

# Hydrolysis of Active Esters by Polymer-Supported Oximes: Influence of Macromolecular Characters

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**ABSTRACT:** Hydrolysis of *p*-nitrophenyl acetate by oximino groups anchored onto two types of supports (i.e., polystyrene and polyacrolein) has been studied. Polystyrene and polyacrolein oximes were prepared using divinylbenzene and tetraethyleneglycol diacrylate as crosslinking agents with a varying extent of crosslinking. The rate of the esterolytic reactions was found to depend on the structural characteristics of the polymer support, which include the hydrophobic or hydrophilic nature of the polymer backbone, solvation of the polymer and the attached functional groups, the nature and extent of crosslinking of the polymer matrix, and also the chemical environments of the oximino groups. The effect of the presence of pyridine residues neighboring the acrolein oxime functionality on the hydrolysis reaction was also studied. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 70: 493–500, 1998

**Key words:** polymer-supported oximes; hydrolysis of active esters; macromolecular characters; degree of crosslinking; hydrophobic–hydrophilic balance

## INTRODUCTION

The solvolysis of ester groups attached to a polymer backbone has been the subject of a large number of investigations.<sup>1–5</sup> The solvolytic reactions of numerous low molecular weight esters, catalyzed by synthetic polymers, have also been reported.<sup>6–8</sup> It has been observed that the rate of the esterolytic reactions depends on the structural characteristics of the polymer support, which include the hydrophilic or hydrophobic nature of the polymer backbone, solvation of the polymer and the attached functional groups, and the extent of crosslinking of the polymer matrix.<sup>3</sup>

One important feature of reactions conducted on crosslinked polymeric supports is the contribution from local concentration effects. The difficulty often encountered in arriving at meaningful quantitative correlation in such studies is due to the heterogeneity of the reaction.<sup>9</sup> This article is concerned with an

attempt to examine the effects of previously described concepts on the kinetics of heterogeneous reactions mediated by crosslinked polymer supports. To understand the intrinsic features of polymer-aided reactions occurring on crosslinked polystyrene and polyacrolein supports, hydrolysis of the chromogenic substrate, *p*-nitrophenyl acetate, by oximino groups anchored on two types of polymeric supports have been studied. Herein, we have tried to analyze the effect of the nature and extent of crosslinking, the relative hydrophobic–hydrophilic nature of the polymer matrix, and the immediate chemical environment of the oximino groups on the reactivity of the polymeric oximes. The hydrolysis of *p*-nitrophenyl acetate can be followed easily by measuring the optical density of the liberated *p*-nitrophenol, which is a direct measure of the extent of reaction.

## EXPERIMENTAL

### Materials and Methods

The monomers [styrene, divinylbenzene (DVB), tetraethyleneglycol diacrylate (TEGDA), acrolein,

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and 4-vinyl pyridine (Aldrich)] were purified by low pressure distillation. Styrene–DVB and styrene–TEGDA copolymer supports were prepared by adopting procedures reported for parallel cases. Polystyrene-bound aldehyde was prepared from polystyrene by chloromethylation and subsequent oxidation. Acetyl, benzoyl, and *p*-nitrobenzoyl polystyrenes were prepared by Friedel Crafts acylation with the respective acyl halides and  $\text{AlCl}_3$ . 3-Nitro-4-chloromethyl polystyrene resins and 3-nitro-4-keto polystyrene resins were prepared by the nitration of chloromethyl resin or keto polystyrene resin with fuming nitric acid at 0°C. Kinetic measurements were done on a Shimadzu model 160 A double beam ultraviolet–visible (UV–vis) spectrophotometer.

#### Preparation of Styrene–Acrolein–DVB Terpolymer: Suspension Polymerization

The monomers were washed with sodium hydroxide solution (1%) (three times) and with water (three times) to remove the inhibitor. Poly(vinyl pyrrolidone) (150 mg) was dissolved in water (100 mL) and heated to 80–90°C. The mixture of monomers, say, styrene (16.78 mL), acrolein (1.11 mL), and DVB (0.95 mL) for 2% crosslinked resin and azobisisobutyronitrile (200 mg) as initiator were added to the hot solution with vigorous stirring. The mixture was heated at 90°C with stirring for 12 h. The precipitated polymer was filtered, washed with water, carbon tetrachloride, benzene, ethanol, and methanol, and dried at 60°C. Yield, 14.5 g. Polymers with crosslink densities of 1, 2, 4, 10, and 20% were prepared by changing the percentage of styrene and DVB. The mole percent of acrolein was kept constant at 10%.

#### Preparation of Styrene–Acrolein–TEGDA Terpolymer: Suspension Polymerization

Poly(vinyl pyrrolidone) (150 mg) was dissolved in water (100 mL) and heated to 80–90°C. The mixture of inhibitor-free monomers [e.g., styrene (16.78 mL), acrolein (1.11 mL), and TEGDA (0.91 mL) for 2% crosslinked resin and azobisisobutyronitrile (200 mg) as initiator] was added to the hot solution with vigorous stirring. The mixture was heated at 90°C with stirring for 12 h. The precipitated polymer was filtered, washed with water, carbon tetrachloride, ethanol and methanol, and dried at 60°C. Yield, 15.8 g. Polymers with crosslink densities of 1, 2, 4, 10, and 20% were prepared by changing the percentage of sty-

rene and TEGDA. The percentage of acrolein was kept constant at 10%.

#### Preparation of Styrene–Acrolein–4-Vinyl Pyridine–DVB/TEGDA Polymer: Bulk Polymerization

Copolymers of styrene–acrolein–4-vinyl pyridine with 2% crosslinking (DVB or TEGDA as crosslinking agent) were prepared by polymerizing a mixture of inhibitor-free monomers [e.g., styrene (5.73 mL), acrolein (0.67 mL), 4-vinyl pyridine (4.09 mL), and DVB (0.57 mL), or TEGDA (0.54 mL)] in a reaction vessel. Nitrogen gas was passed through the reaction mixture, and azobisisobutyronitrile (200 mg) was added as the inhibitor. The mixture was heated on a water bath at 60°C. Heating was continued until all the polymer was precipitated. It was washed with benzene, carbon tetrachloride, water, ethanol, and methanol, and dried in vacuum. Yield, 9.2 g.

#### Preparation of Polymeric Oximes: General Procedure

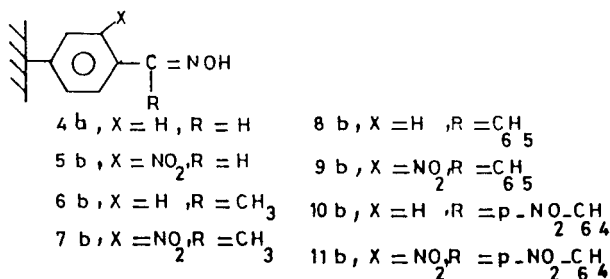
The aldehyde or keto resin (10 g) was mixed with hydroxyl amine hydrochloride (25 g) and pyridine (30 mL) in chloroform (50 mL). The mixture was refluxed at 90°C for 20 h. The resin was filtered and washed successively with chloroform, water, ethanol, and methanol. The resin was dried in vacuum to constant weight. Yield, 11 g.

#### Kinetics of Hydrolysis of *p*-Nitrophenyl Acetate with Differently Crosslinked Oxime Resins: General Procedure

*p*-Nitrophenyl acetate (20 mg, 0.11 mmol) was dissolved in 1 : 1 dioxane–water mixture (20 mL). 0.5 mL of the solution was withdrawn, made up to 10 mL, and used as the blank solution. The oxime resin (0.33 mmol) was added to the *p*-nitrophenyl acetate solution and shaken well. After 10 min, 0.5 mL of the solution was withdrawn, diluted to 10 mL, and the concentration of *p*-nitrophenol liberated was measured by UV–vis spectrophotometer at 400 nm wavelength. The experiment was repeated at different intervals of time. The rate constant for the reaction was calculated.

## RESULTS AND DISCUSSION

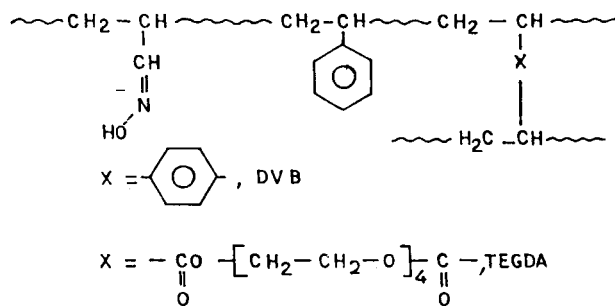
Polystyrene and polyacrolein crosslinked with DVB and TEGDA were prepared and functionalized properly to incorporate the oximino functions as reported earlier.<sup>10,11</sup> These polymeric systems



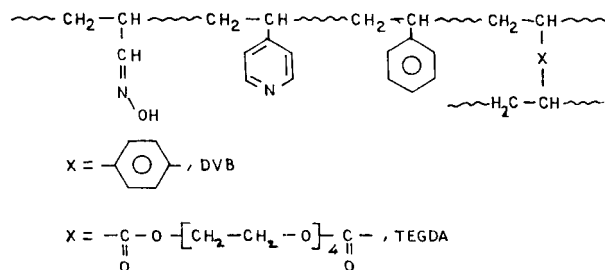
**Figure 1** DVB and TEGDA crosslinked polystyrene-supported oximes. Degree of crosslinking: 1, 2, 4, 10, and 20 mol %.

were prepared in varying crosslink densities. The extent of crosslinking was varied from 1 to 20% (1, 2, 4, 10, and 20%). The structures of the various polymeric oximes used for these studies are represented in Figures 1–3. The hydroxyl group capacity of the various polymeric oximes prepared was determined by the acetylation method.<sup>12</sup>

To study the interdependence of the various macromolecular characters and the reactivity of the attached oximino functions, hydrolysis of *p*-nitrophenyl acetate was conducted as the model reaction. The reaction was followed spectrophotometrically by measuring the amount of *p*-nitrophenol formed in the course of the reaction at a wavelength of 400 nm. The concentration of *p*-nitrophenylacetate was fixed at  $1.1 \times 10^{-4}$  mol, and a 3-fold molar excess ( $3.3 \times 10^{-4}$  moles) of the polymeric oximes was taken. The reaction medium chosen was a 1 : 1 mixture of dioxane and water. The amount of *p*-nitrophenol formed was measured at definite time intervals. The reaction was allowed to continue up to 80 min when appreciable extent of conversion was noticed. The percentage hydrolysis and the rate of the reaction were determined. The results obtained are given in Tables I–III.



**Figure 2** DVB and TEGDA crosslinked polyacrolein-supported oximes. Degree of crosslinking: 1, 2, 4, 10, and 20 mol %.



**Figure 3** DVB and TEGDA crosslinked 4-vinyl pyridine-polyacrolein-supported oximes. Degree of crosslinking: 2 mol %.

It has been reported that the solvolysis of *p*-nitrophenyl esters by polymer-bound nucleophiles follow second-order kinetics.<sup>13</sup> Hydrolysis of *p*-nitrophenyl acetate using polymer-bound amino groups was observed to follow second-order kinetics.<sup>14</sup> In the present case, because the polymeric oximes exist as a discrete phase and because they are crosslinked, it is not easy to calculate the actual rate constants. Equations applicable to homogeneous reactions have been adapted by using the method of log-linear least squares to fit the data to second-order kinetics. The reliability of the data was checked by calculating the coefficient of correlation. The values were very close to unity, which indicated the fitness of the adaptations with second-order kinetics.

### Reactivity of Polystyrene-Supported Oximes

Oximino functions supported on polystyrene resins with varying mole percentages of DVB have been used for studying the hydrolysis reaction of *p*-nitrophenyl acetate. The values of the second-order rate constants and the percentage hydrolysis calculated are presented in Table I.

The values of the rate constant and percentage hydrolysis decreased linearly with an increase in the degree of crosslinking for all the different polymeric oximes. For the polystyrene-supported aldoximes, 1% crosslinked resin gave the highest conversion rate and 20% crosslinked resin, the least. The percentage hydrolysis with the 1% crosslinked resin after a period of 80 min is found to be 45.2%, with the rate constant value coming to  $2.40 \times 10^{-2}$  L mol<sup>-1</sup> s<sup>-1</sup> as against 22.1% for the 20% crosslinked resin having a rate constant value of  $1.04 \times 10^{-2}$  L mol<sup>-1</sup> s<sup>-1</sup>. The other resins having a degree of crosslinking in between these two gave percentage conversion and rate constant values corresponding to their positions in the gradation of the crosslink density values.

**Table I** Rate Constant and Percentage Hydrolysis of *p*-Nitrophenyl Acetate with DVB-Crosslinked Polystyrene Oximes

Polymeric Oxime	Crosslink Density (mol %)	Oxime Capacity (mequiv g <sup>-1</sup> )	Rate Constant × 10 <sup>2</sup> (L mol <sup>-1</sup> s <sup>-1</sup> )	Correlation Coefficient	% Hydrolysis <sup>c</sup>	
Polystyrene aldoxime	1	2.69 <sup>a</sup>	2.40	0.987	45.2	
		2.75 <sup>b</sup>	2.52	0.953	47.8	
	2	2.42 <sup>a</sup>	2.05	0.989	39.1	
		2.52 <sup>b</sup>	2.20	0.993	42.1	
	4	1.82 <sup>a</sup>	1.78	0.985	33.7	
		2.01 <sup>b</sup>	1.91	0.956	36.1	
	10	1.42 <sup>a</sup>	1.38	0.982	25.7	
		1.81 <sup>b</sup>	1.50	0.957	28.1	
	20	0.83 <sup>a</sup>	1.04	0.902	22.1	
		1.21 <sup>b</sup>	1.21	0.942	24.9	
	Polystyrene acetyl oxime	1	2.88 <sup>a</sup>	2.74	0.999	52.7
			2.92 <sup>b</sup>	2.99	0.927	54.4
2		2.66 <sup>a</sup>	2.36	0.989	45.7	
		2.81 <sup>b</sup>	2.48	0.905	48.9	
4		1.88 <sup>a</sup>	2.04	0.983	41.7	
		2.19 <sup>b</sup>	2.27	0.953	44.1	
10		1.49 <sup>a</sup>	1.81	0.979	35.2	
		1.86 <sup>b</sup>	1.94	0.937	38.4	
20		0.94 <sup>a</sup>	1.75	0.998	30.2	
		1.32 <sup>b</sup>	1.81	0.925	33.9	
Polystyrene benzoyl oxime		1	2.57 <sup>a</sup>	1.51	0.988	38.2
			2.71 <sup>b</sup>	1.66	0.937	40.1
	2	2.01 <sup>a</sup>	1.21	0.967	34.8	
		2.12 <sup>b</sup>	1.31	0.965	37.3	
	4	1.75 <sup>a</sup>	1.01	0.914	29.7	
		1.96 <sup>b</sup>	1.12	0.921	32.9	
	10	1.35 <sup>a</sup>	0.72	0.944	19.2	
		1.67 <sup>b</sup>	0.83	0.922	21.1	
	20	0.77 <sup>a</sup>	0.38	0.978	10.1	
		1.18 <sup>b</sup>	0.41	0.973	11.3	
	Polystyrene <i>p</i> -nitrobenzoyl oxime	1	2.42 <sup>a</sup>	1.25	0.965	35.7
			2.48 <sup>b</sup>	1.27	0.925	37.4
2		1.98 <sup>a</sup>	1.02	0.937	32.9	
		2.01 <sup>b</sup>	1.13	0.937	35.1	
4		1.62 <sup>a</sup>	0.85	0.985	27.1	
		1.75 <sup>b</sup>	0.97	0.935	30.2	
10		1.28 <sup>a</sup>	0.23	0.955	15.7	
		1.32 <sup>b</sup>	0.25	0.958	18.2	
20		0.75 <sup>a</sup>	0.15	0.963	5.9	
		1.05 <sup>b</sup>	0.16	0.983	8.2	

<sup>a</sup> Using polystyrene resins without a nitro group at the 3-position.<sup>b</sup> Using polystyrene resins with a nitro group at the 3-position.<sup>c</sup> Percent hydrolysis after 80 min.

Reactivity of polystyrene acetyl oximes also varied inversely with the degree of crosslinking. Resin with 1% crosslinking gave the highest

value of 52.7% conversion, and the rate constant was  $2.74 \times 10^{-2} \text{ L mol}^{-1} \text{ s}^{-1}$ . 20% crosslinked resin gave a conversion of 30.2%, with a rate

**Table II** Rate Constant and % Hydrolysis of *p*-Nitrophenyl Acetate with TEGDA-Crosslinked Polystyrene Oximes

Polymeric Oxime	Crosslink Density (mol %)	Oxime Capacity (mequiv g <sup>-1</sup> )	Rate Constant × 10 <sup>2</sup> (L μmol <sup>-1</sup> s <sup>-1</sup> )	Correlation Coefficient	% Hydrolysis <sup>c</sup>
Polystyrene aldoxime	1	1.34 <sup>a</sup>	2.51	0.939	50.2
		1.42 <sup>b</sup>	2.70	0.991	53.8
	2	1.90 <sup>a</sup>	2.73	0.981	55.3
		2.10 <sup>b</sup>	2.85	0.938	57.4
	4	2.42 <sup>a</sup>	3.01	0.967	61.3
		2.58 <sup>b</sup>	3.16	0.971	64.9
	10	2.10 <sup>a</sup>	1.79	0.978	45.9
		2.25 <sup>b</sup>	1.91	0.981	49.1
	20	1.18 <sup>a</sup>	1.55	0.971	38.7
		1.23 <sup>b</sup>	1.69	0.927	42.3
Polystyrene acetyl oxime	1	1.72 <sup>a</sup>	2.91	0.979	55.9
		1.88 <sup>b</sup>	3.11	0.967	59.1
	2	2.15 <sup>a</sup>	3.18	0.973	61.7
		2.25 <sup>b</sup>	3.31	0.985	63.9
	4	2.89 <sup>a</sup>	3.44	0.937	65.7
		3.28 <sup>b</sup>	3.53	0.932	69.1
	10	2.25 <sup>a</sup>	2.31	0.925	48.3
		2.40 <sup>b</sup>	2.48	0.947	51.7
	20	1.32 <sup>a</sup>	1.92	0.965	40.1
		1.41 <sup>b</sup>	2.03	0.967	43.2
Polystyrene benzoyl oxime	1	1.23 <sup>a</sup>	1.90	0.978	43.7
		1.30 <sup>b</sup>	2.08	0.991	45.1
	2	1.65 <sup>a</sup>	2.24	0.992	47.2
		1.80 <sup>b</sup>	2.26	0.963	48.5
	4	2.75 <sup>a</sup>	2.88	0.987	50.7
		2.90 <sup>b</sup>	2.98	0.972	52.9
	10	1.62 <sup>a</sup>	1.72	0.952	35.7
		1.75 <sup>b</sup>	1.86	0.944	39.1
	20	1.08 <sup>a</sup>	1.08	0.985	31.2
		1.12 <sup>b</sup>	1.31	0.927	34.1
Polystyrene <i>p</i> -nitrobenzoyl oxime	1	1.18 <sup>a</sup>	1.41	0.982	41.7
		1.23 <sup>b</sup>	1.61	0.925	44.4
	2	1.50 <sup>a</sup>	1.52	0.914	45.2
		1.65 <sup>b</sup>	1.69	0.989	47.9
	4	1.90 <sup>a</sup>	1.98	0.972	48.7
		2.10 <sup>b</sup>	2.07	0.965	50.4
	10	1.32 <sup>a</sup>	1.29	0.982	32.7
		1.45 <sup>b</sup>	1.30	0.957	34.4
	20	0.98 <sup>a</sup>	0.88	0.978	25.1
		1.06 <sup>b</sup>	0.99	0.982	28.3

<sup>a</sup> Using polystyrene resins without a nitro group at the 3-position.<sup>b</sup> Using polystyrene resins with a nitro group at the 3-position.<sup>c</sup> Percent hydrolysis after 80 min.

constant value of  $1.75 \times 10^{-2} \text{ L mol}^{-1} \text{ s}^{-1}$ . Polystyrene-supported benzoyl and *p*-nitrobenzoyl oximes also showed similar trends in reactivity toward the hydrolysis reactions.

The decreased reactivity of the highly crosslinked polystyrene-based oximes can be ascribed to the increased rigidity of the polystyrene matrix and hence to the inaccessibility of the ac-



**Table III Rate Constant and % Hydrolysis of *p*-Nitrophenyl Acetate with Polyacrolein Oximes**

Polymeric Oxime	Crosslink Density (mol %)	Oxime Capacity (mequiv g <sup>-1</sup> )	Rate Constant × 10 <sup>2</sup> (L mol <sup>-1</sup> s <sup>-1</sup> )	Correlation Coefficient	% Hydrolysis <sup>a</sup>
DVB-crosslinked polyacrolein oxime	1	2.82	5.11	0.998	75.8
	2	2.76	4.91	0.980	73.1
	4	2.50	4.61	0.999	70.7
	10	2.05	4.14	0.944	60.3
	20	1.82	3.74	0.986	49.8
TEGDA-crosslinked polyacrolein oxime	1	2.69	5.31	0.967	78.3
	2	2.90	5.54	0.972	80.1
	4	3.10	5.95	0.999	82.4
	10	2.82	4.82	0.987	65.3
	20	2.02	4.22	0.985	53.8
DVB-crosslinked 4-vinyl pyridine-acrolein polymer oxime	2	2.85	5.43	0.999	78.9
TEGDA-crosslinked 4-vinyl pyridine-acrolein polymer oxime	2	3.08	6.24	0.999	85.2

<sup>a</sup> Percent hydrolysis after 80 min.

tive oxime functions to the substrate in solution. Increase in the percentage of DVB increases the rigidity of the polystyrene network.<sup>15,16</sup>

Polystyrene-supported oximes with different structural environments have been used to conduct the hydrolysis reaction. The oximino functions were derived from polystyrene-based aldehyde, methyl, phenyl, and *p*-nitrophenyl ketones. Of these different oximes, the acetyl oxime was found to be the most reactive, even more reactive than the aldoxime (Table I). The increased reactivity of the acetyl oxime may be due to the presence of an electron releasing methyl group on the carbonyl carbon, that in turn increases the nucleophilicity of the oxime function. The decreased reactivity of benzoyl and *p*-nitrobenzoyl oximes is due to the steric hindrance offered by the bulky phenyl and *p*-nitrophenyl groups toward the hydrolysis reaction.

Another interesting observation was the increased reactivity of the different polystyrene oximes when a nitro group was introduced on the 3-position of the phenyl residue of the polystyrene

backbone. For the acetyl oxime resin (2% crosslinked), the resin with a nitro group at the 3-position of the phenyl residue gave 48.9% conversion after 80 min, whereas the resin without a nitro group gave only 45.7% conversion. The rate constant values were  $2.48 \times 10^{-2}$  and  $2.36 \times 10^{-2}$  L mol<sup>-1</sup> s<sup>-1</sup>. In the case of polystyrene aldoximes (2% crosslinked), the values were 42.1% and 39.1% respectively; the rate constant values being  $2.20 \times 10^{-1}$  and  $2.05 \times 10^{-2}$  L mol<sup>-1</sup> s<sup>-1</sup>. Similar reactivity patterns were observed for the benzoyl oxime and *p*-nitrobenzoyl oxime resins. In a parallel case of the hydrolysis of *p*-nitrophenyl acetate by oxime groups generated on a quaternized 4-vinyl pyridine-acrolein copolymer, it was suggested that the oximate anion was the nucleophilic species.<sup>17</sup> The presence of a nitro group at the 3-position of the phenyl residue of the polystyrene backbone is believed to facilitate the deprotonation of the oxime, leading to the formation of the more nucleophilic oximate anion. This in turn leads to greater reactivity.

Compared with DVB crosslinked polystyrene oximes, TEGDA crosslinked polystyrene oximes showed considerable difference in the reactivity pattern (Table II). The change in reactivity with a change in the degree of crosslinking was not linear. The 1% crosslinked resin was not the most reactive, but the 4% resin was. The percentage conversion and the rate constant values increased when going from 1 to 4% crosslinked resin, reached a maximum for 4% crosslinked resin; then they decreased gradually. Here, also, the 20% crosslinked resin was the least reactive.

Even though, TEGDA-crosslinked polystyrene is more flexible, compared with DVB-crosslinked polystyrene, at higher extent of crosslinking, as in the 20% crosslinked resin, the rigidity of the polymeric network increases and the functional groups attached to such highly crosslinked resins become more inaccessible to the solvent and soluble substrates. The diffusion-controlled penetration of the solvent and substrate molecules into the interior of the polymer network is made difficult. This leads to decreased reaction rates.<sup>18</sup>

### Reactivity of Polyacrolein-Supported Oximes

Polyacrolein oximes crosslinked with DVB having variable degree of crosslinking were prepared<sup>11</sup> and used in the study of the hydrolysis of *p*-nitrophenyl acetate. The percentage of acrolein was fixed as 10% in the polymerization mixture. The values of the second-order rate constants and the percentage hydrolysis calculated are given in Table III.

In the present case of DVB-crosslinked polyacrolein oximes, the extent of reaction and the corresponding rate constant values showed a gradual decrease upon an increase in the degree of crosslinking. Thus, 1% DVB-crosslinked polyacrolein oxime gave the highest value for the rate constant ( $5.11 \times 10^{-2} \text{ L mol}^{-1} \text{ s}^{-1}$ ) and percentage conversion (75.8%). The 20% crosslinked oxime gave the lowest value of  $3.74 \times 10^{-2} \text{ L mol}^{-1} \text{ s}^{-1}$  for the rate constant and 49.8% conversion. The other resins gave values in between these two extremes. The observed trend in reactivity was in accordance with the results already obtained with regard to the reactivity of acyl-transfer reagents derived from polyacrolein oximes.<sup>11</sup> The 1% resin showed maximum reactivity and the 20% resin least. The reason could be the increased rigidity of the highly crosslinked resins. The structural factors that have been explained in the case of DVB-crosslinked polystyrene oximes are valid in this case also.

In the case of DVB-crosslinked polyacrolein oximes, one significant difference was noticed. It was the considerably higher reactivity of the variously crosslinked polyacrolein oxime resins, compared with the DVB-crosslinked polystyrene system. Even the 20% crosslinked polyacrolein oxime gave 49.8% conversion while the 20% crosslinked polystyrene aldoxime gave only 22.1% conversion under the same reaction conditions. Similar reactivity patterns were observed for all other crosslinked resins. This indicates that the incorporation of almost 10% acrolein units in the crosslinked polymer matrix makes a significant change in the relative polarity of the network. The enhanced reactivity of the polyacrolein oximes shows that the change in the relative polarity of the network as a result of the incorporation of the acrolein units makes the polyacrolein network more hydrophilic; hence, the oxime groups are made more accessible to the substrate, thus increasing the reactivity.

Polyacrolein oximes have also been prepared containing different mole percentage of TEGDA crosslinker. They were used in the study of the hydrolysis of *p*-nitrophenyl acetate. The values of second-order rate constant and the percentage hydrolysis are presented in Table III. TEGDA-crosslinked polyacrolein oximes showed trends of reactivity similar to the earlier case of TEGDA-polystyrene system. The 20% crosslinked resin was found to be the least reactive one and the 4% resin, the most reactive. The reactivity first increased from 1% crosslinked resin to 4% resin, attained a maximum, and then it gradually decreased and reached the minimum value for the 20% crosslinked resin.

The high reactivity at 4% crosslinking may be due to the attainment of the optimum hydrophobic/hydrophilic balance by the polymer network so that it becomes highly compatible with the substrate molecules. The uninhibited motion of the substrate molecules is possible through the solvent swollen polymer matrix, causing enhanced encounter frequencies of substrate molecules with the active sites on the polymer matrix. This leads to enhanced rate of the reaction.<sup>19</sup> The reactivity decreases for the 20% crosslinked resin as the relative rigidity of the polymer network is increased.

When the reactivity of the oxime functions attached to the polyacrolein resins is compared across the series, the TEGDA crosslinked resins are more reactive than the DVB crosslinked ones. But, the variation in reactivity upon changing the crosslinker is not so much pronounced in the case of the polyacrolein

system, compared with the polystyrene system. TEGDA-crosslinked polyacrolein oximes are highly reactive when compared with other polymeric oximes (viz., DVB-crosslinked polyacrolein and DVB- and TEGDA-crosslinked polystyrene oximes). Of the TEGDA-crosslinked polyacrolein oximes, the 4% resin has the highest reactivity. The mechanical and physical forms of this particular resin are found to be best suited for a heterogeneous reaction to be conducted at ease.

The increased reactivity of the TEGDA-crosslinked polystyrene oximes can be ascribed to the greater flexibility of the polymer network as a result of the incorporation of the long and flexible TEGDA units. This can lead to the generation of large volumes of empty space capable of absorbing large quantities of solvents. Thus, the movements of low molecular weight species, both the solvent and substrate molecules, is hardly diffusion-controlled.<sup>16,18</sup>

#### Effect of Neighboring Pyridine Units

Crosslinked polyacrolein resins have also been prepared with appropriate amounts of pyridine units by bulk polymerization of mixture of acrolein, styrene, and 4-vinyl pyridine with the crosslinking agent (either DVB or TEGDA). 2% crosslinked polymers were prepared by taking the monomer ratio as styrene : 4-vinyl pyridine : acrolein : DVB/TEGDA (48 : 40 : 10 : 2). The incorporation of pyridine units in the polymer network was evidenced by nitrogen analysis and infrared spectrum. Absorption peaks at  $1550\text{ cm}^{-1}$  (C=C str),  $1580\text{ cm}^{-1}$ , and  $1480\text{ cm}^{-1}$  (C=N str) are attributed to the nitrogenic heterocyclic pyridine group in the polymer.

The oxime functionality derived from this composite copolymer was used to study the hydrolysis of *p*-nitrophenyl acetate. The reaction conditions remained the same. Second-order rate constant values and the percentage hydrolysis recorded are presented in Table III. When a certain number of pyridine units were introduced into the polyacrolein network, the reactivity of the attached oxime function was found to increase. The enhanced reactivity of the pyridine-containing resins cannot be simply explained by the inductive effects of neighboring pyridine rings. This may be attributed to the microenvironmental nonpolar effects. There was one report regarding the use of linear 4-vinyl pyridine-acrolein copolymers for studying the hydrolysis of *p*-nitrophenyl acetate.<sup>20</sup>

The oxime groups attached to this linear 4-vinyl pyridine-acrolein copolymer were found to be capable of hydrolyzing *p*-nitrophenyl acetate at a faster rate, compared with hydrolysis by the low molecular weight analog, isobutyraldoxime.

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