Conformational Effects and Nonpolar Interactions in Poly[4(5)-vinylimidazole]-Catalyzed Solvolyses of Neutral Substrates

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Abstract: The solvolytic reactions of the neutral esters *p*-nitrophenyl acetate and *p*-nitrophenyl heptanoate catalyzed by poly[4(5)-vinylimidazole] and by imidazole have been investigated in solutions containing varying compositions of ethanol and water. Temperature and pH have been investigated as the perturbing variable in order to elucidate the roles of the effects of nonpolar polymer–substrate interactions and bifunctional catalysis in the synthetic polymeric catalyses. Further, the solution properties of poly[4(5)-vinylimidazole] were investigated in varying ethanol–water compositions and at varying pH values. It was found that the conformation of the polymer chain of poly[4(5)-vinylimidazole] in an ethanol–water mixture is dramatically affected by the ethanol–water composition and by the degree of neutralization of the pendent imidazole groups. The polymeric, catalytic enhancement for the solvolyses of neutral substrates in low and high ethanol compositions at pH *ca.* 8 was attributed to increased bifunctional catalysis which increases with the shrinkage of the macromolecules in solution. The solvolysis of PNPH at low ethanol concentration by poly[4(5)-vinylimidazole] appeared to involve an increased accumulation of the substrate in the polymer domain because of nonpolar polymer–substrate interactions.

The catalytic effects of synthetic, nucleophilic macromolecules in esterolytic reactions have exhibited several similarities with those of enzymic reactions. Although the efficiencies of the synthetic, polymeric reactions are considerably less than those of the enzymic reactions, the former have been characterized by higher reactivity than their monomeric systems, by specificity of substrate hydrolysis, by bifunctional interactions between the pendent groups with the substrate, and by complexation with high and low molecular weight substrates.[1]

In general, two types of effects, *viz.*, the increased concentration of the substrate in the polymer domain by electrostatic or nonpolar interactions and the bifunctional interactions between the catalytically active pendent groups and the substrate, appear to be primarily responsible for the catalytic activities of synthetic macromolecules. It could be expected that bifunctional, catalytic interactions between neutral–neutral or neutral–anionic groups would increase when the pendent, functional groups are held in juxtaposition. In this case polymeric catalysis could depend on the dimensions of the polymer coil in solution. The greatest bifunctional catalytic effect could, therefore, be expected to occur when the polymer chain is in a tight coil in solution.

Recent results have shown that the catalytic rate constants for the poly[4(5)-vinylimidazole]-catalyzed solvolysis of the neutral ester *p*-nitrophenyl acetate (PNPA) increased with increasing water content in several alcohol–water systems.[1-3] This enhancement was attributed to an increase in bifunctional interactions of two neutral, pendent imidazole groups on the polymer with the substrate as well as to an increased accumulation of the substrate in the polymer domain by nonpolar polymer–substrate interactions.[1,2]

In order to study further the effects of alcohol–water solvent composition on the alterations of the conformations of the polymer on bifunctional catalysis and on nonpolar interactions with a substrate, the rates of solvolyses of the neutral esters *p*-nitrophenyl acetate (PNPA) and *p*-nitrophenyl heptanoate (PNPH) were determined in various ethanol–water solvent compositions. A study of the effects of temperature, pH, and polymer concentration in certain solution properties was also undertaken to provide a further insight into the conformation of the polymer in solution.

Experimental Section

4(5)-Vinylimidazole was prepared by the procedure of Overberger and Vorchheimer.[4] The crude product was purified by sublimation at 70–75° ($1-5 \times 10^{-4}$ mm), mp 81.5–83°.

Poly[4(5)-vinylimidazole] (PVIm). A solution of 4(5)-vinylimidazole (1.0 g, 0.011 mol) and azobisisobutyronitrile in 20 ml of methanol or benzene was heated at 65° for 24 hr in a polymerization tube. The polymer prepared in methanol remained in solution while that prepared in benzene precipitated during the polymerization. These solutions were added to a large excess of benzene, and the precipitated polymers were collected by filtration. These polymers were dissolved in methanol and twice reprecipitated into benzene. The ultraviolet spectrum of the obtained poly[4(5)-vinylimidazole] in 90 vol % ethanol–water showed one absorbance: λ_{max} 210–220 mμ (ϵ 3285 at 220 mμ at 26°). The specific viscosity, η_{sp}, for sample no. 1, obtained from the polymerization in methanol, was 0.08 (0.5 g/dl, methanol, 26°) and that for sample no. 2, obtained from the polymerization in benzene, was 0.484 (0.5 g/dl, methanol, 26°).

***p*-Nitrophenyl acetate (PNPA)**, obtained from Eastman Kodak Co., was purified by sublimation, mp 78–79°.

***p*-Nitrophenyl heptanoate (PNPH)** was kindly provided by Dr. I. Cho of this laboratory, mp 82°.

Potentiometric Titrations. 1. Determination of pK$_1$′ in Different Ethanol Compositions at 26°. Solutions of poly[4(5)-vinylimidazole] ($4-10 \times 10^{-3}$ *M*) and imidazole ($4-10 \times 10^{-3}$ *M*) neutralized with HCl were prepared in different ethanol compositions with potassium chloride added to adjust the ionic strength to 0.05. These solutions were titrated with concentrated sodium hydroxide in the same ethanol composition at 26° under a nitrogen atmosphere with stirring by using a microburet and a Beckman pH meter.

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(1) C. G. Overberger and J. C. Salamone, *Accounts Chem. Res.*, **2**, 217 (1969), and the references cited therein.

(2) C. G. Overberger, T. St. Pierre, C. Yaroslavsky, and S. Yaroslavsky, *J. Amer. Chem. Soc.*, **88**, 1184 (1964).

(3) C. G. Overberger and I. Cho, unpublished results.

(4) C. G. Overberger and N. Vorchheimer, *J. Amer. Chem. Soc.*, **85**, 951 (1963).

After stirring for at least 5 min, electrode equilibrium was attained. The volume of added sodium hydroxide solution at the end point was fixed more exactly by estimating the point where the second derivatives of pH with respect to volume (*i.e.*, $\Delta pH^2/\Delta V^2$) becomes zero.

2. Determination of pK_1' in 25 Wt % Ethanol–Water at Different Temperatures (15–45°). Solutions of poly[4(5)-vinylimidazole] (5×10^{-3} *M*) and imidazole (5×10^{-3} *M*) neutralized with HCl were prepared in 25 wt % ethanol–water with potassium chloride added to adjust the ionic strength to 0.05. These solutions and the blank solutions, which do not involve catalyst, were titrated at different temperatures with 0.5 *N* NaOH in 25 wt % ethanol–water in the same manner as described in section 1. The differences of the added volume of 0.5 *N* NaOH in 25 wt % ethanol–water at the same pH between blank and poly[4(5)-vinylimidazole] titrations were evaluated graphically to give differential titration curves.[6] The apparent pK_1' for poly[4(5)-vinylimidazole] was obtained from the value of pH for which $\alpha_1 = 0.5$. The apparent pK_1' for imidazole was obtained according to the procedure described in section 1.

Turbidimetric Titrations. The apparatus used to determine initial precipitation points and to follow the change in turbidities consisted essentially of a light scattering apparatus, with a provision being made for a thermostated glass cell containing the polymer solution to which the precipitant is added from a buret. All precipitations were carried out at 26° from 50 vol % ethanol–water solution (μ 0.13, pH 8.0) using a buffer solution (μ 0.13, pH 8.0) as the precipitant, the initial polymer concentration being 0.0047 g/100 ml (5×10^{-4} *M*). The polymer solution (20 ml) was placed in the cell so that the incident beam (λ 436 mμ) was completely within the solution. The development of turbidity was followed by an increase in right-angled scatter, the photocell output being recorded on a galvanometer-type recorder (range 0–10 mA). The recorder reading is directly proportional to the intensities of light falling on the measuring photocell. A correction for the dilution caused by adding the precipitant was made on the basis of Beer's law. Turbidity, τ, used here was defined as

$$\tau = [i_{90°} - i°_{90°}]/\lambda$$

where $i_{90°}$ is the galvanometer recorder reading perpendicular to the incident beam at each addition of the precipitant (milliamp), $i°_{90°}$ is the recorder reading on a galvanometer for the starting solution of the polymer perpendicular to the incident beam, and λ is the dilution factor based on the starting polymer solution.

Viscosity Measurements. Dilute solution viscosities were measured in an Ubbelohde viscometer (flow time for water at 26°, *ca.* 73 sec) immersed in a water bath at 26.00 ± 0.05°. Freshly prepared solutions were used. They were filtered into the viscometer through a glass filter (M size). The solvent viscosity used in computing the relative viscosity of polymer solutions was taken as that observed for the buffer solution at the same ionic strength, pH, and ethanol composition as those employed in the presence of polymer.

Kinetic Measurements. Catalytst solutions were prepared in ethanol–water buffered with either 0.02 *M* tris(hydroxymethyl)-aminomethane (Tris) and hydrochloric acid (above pH 7.5), 0.02 *M* 2,2-bis(hydroxymethyl)-2,2′,2′′-nitrilotriethanol and hydrochloric acid (pH 6.0–7.0), or 0.02 *M* sodium acetate and acetic acid (below pH 5.0); sufficient potassium chloride was added to adjust the ionic strength to 0.02. The substances PNPA and PNPH were dissolved in the appropriate solvents.

The catalyst solution (3.0 ml, sample no. 2) and the substrate solution (200 μl) were mixed in a quartz cell and the solvolytic rates were studied in a Beckman DU2 spectrophotometer thermostated at 26.0°, by measuring the absorption (A_t) of released phenolate ion as a function of time (t) at one of the following wavelengths: 400 mμ (pH 7–8), 352 mμ (*ca.* pH 6), 348 mμ (*ca.* pH 5).

After at least 10 half-lives the absorption was measured for complete reaction (A_∞). Catalysis by buffer only (blank) was measured in the same manner. The measured data were treated as first-order kinetics by plotting $A_\infty - A_t$ on a logarithm scale *vs.* t on a linear scale. The plots were straight lines for 50% conversion or more. The slope after correcting for natural logarithms was taken as k_{measd}.

The observed rate constant, k_{obsd}, for the catalyzed reaction was obtained by subtraction of k_{blank} for the uncatalyzed reaction from k_{measd}, *i.e.*, $k_{\text{obsd}} = k_{\text{measd}} - k_{\text{blank}}$.

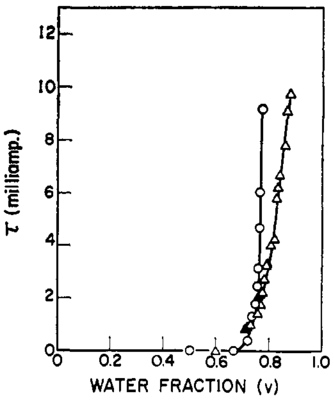

Figure 1. Turbidity of poly[4(5)-vinylimidazole] [samples no. 1 (△) and 2 (○)] at pH 8.0 as a function of increasing water content in ethanol–water solvent systems; buffer (Tris HCl) concentration 0.1 *M*, $\mu = 0.13$, 26°, [PVIm] = 5×10^{-4}.

When k_{obsd} follows first-order reaction against catalyst concentration, $k_{\text{cat.}}$ is obtained by $k_{\text{cat.}} = k_{\text{obsd}}/E_0$ where E_0 is the initial catalyst concentration.

Results and Discussion

The alteration of conformation of poly[4(5)-vinylimidazole] could presumably be elucidated by a study of the solubility of the polymer in varying ethanol–water solvent composition, by a change in the apparent dissociation constant of the pendent imidazole functions with temperature, and by a change in viscosity of the polymer with a variation in solvent composition. These effects could be expected to facilitate an understanding of the conformation of the polymer on the bifunctional interactions of two pendent, catalytically active functions with the substrate.

Turbidimetric Titrations. Poly[4(5)-vinylimidazole] is soluble in a mixed solvent system of ethanol–water, being insoluble in pure water and pure ethanol. Thus, it can be expected that varying the solvent content will lead to alterations in the polymer conformations. The precipitation behavior by turbidimetric titrations was measured in varying ethanol composition. In Figure 1 is shown a plot of the effect of ethanol content on the turbidity of two samples of poly[4(5)-vinylimidazole] [(PVIm) = 5×10^{-4} *M*] at pH 8, $\mu = 0.13$, and 26°. Sample no. 1 had a specific viscosity of 0.08 in methanol at 26° whereas sample no. 2 had a specific viscosity of 0.48. The turbidity of the polymers was also measured at pH 9, under similar conditions. The turbidity behavior for varying ethanol content was similar to the case at pH 8; however, the precipitation started at *ca.* 60 vol % of ethanol content in the solvent.

Since the system employed is on the cationic side of the isoelectric point, with a polyelectrolyte such as poly[4(5)-vinylimidazole], the solubility in a high content of water in mixed solvents generally increases and that in a low content of water in mixed solvents decreases with the net charge density of the polymeric species. Protonated or neutral poly[4(5)-vinylimidazole] has very interesting solubility properties, being soluble in a mixture of the two solvents and not in either component of the mixture.

The determination of the molecular weight of imidazole and 4(5)-methylimidazole by the vapor-density method indicates that these compounds are not associated in the gaseous state. However, when the mo-

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(5) T. V. Parke and J. M. Sturtevant, *J. Amer. Chem. Soc.*, **81**, 2860 (1959).

lecular weights of these compounds are determined by the cryoscopic or ebulliometric methods in nonpolar solvents, striking deviations from ideal behavior are observed. Of importance is the fact that substitution of the imino hydrogen by alkyl, aryl, or carboethoxy groups invariably leads to compounds exhibiting little association.[6] It is of interest to note that imidazole in aqueous solution exhibits a normal molecular weight which changes little with increasing concentration. Solubility, viscosity, and dipole moment measurements support a high degree of association of imidazole and benzimidazole in nonpolar solvents.[7] The spectra of benzimidazole and other derivatives show strong, broad bands from 3300 to 2800 cm^{-1} which indicate association through intermolecular hydrogen bonding.[8]

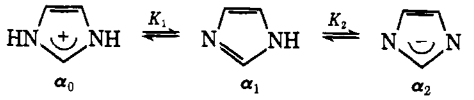
The case of neutral poly[4(5)-vinylimidazole], which is insoluble in absolute ethanol but dissolves in ethanol–water mixtures containing small concentrations of water, might correlate with strong hydrogen bonding between pendent imidazole groups, *i.e.*, with the ability of the solvent to accept a hydrogen bond. On the other hand, protonated or neutral poly[4(5)-vinylimidazole] is insoluble in water or in low contents of ethanol, but dissolves in ethanol–water mixtures. This might be correlated with the strong nonpolar interactions between the long aliphatic backbone chains of polymer rather than van der Waal's interactions.[9–11]

In the above discussion, it should be noted that the intra- or intermolecular interactions of polymer chains are divided into a contribution from nonpolar interactions in solvents of low ethanol content and contributions from hydrogen bonding in solvents of high ethanol content.

Potentiometric Titrations. Conformation studies of poly[4(5)-vinylimidazole] in solution were required in order to understand the bifunctional interactions in the polymeric imidazole catalyzed solvolyses of esters. It was pointed out that the radius of gyration of a polyelectrolyte can be estimated from the values of ΔF_{ele} by means of titration,[12] where ΔF_{ele} is the electrostatic free energy between the charged polymer and proton.

Since the catalytically active imidazole group in the solvolyses of esters is known to be in neutral form in the conditions employed, it was necessary to determine the fraction of pendent, neutral imidazole groups in order to facilitate an interpretation of the reaction kinetics. Therefore, the results of the potentiometric titration are believed to be useful in the studies of conformation and determination of the fraction of pendent imidazole groups in poly[4(5)-vinylimidazole] in ethanol–water mixtures.

The conditions for the titrations in the present investigation, *i.e.*, the effect of ethanol content and the effect of temperature on the dissociation constant, were performed at an ionic strength of 0.05 in order to maintain the ionic strength as constant as possible. The dissociation constant (pK_1') obtained for 30 vol % ethanol–water at 26° at μ 0.05 was 6.17. This value is similar to the previously reported value of pK_1' = 6.20 obtained at room temperature in 28.5 vol % ethanol–water at μ 0.02,[13] but larger than the previously reported value of pK_1' = 5.78 obtained at room temperature in 28.5 vol % ethanol–water at μ 0.015–0.02.[14] The dissociation of imidazole groups has been defined as



(1)

where K_1 and K_2 are the two dissociation constants for the ampholyte and α_0, α_1, and α_2 are the fractions of cationic, neutral, and anionic imidazole.[13] The dissociation constant of neutral, pendent imidazole to its anionic form could not be determined with the glass electrode in these titrations.

A potentiometric method for acid and base dissociation constants and autoprotolysis constants was presented by Grunwald[15] which does not require a knowledge of electrode or liquid junction potentials in organic solvents. Therefore, this method was utilized for poly[4(5)-vinylimidazole].

The apparent dissociation constant of a polymer carrying a large number of ionizable groups will vary with the degree of dissociation, since the charged polymer will interact with hydrogen ions. Therefore, the apparent dissociation constant, K', for polyelectrolytes is defined as follows (based on a consideration of the interaction factor, *i.e.*, the electrostatic free energy $\Delta F_{\text{ele}}(\beta)$ between the charged polymer and proton at a given degree of ionization)[16]

$$\text{pH} = \text{p}K' + \log(\beta/1 - \beta) = \text{p}K^0 + \log(\beta/1 - \beta) - 0.434\Delta F_{\text{ele}}/RT \quad (2)$$

where K^0 is characteristic of the ionizing group under conditions where electrostatic interactions with other ionizing groups are absent, and β is the fraction of the ionizable groups, that is, for this case, $\beta = \alpha_0$ for protonated poly[4(5)-vinylimidazole].

1. Effect of Ethanol Composition. In order to determine the apparent dissociation constants, pK_1', eq 2 was converted to pH = pK_1' + log $(1 - \alpha_1)/\alpha_1$ by the substitution of $1 - \alpha_1$ for β.[13] The apparent dissociation constant is then obtained from the plot of log $(1 - \alpha_1)/\alpha_1$ *vs.* pH at the point where $\alpha_1 = 0.5$. In Figure 2 are shown the apparent first dissociation constants obtained for imidazole and poly[4(5)-vinylimidazole] as a function of the ethanol content.

Figure 2 reveals that the pK_1' values for poly[4(5)-vinylimidazole] show a minimum in the region of 50 vol % ethanol–water, whereas the pK_1' values for imidazole decrease with increasing ethanol content. The behavior of the pK_1' values for imidazole in varying ethanol compositions is consistent with the decreasing pK_1' values of anilinium, *p*-toluidinium, and *N*-methyl-

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[8] D. J. Rabiger and M. M. Joullie, *J. Org. Chem.*, **29**, 476 (1964).

[9] R. G. Shorenstein, C. S. Pratt, C. J. Hsu, and T. E. Wagner, *J. Amer. Chem. Soc.*, **90**, 6199 (1968).

[10] F. Franks in "Physico-Chemical Processes in Mixed Aqueous Solvents," F. Franks, Ed., Elsevier, New York, N. Y., 1967, p 50.

[11] E. M. Arnett, see ref 10, p 50.

[12] E. Wicke and M. Eigen, *Z. Elektrochem.*, **56**, 551 (1952); **57** 319 (1953); N. Ise and M. Hosono, *J. Polym. Sci.*, **39**, 383 (1959).

[13] C. G. Overberger, T. St. Pierre, N. Vorchheimer, J. Lee, and S. Yaroslavsky, *J. Amer. Chem. Soc.*, **87**, 296 (1965).

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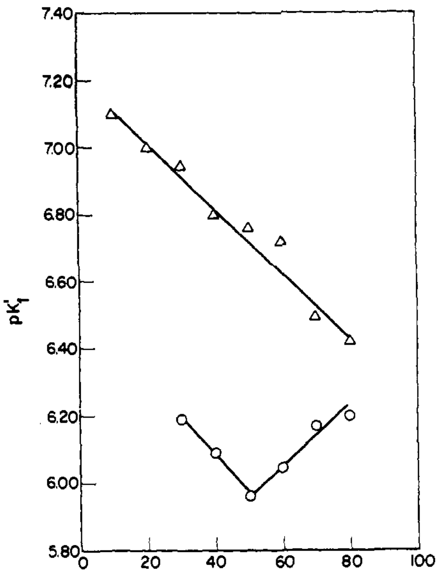

Figure 2. Effect of ethanol composition (ethanol–water) on (apparent) pK_1' values for imidazole (△) and poly[4(5)-vinylimidazole] (○); $\mu = 0.05$, 26°.

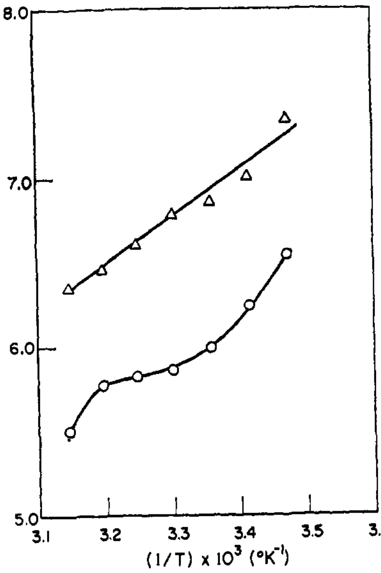

Figure 3. Effect of temperature on (apparent) pK_1' values for imidazole (△) and poly[4(5)-vinylimidazole] (○); $\mu = 0.02$, 25 wt % ethanol–water, $\mu = 0.05$.

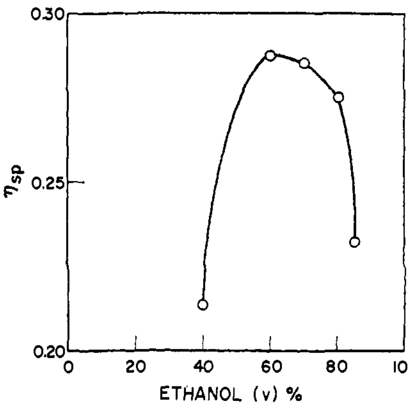

Figure 4. Solution viscosity of poly[4(5)-vinylimidazole] as a function of ethanol composition (ethanol–water); [PVIm] = 0.4229 (g/dl), $\mu = 0.02$, 26°.

anilinium chlorides in ethanol–water mixtures with increasing ethanol content.[17] A similar effect has been noted for the *o*-chloroanilinium ion and the *m*-nitroanilinium ion in methanol–water mixtures.[18] The pK_1' values of poly[4(5)-vinylimidazole] are, on the other hand, decreased by the addition of ethanol to water up to 50 vol % and a minimum value of the pK_1' occurs in the region of 50 vol % ethanol–water; the further addition of ethanol to water leads to an increase in the pK_1' values. This is of interest in connection with electrostatic free energy in eq 2, if the pK_1' for imidazole is assumed to be $pK^{0'}$ for poly[4(5)-vinylimidazole]. The pK_1' is a decreasing function in both poly[4(5)-vinylimidazole] and imidazole up to 50 vol % ethanol. However, the electrostatic free energy contribution, $\Delta F_{\mathrm{ele}}(\beta)$, becomes a decreasing function past 50 vol % ethanol; this accounts for the increasing value of pK_1' of the polymer in the region past 50 vol % ethanol (Figure 2). The drastic decrease in ΔF_{ele} in high ethanol content might be due to the effect of strong intra- and intermolecular interactions between the protonated imidazole groups and the neutral imidazole groups. This point of view could support the specific interaction between imidazole groups in high ethanol content. In an ethanol content of less than 50 vol %, a small interaction of the protonated imidazole groups with the neutral imidazole groups apparently causes only a slight change in ΔF_{ele} under the conditions employed.

2. Effect of Temperature. The effect of temperature on the pK_1' values was measured in 25 wt % ethanol–water with 0.05 *M* KCl. The solutions of poly[4(5)-vinylimidazole] and imidazole were prepared at 25°. The results are given in Figure 3. The pK_1' values of imidazole and poly[4(5)-vinylimidazole] were observed to decrease with increasing temperature, except that in the case of poly[4(5)-vinylimidazole] a plot of pK_1' *vs.* $1/T$ showed a deviation from linearity. The temperature dependence of pK_1' obtained here was more pronounced than that measured by spectrophotometric titration.[13] The differences in pK_1' values between imidazole and poly[4(5)-vinylimidazole] are found to be nearly constant. However, $|\Delta F_{\mathrm{ele}}|$ values for the protonated polymeric base increase with increasing temperature. This result may also be related to the shrinkage of the macromolecule in solution at high temperature under the conditions employed.

Viscosity. The conformational changes in high ethanol composition and low ethanol composition through hydrogen bonding and nonpolar interactions, respectively, have been discussed in preceding sections. In order to study further these problems, the viscosities were measured at a certain polymer concentration (0.4229 g/dl) in different ethanol compositions at $\mu = 0.02$, adjusted with potassium chloride (no buffer) at 26°. Figure 4 is a plot of the specific viscosities at constant polymer concentration, as a function of ethanol composition. The region of *ca.* 60 vol % ethanol composition has a viscosity maximum. The viscosity decrease with decreasing ethanol or increasing ethanol

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(17) B. Gutbezahl and E. Grunwald, *J. Amer. Chem. Soc.*, **75**, 559 (1953).

(18) E. E. Sager, R. A. Bates, *J. Res. Nat. Bur. Stand., Sect. A*, **68**, 305 (1964).

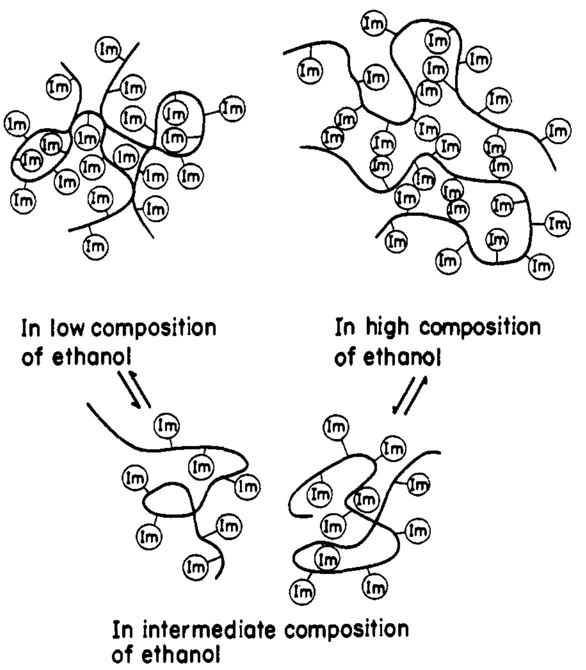

Figure 5. A schematic illustration of conformation for poly-[4(5)-vinylimidazole] in ethanol–water.

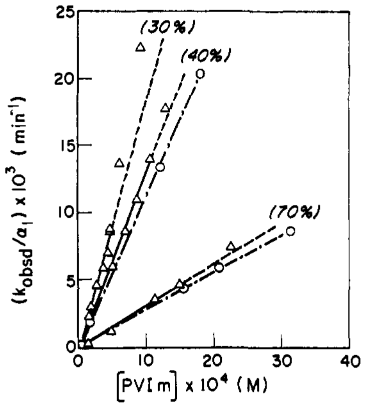

Figure 6. Dependence of the solvolytic rates of PNPA on the concentration of imidazole (○— -) and poly[4(5)-vinylimidazole] (△—); approximate pH 8, μ = 0.02, 26°, in 30, 40, 70 vol % ethanol–water. Dashed lines are extrapolated values for the first-order observed rate constant.

can be attributed to shrinkage of the polymer chain caused by nonpolar interactions and hydrogen bonding, respectively, while at *ca.* 60 vol % ethanol composition the polymer highly expands because of the disappearance of these interactions. Furthermore, the nonpolar interaction between polymer chains in 30 vol % was apparently so strong that the polymer precipitated at the conditions employed.

The specific viscosities were also measured in 30 vol % ethanol–water mixture at various polymer concentrations as a function of the degree of neutralization, using similar conditions as employed for the kinetic measurements. It was found that viscosities increased with an increase in the degree of protonation and with an increase in polymer concentration. The viscosity increase with an increase in the degree of neutralization is ascribed to the expansion of the polymer chain because of the repulsion of the pendent imidazolium ions.

Conformation Change and Catalytic Activity. It is of interest to consider the conformational structure for neutral poly[4(5)-vinylimidazole] chains in ethanol–water mixtures as a simple case. Shrinkage of polymer coils in solvents of low ethanol content might be the result of intra- and intermolecular nonpolar interactions, whereas its shrinkage in solvents of high ethanol content is attributed primarily to intra- and intermolecular hydrogen bonding. Such specific interactions are expected to cause a shrinkage or folding, leading to the exposure of the imidazole groups and the burying of aliphatic chains in solvents of low ethanol composition. The opposite situation is true for solvents of high ethanol composition, *i.e.*, a shrinking or folding, leading to the exposure of aliphatic chains and the burying of the imidazole groups. A schematic illustration of the effect of ethanol composition on the conformational change is given in Figure 5. Esterolytic catalysis in ethanol–water mixtures presumably involves not only a contribution from the change in the macroscopic dielectric constant of the solution, but also a contribution from the change in the conformation of polymer chain. The latter contribution is possibly independent of the former contribution, when the catalyses by poly[4(5)-vinylimidazole] are compared with those by imidazole in the same system. Furthermore, the effect of nonpolar interactions on binding of a specific substrate with polymer will be considerably important in compositions of low ethanol content.

The solvolytic rates of PNPA were first order with respect to both the substrate and polymer concentrations except in the region of high concentration of poly[4(5)-vinylimidazole] (*ca.* 10^{-3} *M*). Since these experiments were not performed at the same pH value, the dependence of the first-order solvolytic rate constants corrected for the neutral imidazole groups, k_{obsd}/α_1, on the polymer concentrations is shown in Figure 6. All of the previous results of the concentration dependence of the rate of solvolysis of PNPA have yielded only a linear relationship of k_{obsd} with the polymer concentrations in the range of concentration investigated (*i.e.*, 5×10^{-5} to 5×10^{-4} *M*).[1,13] It is noted that the imidazole solvolytic rates are directly proportional to the imidazole concentration in a broad concentration range. On the other hand, there is a slightly higher reactivity of poly[4(5)-vinylimidazole] (at high polymer concentrations and especially in low ethanol content) than the reactivity expected with a second-order reaction of catalyst and substrate. This effect could be caused by an increase of the multifunctional catalysis of inter- and intraneutral imidazole groups in the region of the appearance of binary interactions between polymer coils.

In order to ascertain the effects of nonpolar interactions between catalyst and substrate, and the effect of the conformational change in poly[4(5)-vinylimidazole] catalyses, the solvolyses of PNPA and PNPH at approximately pH 8 were investigated in different ethanol–water compositions, with the ionic strength maintained at 0.02. Both of these solvolytic processes were second-order reactions under the conditions investigated, and the effective second-order rate constants and their ratios for polymeric and monomeric imidazole are listed in Tables I and II. Enhancements of the polymer-catalyzed solvolytic rates of PNPA and PNPH were observed in the ethanol composition range less than *ca.*

Table I.[a] Effective Second-Order Catalytic Rate Constants of Imidazole and Poly[4(5)-vinylimidazole] in the Solvolysis of PNPA in Varying Ethanol Compositions (μ = 0.02, 26°)

	Poly[4(5)-vinylimidazole]		Imidazole		
Ethanol, vol %	pH	$k_{\text{cat.}}$ (PVIm), $\text{min}^{-1}\,M^{-1}$	pH	$k_{\text{cat.}}$ (Im), $\text{min}^{-1}\,M^{-1}$	$k_{\text{cat.}}$ (PVIm)/ $k_{\text{cat.}}$ (Im)
10	7.71	60.6	8.03	31.8	1.95
20	8.03	38.2	8.02	23.8	1.60
30	7.95	18.6	7.95	17.1	1.09
40	7.94	12.4	7.94	12.2	1.02
50	7.95	6.06	7.95	7.05	0.861
60	7.95	4.21	7.95	5.19	0.813
70	8.04	2.58	8.04	2.64	0.978
80	7.96	2.19	7.96	1.98	1.10
90	8.02	1.453	8.02	0.861	1.69

[a] It was impossible to obtain the pK_1' of the polymer in 10, 20, and 90 vol % ethanol-water because of its low solubility. Therefore, α_1 values in 10 and 20 vol % ethanol-water were calculated with the pK_1' value obtained in 30 vol % ethanol-water and the α_1 value in 90 vol % ethanol-water was calculated with the pK_1' value obtained in 80 vol % ethanol-water.

Table II.[a] Effective Second-Order Catalytic Rate Constants of Imidazole and Poly[4(5)-vinylimidazole] in the Solvolysis of PNPH in Varying Ethanol Compositions (μ = 0.02, 26°)

	Poly[4(5)-vinylimidazole		Imidazole		
Ethanol, vol %	pH	$k_{\text{cat.}}$(PVIm), $\text{min}^{-1}\,M^{-1}$	pH	$k_{\text{cat.}}$(Im), $\text{min}^{-1}\,M^{-1}$	$k_{\text{cat.}}$ (PVIm)/ $k_{\text{cat.}}$(Im)
20	8.03	34.5	8.03	14.5	2.44
39	7.95	20.6	7.95	9.59	2.15
40	7.94	7.30	7.94	5.96	0.804
50	7.95	2.56	7.95	3.19	0.804
60	7.95	1.54	7.95	2.42	0.637
70	8.04	0.954	8.04	1.44	0.663
80	7.96	0.546	7.96	0.997	0.548
90	8.02	0.488	8.02	0.452	1.08

[a] It was impossible to obtain the pK_1' of the polymer in 10, 20, and 90 vol % ethanol-water because of its low solubility. Therefore, α_1 values in 10 and 20 vol % ethanol-water were calculated with the pK_1' value obtained in 30 vol % ethanol-water and the α_1 value in 90 vol % ethanol-water was calculated with the pK_1' value obtained in 80 vol % ethanol-water.

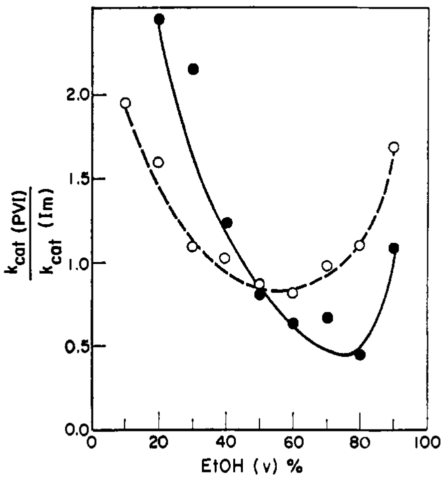

Figure 7. The ratios of the poly[4(5)-vinylimidazole]-catalyzed solvolytic rates of PNPA (O—), PNPH (●—), k_{cat}(PVIm), with its monomeric analog imidazole, k_{cat}(Im), in varying ethanol compositions; approximate pH 8, μ = 0.02, 26°.

40 vol % and more than *ca.* 90 vol % in comparison with its monomeric analog imidazole; however, a rate depression was obtained in the range of 40–90 vol % ethanol-water mixtures (Figure 7). The enhancements appear to reflect increased bifunctional catalysis through shrinkage of the polymer chain as a result of the change in ethanol composition, whereas the marked decrease in the catalytic activity of the polymer in the intermediate range of ethanol composition can be attributed to a decrease in such bifunctional interactions because of the expansion of the polymer chain. It is of interest to compare the solvolysis of PNPA catalyzed by poly[4(5)-vinylimidazole] and imidazole, where at values below pH 8 the polymer was a less efficient catalyst than imidazole in 28.5 vol % ethanol-water.[1,13] The same results were obtained in this investigation in the poly[4-(5)-vinylimidazole]-catalyzed solvolyses of PNPA in different ethanol-water mixtures with the exception of 10 and 20 vol % ethanol compositions, in which slight enhancement was still observed, even at approximately pH 7, in comparison with imidazole.

It is noted that the poly[4(5)-vinylimidazole]-catalyzed solvolyses of PNPH (relative to imidazole) are faster in the ethanol composition of less than 50 vol % than those of PNPA (relative to imidazole), in spite of the steric hindrance factor for PNPH. Also, a smaller rate enhancement is observed for PNPH in *ca.* 90 vol % ethanol-water than for PNPA. This behavior in the polymeric solvolysis of PNPH in the ethanol composition less than 50 vol % may be rationalized by the nonpolar interaction between the long aliphatic chain in PNPH and the polymer, which would account for an increase in the binding of the substrate to the polymer chain.

The solvolytic rates of PNPA and PNPH catalyzed by imidazole and by poly[4(5)-vinylimidazole] decrease with increasing ethanol composition (Tables I and II). These results can be explained as a solvent effect—the hypothesis being that the tetrahedral intermediate complex[1,2,13] is more polar than the reactants. An ionizing, high dielectric solvent would promote the formation of the more polar complex, thus increasing its concentration and enhancing the reaction rate.[19]

Conclusion

From the results of this study it seems apparent that bifunctional interactions of pendent, catalytically active groups on the polymer chain and substrate are directly related to the conformation of the polymer in solution. When the polymer exists as a tight coil in solution, the probability of catalytic groups being in juxtaposition is increased, and the solvolytic rate (relative to monofunctional catalysis) is enhanced. Furthermore, it also seems likely that nonpolar interactions between polymer and substrate increase with increasing water concentration, particularly with a long paraffinic chain substrate. Although it is difficult to obtain saturation kinetics of the Michaelis–Menten type in this system because of the low solubility of the neutral esters in solvents of low ethanol composition, it could be expected that polymer–substrate complexation through nonpolar interactions could occur with highly paraffinic substrates.

Acknowledgment. The authors are grateful to Dr. J. C. Salamone for his helpful discussions and invaluable assistance in composing this manuscript. We

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also gratefully acknowledge the valuable discussions with Visiting Professor Ephraim Katchalski and the financial support by the Research Laboratory, U. S. Army, Edgewood Arsenal (Grant No. DAA-15-67-C-0567) and the National Institutes of Health (Grant No. GM-15256-02).

The Effect of Ethanol–Water Solvent Composition on the Poly[4(5)-vinylimidazole]-Catalyzed Solvolysis of an Anionic, Long-Chain Substrate[1]

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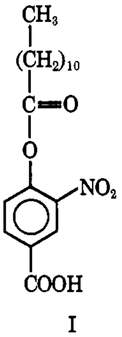
Received August 18, 1970

Abstract: The solvolytic reactions of the anionic, long-chain substrate 3-nitro-4-dodecanoyloxybenzoic acid (NDBA) catalyzed by poly[4(5)-vinylimidazole] (PVIm) have been investigated as a function of temperature and pH in aqueous solutions containing varying compositions of ethanol and water. It was found that the polymeric solvolytic reaction of NDBA follows the Michaelis–Menten mechanism in low ethanol composition based on the assumption of a catalyst–substrate complex formation. The maximum catalytic activity of the polymer was observed in *ca.* 30 vol % ethanol–water, relative to that of its monomeric analog imidazole, and this was attributed to the extremely large value of the first-order rate constants, k_2, rather than a favorable Michaelis constant, K_m. The solvolytic reaction of NDBA catalyzed by poly[4(5)-vinylimidazole] in 43.7 vol % ethanol–water presented unusual kinetic features in which a retardation behavior was noted for [NDBA] > [PVIm] and an acceleration behavior for [PVIm] > [NDBA]. These results were related to the formation of the long-lived intermediate compound, dodecanoylpoly[4(5)-vinylimidazole]. This formation also indicates that the deacylation step is an overall rate-determining step in the solvolysis of NDBA catalyzed by poly[4(5)-vinylimidazole]. Nonpolar interactions between the substrate and the catalyst are discussed, based upon the structuredness of the solvent in varying compositions of ethanol.

The enhanced esterolytic action of synthetic, vinyl polymers containing pendent imidazole or benzimidazole groups (in comparison to their monomeric analogs) has been attributed to a variety of cooperative interactions between the pendent catalytic groups and the substrate. Although the efficiencies of the synthetic macromolecular catalysts have been found to be several orders of magnitude less than those of natural enzymes in esterolytic reactions,[2,3] it could be expected that the reactivity of the synthetic macromolecular catalyst could be improved by complex formation with the substrate through either electrostatic or nonpolar interactions followed by a bifunctional interaction from the catalytic functions.

In recent years, contributions of nonpolar interactions on complexation or binding of catalytically active, synthetic macromolecules with low and high molecular weight reagents have been discussed by several workers.[4–6] Recently, we have reported a dramatically large catalytic enhancement for the solvolysis of the long-chain, anionic substrate 3-nitro-4-dodecanoyloxybenzoic acid (NDBA, I) catalyzed by poly[4(5)-vinylimidazole] in an ethanol-water solvent composition of less than *ca.* 40 vol % ethanol in relation to its monomeric analog, imidazole.[1]



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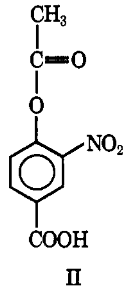

II

Reactivity studies on solvolytic reactions in the presence of detergent micelles have been carried out in order to ascertain the analogies to biological systems.[7–10]

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