Communications to the Editor

The Effect of Ethanol–Water Solvent Composition on Poly-4(5)-vinylimidazole-Catalyzed Esterolytic Reactions

The complexation or binding of catalytically active, synthetic macromolecules with low and high molecular weight reagents has been investigated by several workers.[1–5] These processes presumably involved an accumulation of the substrate in the vicinity of the polymer chain by either an electrostatic interaction between a charged macromolecule and an oppositely charged substrate or by apolar bonding between the interactant hydrocarbon components. Similar results have been noted in the presence of catalytically active detergents.[6–8]

It has recently been found that partially protonated poly-4(5)-vinylimidazole was able to complex with the negatively charged ester sodium 3-nitro-4-acetoxybenzenesulfonate (NABS) in 28.5% ethanol–water; in contradistinction, this saturation effect could not be achieved when the neutral ester *p*-nitrophenyl acetate (PNPA) was employed.[3] These results suggested that saturation of poly-4(5)-vinylimidazole with NABS was facilitated by electrostatic forces, whereas the lack of saturation with PNPA indicated that apolar interactions were insufficient to accumulate the neutral ester in the vicinity of the polymer domain.

Since the composition of a binary mixture of polar and nonpolar solvents could be expected to alter the effects of electrostatic and apolar interactions, we have investigated the poly-4(5)-vinylimidazole-catalyzed solvolysis of the long aliphatic chain, anionic ester 3-nitro-4-dodecanoyloxybenzoic acid (NDBA)[9, 10] in solvent systems of varying ethanol–water content. As comparisons for the polymeric systems, similar reactions were performed with the monomeric analog imidazole.

TABLE I[a]
EFFECT OF ETHANOL–WATER SOLVENT COMPOSITION ON TIME FOR HALF-SOLVOLYSES OF NDBA CATALYZED BY POLY-4(5)-VINYLIMIDAZOLE AND IMIDAZOLE

Ethanol, vol %	Poly-4(5)-vinylimidazole $t_{1/2}$, min	Poly-4(5)-vinylimidazole α_1	Imidazole $t_{1/2}$, min	Imidazole α_1	$\frac{\alpha_1 t_{1/2\text{PVIm}}}{\alpha_1 t_{1/2\text{Im}}}$
20	0.125	0.86	197	0.89	1630
30	0.210	0.86	352	0.89	1730
40	15	0.89	635	0.92	44.0
60	454	0.89	1,610	0.94	3.8
80	861	0.88	4,146	0.97	5.3
90	826		11,093		

[a] All solutions were buffered at pH 7.9 with 0.02 *M* tris(hydroxymethyl)aminomethane and hydrochloric acid; ionic strength was maintained at 0.02 with potassium chloride; half-solvolyses times were determined for total catalyst concentrations of 1.90×10^{-4} *M* and substrate concentration of 1.78×10^{-4} *M*. The substrate concentration is below the critical micelle concentration.

In Table I are listed the times for half-solvolyses of NDBA catalyzed by poly-4(5)-vinylimidazole and by imidazole for several ethanol–water solvent systems. The solutions were buffered at pH 7.9 with tris(hydroxymethyl)aminomethane and hydrochloric acid and the ionic strength was maintained at 0.02 with potassium chloride. The fractions of neutral, catalytically active imidazole functions (α_1) for the polymer and its monomeric analog are also given in Table I, as well as the efficiency factors $\alpha_1 t_{1/2\text{PVIm}}/\alpha_1 t_{1/2\text{Im}}$ for the polymeric and monomeric reactions, respectively. For each solvent system the catalyst concentration was greater than the substrate concentration such that the reaction system would not be significantly affected by the formation of a long-lived intermediate (dodecanoylimidazole) or by the solvolysis products.

The imidazole-catalyzed reactions were found to be second-order processes in all solvent systems, and it is noted that the half-lives for NDBA solvolyses increased considerably with increased ethanol content. The poly-4(5)-vinylimidazole-catalyzed reactions were, however, more complex. At ethanol contents of 60, 80 and 90%, the polymeric reactions were second-order processes, and they were slightly more efficient than the monomeric processes. These minor increases in reactivity could in part be caused by a contribution of electrostatic forces between the partially protonoted polymer and the oppositely charged substrate. An effect of this type is not possible for monomeric (neutral) imidazole and NDBA. Since we have also observed a rate enhancement of the poly-4(5)-vinylimidazole catalyzed solvolysis of the neutral ester PNPA in solvents of high ethanol content,[11] it would appear that the polymer-catalyzed solvolysis of NDBA (as well as of PNPA) also involves a cooperative interaction between pendent, neutral imidazole functions as has been previously reported.[12]

It can also be noted that the reactivity of poly-4(5)-vinylimidazole, relative to imidazole, increases dramatically at ethanol contents of 20–40%. The solvolytic reactions at 20 and 30% ethanol required measurement by the method of stopped-flow spectroscopy.

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(9) This substrate was prepared according to the procedure of Overberger and Cho,[10] and was recrystallized from cyclohexane, mp 82°.

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These exceptionally large rate enhancements appear to be related to the "structuredness" of the solvent medium. The addition of ethanol to water has been shown to increase the structuredness of the system, and the degree of structuredness reached a maximum at an ethanol mole fraction (x_2) of 0.1 (*ca.* 27% ethanol by volume at 25°).[13,14] Beyond this maximum point the degree of the structured system decreased until the system became an ordinary binary mixture at $x_2 > 0.25$ (*ca.* 54% ethanol by volume at 25°).

Although our ethanol-water solvent systems contain additional components, it would appear that the polymeric reactivities are in part related to apolar interactions which are based on the structuredness of the solvent, especially for the catalytic rate enhancement in the region of 30% ethanol. Another factor which is apparently involved in the polymeric reaction and which is lacking in the monomeric reaction is the complexation between poly-4(5)-vinylimidazole and NDBA. Initial results of the poly-4(5)-vinylimidazole catalyzed solvolysis of NDBA in 43.7% ethanol-water have shown kinetic evidence for complex formation which could be represented by the Michaelis-Menten mechanism.[3] This saturation effect could be achieved when either the varying polymer concentration was in excess of the fixed substrate concentration or *vice versa.* The Michaelis constants (K_m) for these reactions were determined to be $(4.77 \pm 0.57) \times 10^{-4}$ *M* for [PVIm] > [NDBA] and $(4.53 \pm 0.64) \times 10^{-4}$ *M* for [NDBA] > [PVIm]. The first-order rate constants (turnover numbers) were determined to be 0.032 ± 0.004 min^{-1} for the former system and 0.088 ± 0.013 min^{-1} for the latter system. The novel similarity of these K_m values would appear to suggest that the mechanisms of complexation between poly-4(5)-vinylimidazole and NDBA involve both electrostatic and apolar interactions, a circumstance which would lead to a lowering of the free energy of activation of the solvolytic reaction. This factor in conjunction with the effect of an ordered solvent structure could be responsible for the exceptionally large esterolytic reactivities achieved with a synthetic, vinyl polymer, reactivities which approach the order of enzymic processes. These results may suggest that the high reactivity of an enzymic process could be in part related to an ordered water structure at the enzymes' active site.

Although the values of K_m determined for 43.7% ethanol-water are of the same order as those of certain enzyme-substrate reactions, the turnover numbers of this system are indicative of a rather inefficient solvolytic process. We hope to report in the near future detailed results of the rapid solvolysis of NDBA at low ethanol contents, as well as the effects of temperature, pH and ionic strength on these reactions.

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Thin Layer Chromatographic Studies on Specific Interactions between Stereoisomeric Chains of Poly(methyl methacrylate)

In our preceding papers it has been reported that thin layer chromatography (tlc) can be applied successfully to studies on the chemical structure of binary copolymers,[1] as well as on the stereoisomerism of poly(methyl methacrylate) (PMMA).[2] This short communication deals with further applications of tlc to the investigation of specific interactions between isotactic and syndiotactic PMMA chains. The problem treated here is divided into two subjects, *viz.*, stereocomplex formation in dilute solution,[3-7] and the structure of crystallizable PMMA, which was first thought to be a stereoblock PMMA.[8,9] For this first subject, stereocomplexes were formed in dilute solution in different mixing ratios of isotactic and syndiotactic PMMA, and the chromatographic behavior of the complexes was observed. For the second subject, the tlc method was utilized to separate the so-called stereoblock polymer into components without conversion to the polymeric acid, such was done by Liquori, *et al.*[10]

Fractionated samples of isotactic and syndiotactic PMMA designated iMA-3 ($M_v = 3.64 \times 10^5$) and sMA-2 ($M_v = 2.46 \times 10^5$), respectively, were used in this investigation. The preparation and the characterization of these samples have been reported in the previous paper.[2] To obtain the so-called stereoblock polymers, two different polymerization runs of MMA in toluene at −50° were made by using different catalysts, *n*-butylmagnesium chloride and diphenylmagnesium, respectively. The products were extracted with boiling acetone[4] and the insoluble portions were used for the subsequent experiments, being designated Bmc-M ($M_v = 2.66 \times 10^5$) and Dpm-M ($M_v = 2.02 \times$

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