employed in this research. The relationship between viscosity and concentration was determined at 25° for poly(1-Me-5-VIm) in methanol, 28.5% ethanol/H_2O; 28.5% ethanol/H_2O buffered to pH 3.90, μ = 0.02; 28.5% ethanol/water buffered to pH 7.75, μ = 0.02; 28.5% EtOH/H_2O, 0.5 M KCl and H_2O, buffered to pH 7.90, μ = 0.02.

Poly(1-Me-5-VIm) in methanol solution exhibited an intrinsic viscosity of 0.28. In 28.5% EtOH/H_2O, a slight polyelectrolyte effect[8] was evident, the reduced viscosity at 0.11 g/dl being 0.225. This polyelectrolyte effect was more pro-

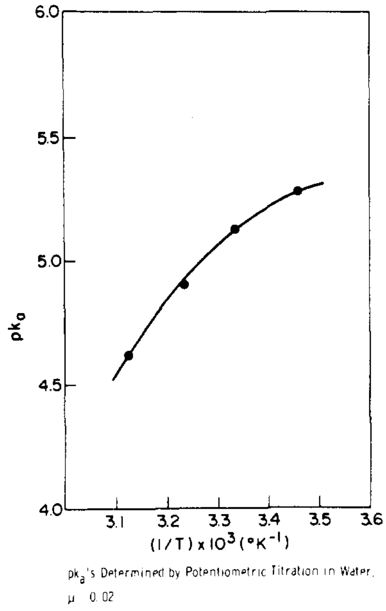

Figure 1. Effect of temperature on (apparent) pK_a of poly(1-Me-5-VIm). pK_a's determined by potentiometric titration in water, μ = 0.02.

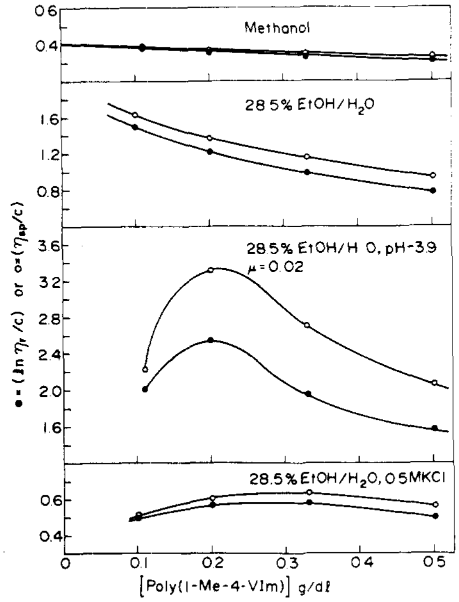

Figure 2. Relationship between viscosity and concentration of poly(1-Me-4-VIm) in various solvents at 25°.

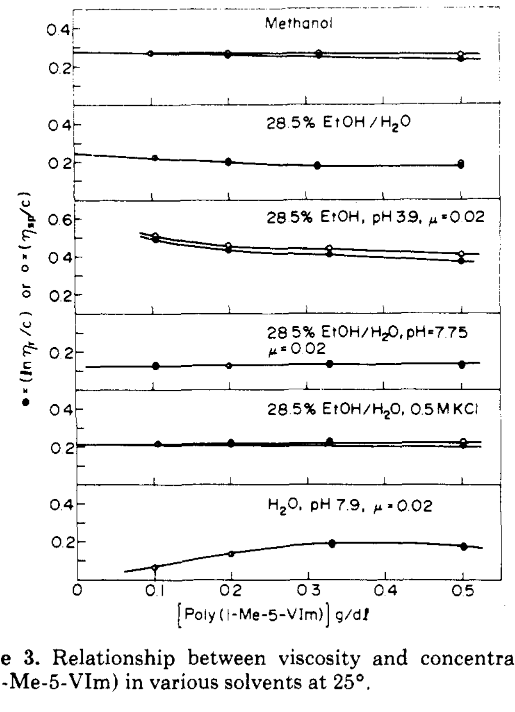

Figure 3. Relationship between viscosity and concentration of poly(1-Me-5-VIm) in various solvents at 25°.

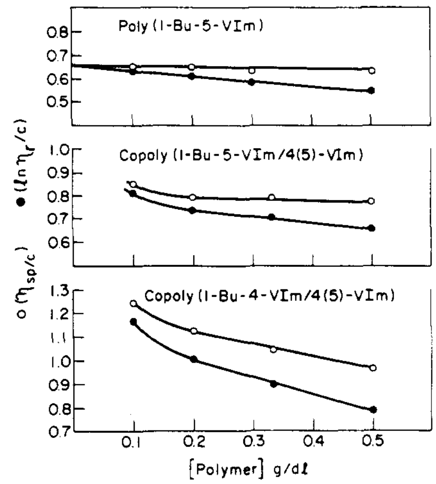

Figure 4. Relationship between viscosity and concentration at 25° in methanol.

nounced in pH 3.90, μ = 0.02, 28.5% EtOH/H_2O, the reduced viscosity at 0.11 g/dl climbing to 0.50. In pH 7.75, 28.5% EtOH/H_2O, μ = 0.2 buffer, and in 0.5 *M* KCl 28.5% EtOH/H_2O the polyelectrolyte effect was absent, and the intrinsic viscosities dropped to values of 0.12 and 0.21, respectively. The viscosity characteristics of poly(1-Me-5VIm) in pH 7.90, μ = 0.02, aqueous buffer were somewhat anomalous. Apparently, at high polymer concentrations (0.5 g/dl) there is some association of macromolecules leading to a low viscosity value. Upon dilution these macromolecules dissociate; thus, the curve for the relationship between viscosity and concentration is concave. At the lowest concentration, 0.11 g/dl, the reduced viscosity in pH 7.90 aqueous buffer was only 0.063.

The viscosity vs. concentration characteristics of poly(1-Me-4-VIm) were determined at 25° in methanol; 28.5% EtOH/H_2O; 28.5% EtOH/H_2O buffered to pH 3.90, μ = 0.02; and 28.5% EtOH/H_2O, 0.5 *M* KCl. The intrinsic viscosity of poly(1-Me-4-VIm) in methanol was 0.41. In 28.5% EtOH/H_2O and in pH 3.90, 28.5% EtOH/H_2O, μ = 0.02, definite polyelectrolyte behavior was observed; the inherent viscosities at 0.1 g/dl were 1.38 and 2.21, respectively. This polyelectrolyte behavior was mediated in 0.5 *M* KCl, 28.5% EtOH/H_2O; however, the curve was still anomalous, having a concave shape. In this case, too, the concavity is attributed to association of macromolecules at higher concentrations. The inherent viscosity at 0.11 g/dl in 0.5 *M* KCl, 28.5% EtOH/H_2O, was 0.50.

In the cases of poly(1-Bu-5-VIm), copoly(1-Bu-5-VIm/4(5)-VIm) and copoly(1-Bu-4-VIm/4(5)VIm), the relationship between viscosity and concentration was determined only in methanol. The relationship in the case of poly(1-Bu-5-VIm) was linear and the intrinsic viscosity was determined to be 0.66. Copoly(1-Bu-5-VIm/4(5)VIm) and copoly(1-Bu-4-VIm/4(5)VIm) displayed nonlinear curves, probably due to some H-bonded association of the macromolecules at the higher concentrations. The inherent viscosities at 0.11 g/dl were 0.85 and 1.25, respectively. The data for all systems are summarized in Figures 2, 3, and 4, and in Table III.

Table III
Viscosity Characteristics of Polymeric Catalysts[a]

	Methanol		28.5% EtOH		28.5% EtOH buffered pH 3.90		28.5% EtOH buffered pH 7.75		28.5% EtOH buffered 0.5 *M* KCl		H_2O pH 7.90	
	η_{red}	$[\eta]$	η_{red}	$[\eta]$	η_{red}	$[\eta]$	η_{red}	$[\eta]$	η_{red}	$[\eta]$	η_{red}	$[\eta]$
Poly(1-Me-5-VIm)	0.270	0.275	0.225		0.504		0.126	0.120	0.287	0.212	0.063	
Poly(1-Me-4-VIm)	0.387	0.405	1.631		2.216				0.504			
Poly(1-Bu-5-VIm)	0.649	0.655										
Copoly[1-Bu-5-VIm/4(5)-VIm]	0.847											
Copoly[1-Bu-4-VIm/4(5)-VIm]	1.24											

[a] η_{red} at 0.11 g/dl.

It should be noticed that viscosities are highest in methanol, intermediate in 28.5% EtOH/H_2O, and lowest in water. This, of course, reflects the smaller macromolecular dimensions and the increased compactness of the polymers in a totally aqueous medium.

Protonation of some of the imidazole residues along the chain can serve to increase the macromolecular dimensions through charge repulsion. This is evidenced by the higher viscosity of poly(1-Me-5-VIm) in pH 3.90, 28.5% EtOH/H_2O buffer as compared to that in pH 7.75 EtOH/H_2O buffer.

The Effect of Ester Chain Length on the Rate of Solvolysis. A convenient method through which to qualitatively ascertain the contribution of apolar binding to rate enhancements is to follow the rate of hydrolysis of increasingly longer chain ester substrates.

Thus, the polymer-catalyzed hydrolysis of a series of 3-nitro-4-acyloxybenzoic acids,[9] S_n^-, where *n* denotes the acyl chain length, was carried out at 26° in pH 6.85, 26.7% (v) ethanol, 3.3% (v) acetonitrile, 70% water buffer, $\mu = 0.02$ *M* KCl. The catalysts employed were poly(N-VIm), poly(1-Me-5-VIm), poly(1-Bu-5-VIm), poly[4(5)-VIm], copoly[1-Bu-5-VIm/4(5)-VIm] (1:1) *M*, and copoly[1-Bu-4-VIm/4(5)-VIm] (1:1) *M*.

The kinetics were typically carried out in a tenfold excess of catalyst. 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 psuedo-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.

$$k_{obsd} = k_{meas} - k_{blank} \quad (2)$$

$$k_{cat} = k_{obsd}/[\text{catalyst}] \quad (3)$$

In certain instances, the poly(1-Bu-5-VIm)-catalyzed hydrolyses of the S_n^- series and the poly(*N*-VIm)-catalyzed hydrolysis of S_{18}^-, precipitation was observed late in the kinetic run. In these cases, the initial rate (V_i) was obtained from the plot of absorbance vs. time. The initial rate can be related to k_{obsd} via the following equation.

$$k_{meas} = V_i/[\text{substrate}] \quad (4)$$

Poly[4(5)-VIm] and copolymers of 4(5)-VIm exhibited accelerative kinetic behavior toward S_7^- and S_{12}^-; thus, initial rates were determined in catalysis by these polymers as well. At no time were substrate concentrations in excess of their determined critical micelle concentrations, cmc, utilized.[9]

(a) The Poly(*N*-alkylimidazole)-Catalyzed Hydrolysis of the S_n^- Series. The *N*-substituted imidazole homopolymers comprise something of a homologous series with respect to increasing hydrophobicity of catalyst. Figure 5 graphically illustrates the rate enhancement achieved in the polymer-catalyzed hydrolysis of long-chain substrates. Poly(1-Me-5-VIm) is a more effective catalyst than the model compound, 1,5-DMIm, over the entire S_n^- series. The rate of the poly(1-Me-5-VIm)-catalyzed hydrolysis of S_{18}^- is almost eight times faster than the rate of hydrolysis of S_2^-. More dramatic is the fact that while poly(1-Me-5-VIm) catalyzes the hydrolysis of S_2^- only 1.4 times faster than does 1,5-DMIm, it hydrolyzes S_{18}^- 88 times faster than does 1,5-DMIm.

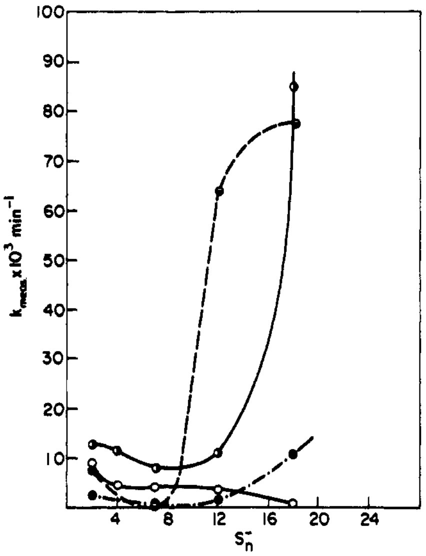

Figure 5. Solvolysis of the S_n^- series by poly(*N*-alkylimidazoles). Hydrolysis of S_n^-, 26.7% ethanol, 3.3% CH_3CN, 70% H_2O (v), pH 6.85 buffer; $\mu = 0.02$; 26°; [catalyst] 5×10^{-4} *M*; $[S_n^-] = 5 \times 10^{-5}$ *M*: (○) 1,5-DMIm; (●) poly(1-*N*-VIm); (◑) poly(1-Me-5-VIm); (◒) poly(1-Bu-5-VIm).

Poly(*N*-VIm) is a less effective catalyst than 1,5-DMIm toward S_2^-, S_7^-, and S_{12}^-. A significant rate enhancement was finally realized in the hydrolysis of S_{18}^-.

Poly(1-Bu-5-VIm) presents an interesting case, being a less efficient catalyst than 1,5-DMIm toward S_2^- and S_7^-, a better catalyst than poly(1-Me-5-VIm) toward S_{12}^-, and less efficient than poly(1-Me-5-VIm) toward S_{18}^-. This is reasonable if it is realized that poly(1-Bu-5-VIm) is probably more sterically hindered than poly(1-Me-5-VIm) and that there is a limit to the rate enhancement one can achieve through increasing the binding of substrate to catalyst. The data in Figure 5 are given in tabular form in Table IV.

Table IV
Solvolysis of the S_n^- Series by Poly(*N*-alkylimidazoles)[a]

		S_2^-		S_7^-		S_{12}^-		S_{18}^-	
Catalyst	pK_a	k_{meas},[b] 10^3 min^{-1}	r[c]	k_{meas},[b] 10^3 min^{-1}	r	k_{meas},[b] 10^3 min^{-1}	r	k_{meas},[b] 10^3 min^{-1}	r
1,5-DMIm	7.35	8.93		4.12		3.64		0.957	
Poly(*N*-VIm)	4.62	2.46	0.275	1.09	0.265	1.61	0.442	10.6	11.1
Poly(1-Me-5-VIm)	4.70	12.8	1.43	7.88	1.91	11.15	3.06	85.0	88.8
Poly(1-Bu-5-VIm)	4.20	7.78	0.87	0.78	0.019	64.10	17.6	77.2	80.7

[a] Hydrolysis of S_n^-, 27.6% ethanol/3.3% CH_3CN/69.1% H_2O (v), pH 6.85 buffer, $\mu = 0.02\ M$, 26°, [catalyst] = $5 \times 10^{-4}\ M$, [S_n^-] = $5 \times 10^{-5}\ M$. [b] $k_{meas} = k_{obsd}$, k_{blank} negligible. [c] $r = k_{meas}$ of polymer/k_{meas} of 1,5-DMIm.

Table V
Solvolysis of the S_n^- Series by 4(5)-Vinylimidazole-Containing Polymers[a]

			Substrate			
Catalyst	pK_a[d]	Rate[b] or rate constant[c]	S_2^-	S_4^-	S_7^-	S_{12}^-
Poly[4(5)-VIm]	6.19[e]	V_i, $10^7\ M$ min^{-1}	27.8	21.4	22.7	550[f]
	$\alpha_1 = 0.79$	k_{meas}, 10^3 min^{-1}	55.6	42.8	45.3	1100
		k_{cat}, M^{-1} min^{-1}	111	85.6	90.6	2200
Copoly[1-Bu-4-VIm/ 4(5)-VIm]	5.12	V_i, $10^7\ M$ min^{-1}	15.2	13.6	27.1	562
		k_{meas}, 10^3 min^{-1}	30.5	27.1	54.1	1124
		k_{cat}, M^{-1} min^{-1}	122	108	216	4500
Copoly[1-Bu-5-VIm/ 4(5)-VIm]	5.00	V_i, $10^7\ M$ min^{-1}	12.6	10.6	28.7	562
		k_{meas}, 10^3 min^{-1}	25.3	21.2	57.5	1124
		k_{cat}, M^{-1} min^{-1}	101	84.9	230	4500

[a] Solvolysis in 26.7% ethanol, 3.3% CH_3CN, 70% H_2O by volume, pH 6.85, $\mu = 0.02$, 26°, [catalyst] = $5 \times 10^{-4}\ M$, [S_n^-] = $5 \times 10^{-5}\ M$. [b] Initial rate from the plot of absorbance vs. time. [c] Calculated: $k_{meas} = V_i/[S_n^-]$, $k_{cat} = k_{meas}$/[4(5)-VIm] residues only. [d] In 28.5% ethanol–water, $\mu = 0.02$, 26°. [e] Taken from ref 6, 30% ethanol–water, $\mu = 0.02$. [f] Calculated from data in ref 10.

(b) The Hydrolysis of the S_n^- Series by 4(5)-Vinylimidazole-Containing Polymers. Partially acylated poly[4(5)-VIm] was shown by Overberger and Glowaky to be a better catalyst for the hydrolysis of nitrophenyl esters than unacylated polymer.[2] It therefore seemed that copolymers of 1-butyl-4-vinylimidazole or 1-butyl-5-vinylimidazole with 4(5)-vinylimidazole might also be better catalysts than poly[4(5)-VIm]. Such copolymers were prepared containing 50 mol % 1-butyl-4-vinylimidazole or 1-butyl-5-vinylimidazole, and the hydrolysis of the S_n^- series in a tenfold excess of catalyst was monitored. The results, as compared to poly[4(5)-VIm], are shown in Table V and Figure 6.

With all three polymers, accelerative kinetics were encountered when hydrolyzing esters of seven carbons or longer. Since the purpose of these experiments was to study the activity of unacylated polymers, initial rates were obtained from the respective asorbance vs. time plots and k_{meas} and k_{cat} were calculated. The concentration of only the 4(5)-vinylimidazole residues was utilized in calculating k_{cat}, because it appears from the data for the hydrolysis of S_7^- in excess substrate that for all practical purposes only the 4(5)-vinylimidazole residues are catalytically active (see Figure 7).

In Figure 6, it can be seen that there is little difference in the activity of poly[4(5)-VIm] or its copolymers toward S_2^- or S_4^-. Toward S_7^- the copolymers are twice as active as the homopolymer. This is no doubt due to the increased hydrophobic character of the vinylbutylimidazole-containing polymers. The rate of the copolymer catalyzed hydrolysis of S_{12}^- was extremely fast, necessitating the use of the stopped flow spectrophotometer. The initial rates of the hydrolysis of S_{12}^- by copoly[1-Bu-4-VIm/4(5)-VIm] and by copoly[1-Bu-5-VIm/4(5)-VIm] were identical, k_{cat} = 4500 M^{-1}min^{-1}, twice that exhibited by poly[4(5)-VIm].[10]

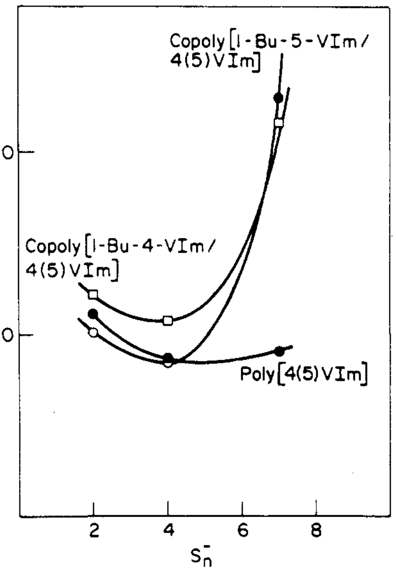

Figure 6. Solvolysis of S_n^- series by 4(5)-VIm containing polymers. Solvolysis in 26.7% ethanol; 3.3% CH_3CN; 70% H_2O; pH 6.85, $\mu = 0.02$, 26°, [catalyst] = $5 \times 10^{-4}\ M$; [S_n^-] = $5 \times 10^{-5}\ M$. k_{cat} was calculated on the basis of 4(5)vinylimidazole residues.

As was mentioned previously, the solvolysis of S_7^-, in excess catalyst, by poly[4(5)-VIm] or its vinyl-*N*-butylimidazole copolymers proceeds in an accelerative manner. This accelerative behavior results from the accumulation of acylated imidazole residues on the polymer.[2] Overberger and

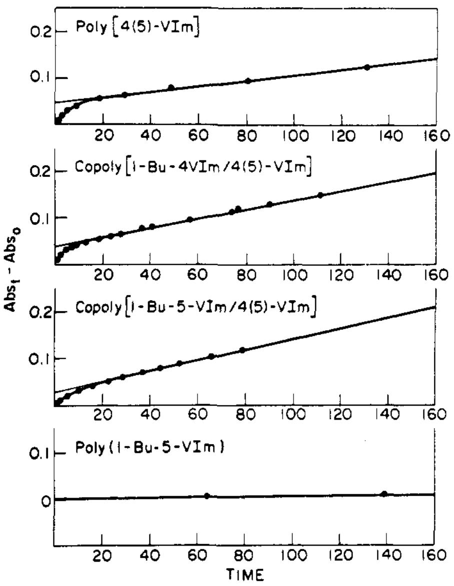

Figure 7. Polymer catalyzed hydrolysis of S_7^- in excess: pH 6.85, 27.6% ethanol, 3.3% CH_3CN, 69.1% H_2O buffer, μ = 0. 26°, [catalyst] = 2.5×10^{-5} *M*; [S_7^-] = 2.5×10^{-4} *M*.

Sannes[11] have shown that, in cases exhibiting accelerative behavior, one can study the acylation–deacylation behavior of poly[4(5)-VIm] by following the solvolysis in excess substrate, ca. poly[4(5)-VIm] = 2.5×10^{-5} *M*, [S_n^-] = 2.5×10^{-4} *M*. The plots of absorbance vs. time (Figure 7) show an initial burst region followed by a slow zero-order steady state deacylation region. Assuming a Michaelis–Menten type mechanism

$$E + S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} E\cdot S \xrightarrow{k_2} E' + P_1 \xrightarrow{k_3} E + P_2 \qquad (5)$$

the curves can be described by the equation[12]

$$[P_1] = At + B(1 - e^{-bt}) \qquad (6)$$

where

$$A = \frac{k_{cat}[E]_0[S]_0}{[S]_0 + K_m(\text{apparent})} \qquad (7)$$

$$B = [E]_0\left(\frac{k_2}{k_2 + k_3}\right)^2 \Big/ \left(1 + \frac{K_m(\text{apparent})}{S_0}\right)^2 \qquad (8)$$

and

$$b = k_3 + \frac{k_2}{1 + (K_s/[S]_0)} \qquad (9)$$

At *t* approaching infinity

$$[P_1] = At + B \qquad (10)$$

This is a linear relationship which when extrapolated to *t* = 0 gives the value of *B*.[12] The value of *B* is a measure of the steady state concentration of acylated imidazole residues. The slope of this line, *A*, is a measure of the steady state rate of deacylation.

Copoly[1-Bu-5-VIm/4(5)-VIm] displays the fastest rate of deacylation, k_3 = 47×10^{-3} min^{-1}, and a steady state concentration of acylimidazole residues of 0.961×10^{-5} *M*. This constitutes almost 77% of the 4(5)-vinylimidazole residues. Copoly[1-Bu-4-VIm/4(5)-VIm] exhibits a k_3 value of 39.0×10^{-3} min^{-1} and a steady state concentration of acylimidazole residues of 0.874×10^{-5} *M*, or 70% of the 4(5)-vinylimidazole residues. Poly[4(5)-VIm] deacylates slowest, k_3 = 12.1×10^{-3} min^{-1}; the steady state concentration of acylated residues in the homopolymer is 1.75×10^{-5} *M* or 70% of the imidazole residues. The data are presented in Table VI.

Table VI
Steady State Rate of Release of Phenolate Anion by 4(5)-Vinylimidazole-Containing Polymers During the Hydrolysis of S_7^- [a]

Catalyst	Rate of release of phenolate, 10^7 *M* min^{-1}	Concn of acylated residues, 10^5 *M*	k_3, 10^3 min^{-1}
Poly[4(5)-VIm]	2.11	1.75	12.1
Copoly[1-Bu-4-VIm/4(5)-VIm]	3.75	0.87	39.0
Copoly[1-Bu-5-VIm/4(5)-VIm]	4.33	0.96	47.0

[a] Solvolysis in 26.7% ethanol, 3.3% CH_3CN, 70% H_2O by volume, pH 6.85, μ = 0.02, 26°, [catalyst] = 2.5×10^{-5} *M*, [S_7^-] = 2.5×10^{-4} *M*.

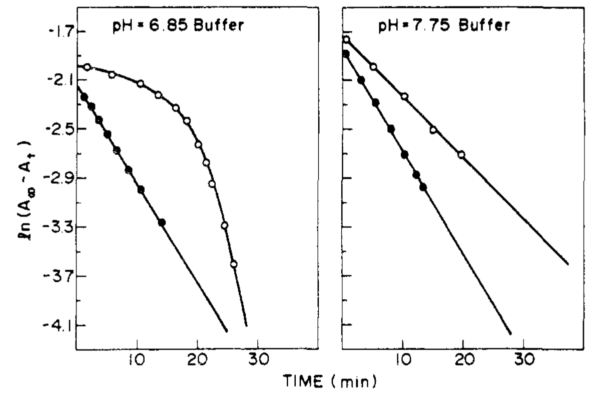

Figure 8. The poly(1-Me-5-VIm)-catalyzed hydrolysis of S_{18}^- as a function of [catalyst], [S_{18}^-] = 5×10^{-5} *M*, μ = 0.02, 26°: (○) [catalyst] = 0.33×10^{-4} *M*; (●) [catalyst] = 9.67×10^{-4} *M*.

Saturation Kinetics. The Poly(1-Me-5-VIm)-Catalyzed Solvolysis of S_{18}^-. It would not seem possible for rate enhancements as dramatic as those observed in the polymer-catalyzed solvolysis of the S_n^- series to be achieved without some change in mechanism for the hydrolysis of the long chain substrates. Indeed, Overberger, Morimoto, Cho, and Salamone[13] have shown that the poly[4(5)-VIm]-catalyzed hydrolysis of S_{12}^- in solvents of low ethanol content exhibits saturation behavior and proceeds in accordance with a Michaelis–Menten mechanism. In order to investigate the possibility of such a phenomenon, the poly(1-Me-5-VIm)-catalyzed hydrolysis of long chain substrates was investigated as a function of the concentration of catalyst and/or substrate in excess catalyst and/or excess substrate, respectively. The poly(1-Bu-5-VIm)-catalyzed solvolysis of S_{18}^- was also followed as a function of the catalyst concentration in excess catalyst.

These studies of the rate of solvolysis of long chain substrates were most often carried out at pH 7.75 and not pH 6.85. This practice was followed because at pH 6.85 accelerative kinetic patterns were observed when the substrate concentration approached that of the polymer in the poly(1-Me-5-VIm)-catalyzed hydrolysis of S_{18}^-. The left part of Figure 8 shows this autocatalytic behavior. By merely increasing the pH of the buffer to 7.75, the rate of deacylation was increased and the accelerative behavior was totally eliminated (see the right part of Figure 8).

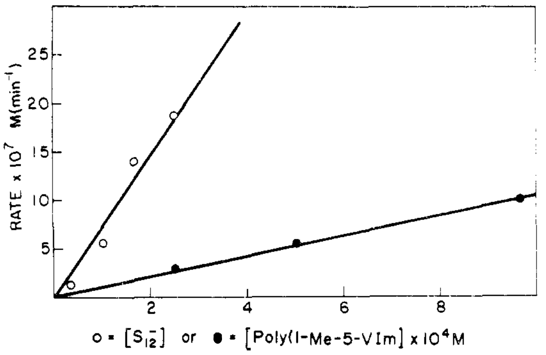

Figure 9. The poly(1-Me-5-VIm)-catalyzed hydrolysis of $[S_{12}^-]$ as a function of the concentration of both catalyst and substrate: hydrolysis in 26.7% ethanol, 3.3% CH_3CN, 70% H_2O by volume; pH 7.75 buffer, $\mu = 0.02$, 26°

Table VII
The Poly(1-Me-5-VIm)-Catalyzed Solvolysis of S_{12}^- [a]

[Poly(1-Me-5-VIm)], 10^4 *M*	k_{meas}, 10^3 min^{-1}	Rate = $[S_{12}^-]k_{\text{meas}}$, 10^7 *M* min^{-1}
	Excess Catalyst[b]	
2.50	5.57	2.79
5.00	10.8	5.40
9.67	20.3	10.0
$[S_{12}^-]$, 10^4 *M*		Initial rate V_i, 10^7 *M* min^{-1}
	Excess Substrate[c]	
0.33	4.97	1.22
1.00	6.23	5.64
1.67	9.03	14.0
2.50	10.65	18.7

[a] Solvolysis in 26.7% ethanol, 3.3% CH_3CN, 70% H_2O by volume, pH 7.75 buffer, $\mu = 0.02$, 26°. [b] $[S_{12}^-] = 5 \times 10^{-5}$ *M*. [c] [Poly(1-Me-5-VIm)] = 5×10^{-5} *M*.

The poly(1-Me-5-VIm)-catalyzed hydrolysis of S_{12}^- in pH 7.75, 26.7% ethanol, 3.3% CH_3CN, 70% water buffer was followed both as a function of catalyst concentration in excess catalyst and as a function of substrate concentration in excess substrate. Over the range of concentrations employed, the kinetics were ostensibly first order in both substrate and catalyst. Figure 9 and Table VII display these data.

The hydrolysis of S_{12}^- by poly(1-Me-5-VIm) in excess substrate and in excess catalyst is not symmetrical as would be predicted by a simple Michaelis-Menten mechanism. This is most likely due to the fact that the binding of a large amount of substrate must have a profound effect on the conformation of a multisite macromolecular catalyst such as poly(1-Me-5-VIm).

In marked contrast, the poly(1-Me-5-VIm)-catalyzed hydrolysis of S_{18}^- in pH 7.75 ethanol-water buffer exhibited saturation in excess catalyst (see Figure 10). The kinetic parameters (V_{max}, K_{m}, and K_2) were evaluated by analysis of the modified Lineweaver-Burk plot

$$\frac{E_0}{\text{rate}} = \frac{K_{\text{m}}}{V_{\text{max}}} + \frac{E_0}{V_{\text{max}}} \qquad (11)$$

where E_0/V_{max} is the *Y* intercept, $1/V_{\text{max}}$ is the slope, and $-K_{\text{m}}$ is the *X* intercept. Figure 11 displays the double reciprocal plot and Table VIII presents the data.

The poly(1-Me-5-VIm)-catalyzed hydrolysis of S_{18}^- in pH 7.75, 28.5% EtOH/H_2O buffer can be interpreted according to a simple Michaelis-Menten mechanism.

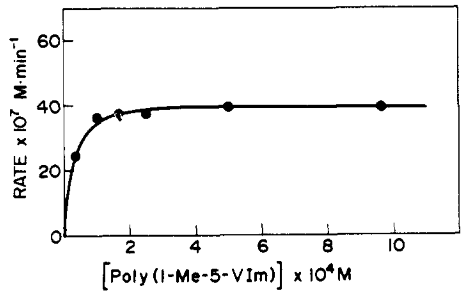

Figure 10. Saturation curve poly(1-Me-5-VIm)-catalyzed hydrolysis of S_{18}^-. Rate (k_{meas}[S]) of the poly(1-Me-5-VIm)-catalyzed solvolysis of S_{18}^- in 26.7% EtOH, 3.3% CH_3CN, 70% H_2O, $[S_{18}^-] = 5 \times 10^{-5}$ *M*, $\mu = 0.02$, pH = 7.75, 26°.

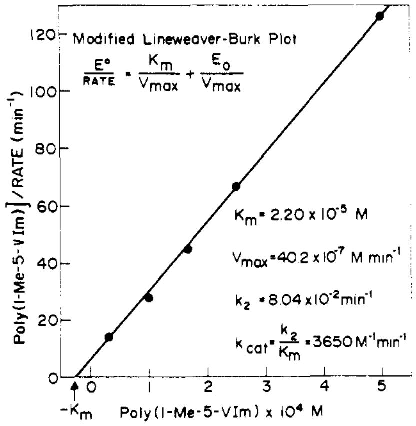

Figure 11. Poly(1-Me-5-VIm)-catalyzed solvolysis of S_{18}^-. Modified Lineweaver-Burk Plot of rate vs [poly(1-Me-5-VIm)] for the poly(1-Me-5VIm)-catalyzed solvolysis of S_{18}^- in 26.7% EtOH, 3.3% CH_3CN, 70% H_2O, $[S_{18}^-] = 5 \times 10^{-5}$ *M*, $\mu = 0.02$, pH 7.75, 26°.

Table VIII
The Poly(1-Me-5-VIm)-Catalyzed Solvolysis of S_{18}^- [a]

[Poly(1-Me-5-VIm)], 10^4 *M*	k_{meas}, 10^3 min^{-1}	$k_{\text{meas}} \times [S_{18}^-]$,[b] 10^7 *M* min^{-1}	Poly(1-Me-5-VIm)
0.33	48.4	24.2	13.6
1.00	73.1	36.5	27.4
1.67	74.6	37.3	44.8
2.50	74.6	37.3	66.7
5.00	79.2	39.6	126.2
9.67	79.2	39.6	244.2

Kinetic parameters			
V_{max}	K_{m}	k_2	$k_{\text{cat}} = k_2/K_{\text{m}}$
40.2×10^{-7} *M* min^{-1}	2.20×10^{-5} *M*	8.04×10^{-2} min^{-1}	3650 M^{-1} min^{-1}

[a] Solvolysis in 26.7% ethanol, 3.3% CH_3CN, 70% H_2O by volume, pH 7.75 buffer, $\mu = 0.02$, 26°, $[S_{18}^-] = 5 \times 10^{-5}$ *M*. [b] $k_{\text{meas}}[S_{18}^-]$ = rate.

$$E + S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} E \cdot S \xrightarrow{k_2} E' + P_1 \xrightarrow{k_3} E + P_2$$

where K_2 is the rate-determining step. K_3 is fast because of the extreme reactivity of the 1-methyl-3-acylimiazolium ion, E′. Poly(1-Me-5-VIm) is thus a true catalyst capable of rapidly turning over large amounts of substrate. This was, in fact, demonstrated by the poly(1-Me-5-VIm)-catalyzed

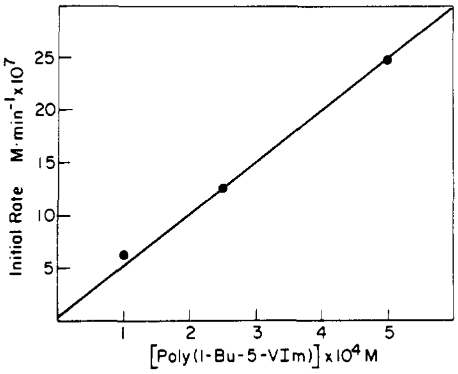

Figure 12. The poly(1-Bu-5-VIm)-catalyzed hydrolysis of S_{18}^-. Solvolysis in 26.7% ethanol, 3.3% CH_3CN, 70% H_2O by volume, pH 7.75 buffer $\mu = 0.02$, 26°, $[S_{18}^-] = 5 \times 10^{-5}$ *M*.

Table IX
The Poly(1-Bu-5-VIm)-Catalyzed Solvolysis of S_{18}^- [a]

[Poly(1-Bu-5-VIm)], 10^4 *M*	Initial rate V_i, 10^7 *M* min^{-1}	$k_{meas} = V_i/[S_{18}^-]$, 10^3 min^{-1}
5.0	24.9	49.8
2.5	12.6	25.2
1.0	6.19	1.24

[a] Solvolysis in 26.7% ethanol, 3.3% CH_3CN, 70% water by volume, pH 7.75 buffer, $\mu = 0.02$, 26°, $[S_{18}^-] = 5 \times 10^{-5}$ *M*.

hydrolysis of S_{12}^- in excess substrate (Table VIII, Figure 9).

Since the poly(1-Me-5-VIm)-catalyzed hydrolysis of S_{18}^- in ethanol-water exhibited saturation kinetics, it was expected that poly(1-Bu-5-VIm) would also. Surprisingly, it was found that over the range of concentration followed, poly(1-Bu-5-VIm) displayed essentially first-order kinetics (see Figure 12 and Table IX).

Poly(1-Bu-5-VIm) evidently has a higher binding capacity than poly(1-Me-5-VIm). Thus, it is not possible to saturate the polymer with a mere tenfold excess of substrate.

Experimental Section

A. Synthesis. 1. 1-Butyl-4-vinylimidazole (1-Bu-4-VIm) and 1-Butyl-5-vinylimidazole (1-Bu-5-VIm). Synthesis via Alkylation of 4(5)-VIm with Butyl Iodide. Crude 4(5)-VIm, 0.94 g (0.01 mol), was charged to a 20 ml pressure bottle along with 2 ml of *n*-butyl alcohol and 1 ml of 10 *N* aqueous sodium hydroxide. The bottle was capped with a crown cap and neoprene gasket and immersed in a constant temperature bath at 100°. After 0.5 hr, 0.2 ml of a 50% solution of butyl iodide in butanol was added. Another 0.2 ml was added 15 min thereafter. Subsequently, 0.1-ml aliquots were injected at 15-minute intervals over a 4-hr period. The total amount of butyl iodide added was 1.84 g (0.01 mol).

After holding at 100° for 16 hr, the reaction mixture was quenched in aqueous hydrochloric acid and extracted with ethyl ether to remove any unreacted butyl iodide. The aqueous layer was neutralized by saturating with potassium carbonate and was extracted with chloroform. The chloroform extract was dried over anhydrous potassium carbonate prior to removal of the chloroform in vacuo. The resulting oily residue was vacuum distilled yielding 0.2 g (20%) of the mixed isomers of 1-Bu-4-VIm and 1-Bu-5-VIm in a ratio of 90:10, (1,4:1,5) by NMR. The isomers could be separated by GLC on a 25% QF-1 on 60–40 Chromosorb W column.[14] Typical separation conditions are: oven temperature, 200° isothermal; injector temperature, 250°; detector temperature, 270°; helium flow rate, 8 ml/sec.

2. Synthesis via Quaternization of 1-Trimethylsily-4-vinylimidazole. 1-Trimethylsilyl-4-vinylimidazole was prepared by the reaction of 1,1,1-3,3,3-hexamethyldisilazane with 4(5)-VIm. Crude 4(5)-VIm (4.7 g, 0.05 mol), hexamethyldisilazane (8.05 g, 0.05 mmol), and 10 ml of benzene were charged to a 50-ml round-bottomed flask equipped with a reflux condenser and a calcium sulfate drying tube.

A trace of ammonium sulfate was added and the reaction mixture was refluxed for 16 hr. Ammonia was given off from the reaction. The reaction mixture was evaporated to an oily residue which NMR proved to be exclusively 1-trimethylsilyl-4-vinylimidazole: NMR($CDCl_3$) δ_{TMS} 0.217 (9 H, s, $(CH_3)_3$–Si), 4.92 (1 H, q, *cis*-vinyl H), 5.73 (1 H, q, *trans*-vinyl H), 6.55 (1 H, q, vinyl H–C), 6.78 (1 H, s, C-5H), 7.30 (1 H, S, C-2H).

Crude 1-trimethylsilyl-4-vinylimidazole from the previous reaction was transferred to a 10 ml pressure bottle and the bottle was capped with a crown cap and neoprene gasket. Butyl iodide was added by syringe and the bottle was immersed in an oil bath at 65°. After 16 hr at 65°, the reaction was quenched by hydrolysis with water. The aqueous layer was saturated with potassium carbonate and the reaction mixture was extracted with chloroform. The chloroform was removed in vacuo and the resulting oil was eluted over a Florisil column with chloroform in order to remove any unreacted 4(5)-VIm. The column eluent was evaporated to dryness, yielding 5.5 g (62.7%) of the mixed isomers of 1-Bu-4-VIm and 1-Bu-5-VIm.

An attempt was made to separate the mixed butyl isomers by preparative thin-layer chromatography on alumina Brinkman, Alox-100 uv_{254}, 1.0 mm plates or Brinkman, $Al_2O_3F_{254}$(type T) 1.5 mm plates, eluting with acrylonitrile. Approximately 250 mg of the mixed isomers was applied per plate. The sample was applied to the plates by the method of Weaver and Teegarden.[15]

After developing each plate 2–3 times, only a slight separation could be achieved. The separate bands were removed from the plates and extracted with methanol. A drop of saturated picric acid solution was added to the extract of each fraction, the methanol was removed in vacuo, and the respective fractions were distilled. The overall distilled yield of both fractions was 26.7% based on 4(5)-VIm.

The first band, bp 82° (0.025 nm), was a mixture estimated to be 85% 1-Bu-4-VIm and 15% 1-Bu-5-VIm: yield 0.3 g; ir (neat film) cm^{-1} 1640 s (C=C); NMR ($CDCl_3$) δ_{TMS} 0.734 (3 H, t, CH_3), 0.8–1.6 (4 H, broad m, $(CH_2)_2$), 3.64 (2 H, t, $-N-CH_2-$), 4.87 (1 H, q, *cis*-vinyl H), 5.70 (1 H, q, *trans*-vinyl H), 6.52 (1 H, q, vinyl HC), 6.87 (1 H, s, C-5H), 7.32 (1 H, S, C-2H); mass spectrum *m/e* 150. The second band, bp 82° (0.025 mm), was, essentially, pure 1-Bu-5-VIm: yield 1.7 g; ir (neat film) cm^{-1} 1630 s (C=C); NMR ($CDCl_3$) δ_{TMS} 0.933 (3 H, t, CH_3), 1–1.8 (4 H, broad m, $(CH_2)_2$), 3.89 (2 H, t, $-N-CH_2-$), 5.12 (1 H, d, *cis*-vinyl H), 5.50 (1 H, d, *trans*-vinyl H), 6.53 (1 H, q, vinyl, HC=), 7.12 (1 H, s, C-4H), 7.42 (1 H, s, C-2H), mass spectrum *m/e* 150. Anal. Calcd for $C_9H_{14}N_2$: C, 72.00; H, 9.33; N, 18.66. Found: C, 71.29; H, 9.56; N, 18.65.

3. Poly(*N*-Vinylimidazole). One milliliter of freshly distilled *N*-vinylimidazole was charged to a Carius tube along with 0.0164 g of 2,2′-azobis(2-methylpropionitrile), AIBN, and 5 ml of reagent grade benzene. The materials were degassed by the standard freeze–thaw method before sealing the evacuated tube. The tube (properly sheathed) was placed in an oil bath at 65°. After 16 hr the vessel was removed from the 65° bath. The benzene solution of polymer was evaporated to dryness, taken up in methanol, and precipitated into acetone. The polymer was isolated by filtration onto a medium porosity sintered glass funnel and dried at ambient temperature, yield 0.9 g. The polymer was further purified by passage over a Sephadex LH-20 column eluting with methanol. The eluent was monitored by uv and the polymer was observed to elute in a band of less than 200 ml of solvent. The methanol was removed in vacuo and the polymer was taken up in benzene. Lyophilization of the benzene solution yielded the poly(*N*-vinylimidazole) used in these studies.

4. Poly(1-butyl-5-vinylimidazole). Poly(1-Bu-5-VIm) was prepared in bulk by a procedure analogous to that employed for poly(1-Me-4-VIm).[1] Thus, 0.50 g of freshly distilled 1-butyl-5-vinylimidazole and 0.00054 g of AIBN yielded 225 mg of poly(1-Bu-5-VIm). Elution over Sephadex LH-20 and lyophilization of a benzene–methanol solution yielded the poly(1-Bu-5-VIm) utilized in these studies: $[\eta]$(methanol, 26°) = 0.655.

5. Copoly(1-butyl-5-vinylimidazole/4(5)-vinylimidazole) (1:1) *M*. Copoly[1-Bu-5-VIm/4(5)-VIm] was prepared in bulk by a procedure analogous to that employed for poly-(1-Me-4-VIm). Thus, 0.50 g of freshly distilled 1-butyl-5-vinylimidazole, 0.31 g of sublimed 4(5)-vinylimidazole, and 0.00109 g of AIBN yielded 0.5 g of polymer. Elution over Sephadex LH-20 and lyophilization of a benzene–methanol solution yielded the copoly[1-Bu-5-VIm/4(5)-VIm] utilized in these studies: η_{red} (0.11 g/dl, methanol, 26°) =

0.847; NMR ratio of $-NCH_2-$ to all aliphatic H's, found, 20:130. Anal. Found: C, 64.37; H, 8.35; N, 20.26; C, 64.25; H, 8.15; N, 20.27.

6. **Copoly[1-Butyl-4-Vinylimidazole/4(5)-Vinylimidazole] (1:1)** ***M.*** Copoly[1-Bu-4-VIm/4(5)-VIm] was prepared in bulk by a procedure analogous to that employed for poly(1-Me-4-VIm). Thus, 0.3 g of freshly distilled 1-butyl-4-vinylimidazole, 0.188 g of sublimed 4(5)-VIm, and 0.00066 g of AIBN yielded 0.383 g of polymer. Elution over Sephadex LH-20 and lyophilization of a benzene–methanol solution yielded the copoly[1-Bu-5-VIm/4(5)-VIm] utilized in these studies: η_{red} (0.11 g/dl, methanol, 26°) = 1.24; NMR ratio of $-NCH_2-$ to all aliphatic H's, found, 20:130. Anal. Found: C, 62.34; H, 7.96; N, 20.80; C, 62.54; H, 8.06; N, 21.02.

7. **Poly[4(5)-vinylimidazole].** Freshly sublimed 4(5)-vinylimidazole, 0.47 g, was charged to a Carius tube along with 0.0076 g of AIBN in benzene solution. The materials were degassed by standard freeze–thaw techniques and the benzene was removed by lyophilization. Subsequently, the evacuated Carius tube was sealed. The tube (properly sheathed) was placed in an oil bath at 70°. After 16 hr the vessel was removed from the bath. The polymer was dissolved in methanol and precipitated into benzene. The precipitate was isolated by filtration onto a medium porosity sintered glass funnel. The polymer was dried at ambient temperature, yielding 0.45 g. The polymer was further purified by passage over a Sephadex LH-20 column eluting with methanol. The eluent was monitored by uv and the polymer was observed to elute in a band of less than 200 ml of solvent. The methanol solution was concentrated in vacuo, reprecipitated into benzene, and dried in an Abderhalden over P_2O_5 at 110°. This then is the poly[4(5)-VIm] utilized in these studies. Anal. Calcd for $C_5H_6N_2$: C, 63.80; H, 6.38; N, 29.80. Found: C, 61.20; H, 6.56; N, 27.24; C, 61.30; H, 6.51; N, 27.33.

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 Arbor, 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 or a Jaspar Electronic Optics Laboratory (JEOL) 100 MHz NMR spectrophotometer, both in continuous wave and Fourier transform modes.

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 (Δml) were plotted as a function of pH to give the differential titration curves.[6] 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[6]

$$\text{pH} = \text{p}K_a + n \log \alpha_1/(1 - \alpha_1)$$

D. Kinetic Measurements. 1. Slow Reactions in Excess Catalyst. (a) 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 or 96.7% water and 3.3% acetonitrile 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.

(b) 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, $k_{\text{obsd}} = k_{\text{meas}} - k_{\text{blank}}$. The second-order-rate constant k_{cat} was calculated either from k_{meas} or from k_{obsd}: $k_{\text{cat}} = k_{\text{obsd}}/[\text{catalyst}]$.

2. Fast Reactions in Excess Catalyst. All reactions which had a half-life of less than 2 min were followed on a Durrum-Gibbs Stopped Flow Spectrophotometer. The data were obtained on an oscilloscope trace of % *T* vs. time; this trace was photographed to supply a permanent record. The % *T* was read off the photographs at certain time intervals, then converted to absorbance.

With respect to the poly(1-Me-5-VIm)-catalyzed hydrolysis of S_{12}^- in water, the data were treated as pseudo-first-order kinetics by plotting ln $(A_\infty - A_t)$ vs. time. With respect to the 4(5)-VIm-containing copolymer-catalyzed solvolysis of S_{12}^- in 28.5% ethanol–water initial rates were obtained from plots of absorbance vs. time.

3. Reactions in Excess Substrate and Anomalous Reactions. (a) Preparation of Solutions for Kinetics. Essentially the same procedure was followed as described in section D1a except the catalyst concentration was held constant and the substrate concentration was variable.

(b) Treatment of Data. In all cases in excess substrate, initial rates were obtained from plots of absorbance vs. time. This was done even when the reaction in excess substrate obeyed psuedo-first-order kinetics, as determined by the linearity of plots of ln $(A_\infty - A_t)$ vs. time.

Reactions in excess catalyst which were anomalous, either because of accelerative kinetic behavior or because of other effects, were also analyzed by monitoring the initial rate.

For purposes of comparison, the initial rate could be related to k_{obsd} by the following relationship: $k_{\text{obsd}} = V_i/[\text{substrate}]$.

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